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Award ID: 9810367
Organization: Columbia University
Title:
Environmental Molecular Science Institute on Chemical Sources and Sinks at Liquid/Solid Interfaces

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Chemical Structure and Dynamics Group

DuPont Chemicals

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Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)
See PDF version submitted by PI at the end of the report.

Findings: (See PDF version submitted by PI at the end of the report)
See PDF version submitted by PI at the end of the report.

Training and Development:
Research Training

Research under the EMSI program at Columbia University, sponsored by the National Science Foundation and the Department of Energy, contributed to the training of many graduate students almost all of whom have gone on to receive their Ph.D. degrees. In addition a number of post-doctoral fellows received post-graduate experience under the EMSI program. Typically this training emphasized hands on laboratory work, the writing of first drafts of publishable manuscripts, significant library research, and some development of theoretical concepts. Post-doctoral fellows participated in research and helped to supervise graduate and undergraduate students. Undergraduates became involved in research mainly during the summer and occasionally during the academic term through junior and senior year research projects. (See the descriptions of the EMSI Research Experience for Undergraduates and Langmuir Scholars programs under Education and Outreach.) Exchange of ideas and scientific skills was fostered via frequent group meetings and a number of seminar programs. These seminars included an EMSI sponsored series focused on issues of fundamental science related to the environment. Access to the facilities of the Columbia Center for Integrated Science and Engineering (CISE) and the Lamont-Doherty Earth Observatory (L-DEO) enhanced the exchange of interdisciplinary research ideas. This provided students, post-doctoral fellows, and faculty contact with research scientists in the Columbia Graduate School of Arts and Sciences, the Columbia School of Engineering and Applied Science, and the Columbia Earth Institute.

A) EMSI Research Group Meetings
Meetings with all members of the EMSI group were held regularly to insure good communication on scientific issues within the Institute. These meetings were typically 1-2 hours in length and consisted of one or two featured speakers from within Columbia's EMSI group. Presentations were given by faculty, post-doctoral fellows and graduate students.

B) EMSI Seminar Series:
The following seminars, held on the main Columbia campus, were sponsored by the EMSI research program:

February 9, 1999 û Dr. Matt Simcik, Barnard College and Lamont-Doherty Earth Observatory
'Environmental Chemistry in the Great Lakes: The PCB Story'

February 10, 1999 û Dr. Matt Simcik, Barnard College and Lamont-Doherty Earth Observatory
'Fate and Transport of Organic Contaminants in the Great Lakes'

March 10, 1999 û Dr. Matt Simcik, Barnard College and Lamont-Doherty Earth Observatory
'Polycyclic Aromatic Hydrocarbon (PAH) Distributions within Coastal Sediments; a Case Study of the Lower Hudson River Estuary'

March 11, 1999 û Dr. Sid Mitra, Institute for Earth and Ecosystem Sciences, Tulane University
'Polycyclic Aromatic Hydrocarbon (PAH) Source, Sediment Deposition Patterns, and Particle Geochemistry as Factors Influencing PAH Distribution'

April 5, 1999 û Prof. Stefan Bossman, University of Karlsruhe
'Exploration of Humic Substances by Means of Photochemical Engineering'

April 13, 1999 û Prof. Dan Strongin, Drexel University
'Surface Chemistry of Pyrites'

October 5, 1999 û Dr. James D. Myers, William R. Wiley Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory
'eResearch: The Rise of Scientific Virtual Facilities'

November 15, 1999 û Prof. Joseph Francisco, Purdue University
'Atmospheric Fate of Next Generation Chlorofluorocarbon Replacement Materials: Are They Better or Worse for the Environment?'

December 21, 1999 û Dr. Doug Ray, Environmental Molecular Sciences Laboratory and Pacific Northwest National Laboratory
'ransport of Small Molecules Across the Liquid/Vapor Interface of Water'

January 19, 2000 û Dr. Klaus Lackner, Los Alamos National Laboratory
'Zero Emission Coal û Chemical Processes for Carbon Dioxide Disposal'

February 18, 2000 û Dr. Chris Michaels, National Institute of Standards and Technology
'Chemical Imaging with Near-Field Vibrational Spectroscopy'

May 15, 2000 û Dr. Maxim Pshenichniko, Department of Chemistry, University of Groningen, The Netherlands
'Water, Light, and Electrons: Probing the dynamics of electrons in water with femtosecond spectroscopy'

April 17, 2001 û Prof. Charles Langmuir, Arthur D. Storke Professor, Department of Earth & Environmental Science, Lamont-Doherty Earth Observatory
'Volcanoes as Windows to the Earth's Interior'

April 19, 2001 û Prof. Christian Meyer, Department of Civil Engineering and Engineering Mechanics, Columbia University
'Beneficiation of New York Harbor Dredge Material'

April 23, 2001 û Prof. Jeanne Pemberton, Department of Chemistry, University of Arizona
'New Approaches for Laboratory Studies of Heterogeneous Atmospheric Chemistry'

April 27, 2001 û Dr. Diego Diaz, Department of Chemistry, Cornell University
'Imaging and Modification of Redox Active Surface Structures with SPM Techniques'

May 8, 2001 û Dr. Ryan Pearman, Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois at Champaign-Urbana
'Toward the Understanding of Intramolecular Energy Transfer'

May 29, 2001 û Prof. Walter Harrison, Stanford University
'How Electronic Structure Got Simple'

June 19, 2001 û Dr. Patrick Dupre, Grenoble High Magnetic Field Laboratory
'Dynamics and Spectroscopy of the NO2 Molecule by the CW-CRLAS Technique: Linear and Non-linear Behavior'

July 26, 2001 - Dr. Daniel Sarewitz, Senior Research Scholar at Columbia University
'Why Being Right Doesn't Matter: Science Politics, and the Excess of Objectivity'

November 14, 2001 - Professor Barney Ellison, Department of Chemistry and Biochemistry, University of Colorado
'Organic Aerosols, Free Radicals, and the Fate of the Earth'

March 11, 2002 - Dr. Peter J. Feibelman, Sandia National Laboratories
'Density Functional Modeling of Metal Surfaces in an Aqueous Environment: Application to Ru(0001)'

March 26, 2002 - Gina Florio, Department of Chemistry, Purdue University
'Shedding Light on the Molecule of Darkness: Conformational Preferences, Solvation, and Dynamics of Jet-cooled Melatonin'

May 9, 2002 - Professor George Flynn, Columbia University
'Raising Flags: Chemical Marker Group STM Probes of Self-Assembly and Chirality at Liquid-Solid Interfaces and Reactions of Environmentally Important Contaminants on Iron Oxide Surfaces'

May 14, 2002 - Dr. David Senn, Department of Environmental Science and Engineering at Harvard University
'Contaminant Interactions in an Urban Lake: Nitrogen Controls Arsenic'

September 10, 2002 û Markus Lackinger, Chemnitz University of Technology, Germany
'Organic Molecules on Crystalline Surfaces-A Facinating Nanoworld Accessable by STM'

September 24, 2002 û Prof. Simon North, Texas A&M University
'Atmospheric Oxidation Mechanisms of Biogenic Haydrocarbons: Insights from Experiment and Theory'

November 19, 2002 û Dr. Robert Walker, Department of Chemistry & Biochemistry, University of Maryland
'Solvation at Surfaces: Profiling Interfacial Solvent Polarity with Molecular Rulers'

July 16, 2003 û Prof. John Fourkas, Eugene F. Merkert Chemistry Center, Boston College
'Seeing and Shaping the Microscopic World with Multiphoton Absorption'

October 8, 2003 û Prof. Richard A. Loomis, Department of Chemistry, Washington University
'The somewhat complicated interactions and dynamics of dihalogen molecules with rare gas atoms at low temperatures'

May 9, 2004 û Dr. Marcus D. Lay, National Research Council
'Atomic-Level Studies of Reactions Used in the Electrochemical Formation of Compound Semiconductors'

July 23, 2004 û Dr. Peter Schwartz, California Polytechnici State University
'Environmental Effects on Molecular Transport from an AFM Tip; and the Use of DNA to Direct the Self Assembly of Microspheres: Investigations in Nanoconstruction'

C) EMSI Langmuir Visiting Scholars Program
Columbia's EMSI sponsored a seminar/visitors program that brought to the New York area scholars expert in scientific problems of the environment. Visitors typically were in residence for 3 days to a week. As part of their responsibilities, the Langmuir visitors gave at least one public seminar and met with EMSI faculty for extended periods of time. In addition these longer stays allowed visitors to interact extensively with students and post-doctoral fellows doing research within the Environmental Molecular Sciences Institute. The program received strong, positive reviews from both visitors and EMSI participants.

The EMSI Langmuir Visiting Scholars were:

October 4-7, 1999 - Dr. James Myers, Computational Science and Mathematics Department, Pacific Northwest National Labs
Seminar: 'eResearch: The Rise of Scientific Virtual Facilities' (October 5, 1999)

April 10-11, 2000 û Dr. James Cowin, Pacific Northwest National Labs
Seminar: 'Proton Transport at the Oil/Water Interface' (April 11, 2000)

April 16-20, 2001 û Prof. Stefan Bossman, Environmental Analysis and Technology Department, University of Karlsruhe, Germany
Seminar: 'A Chemist's Approach to Iron III Induced Photooxidation Reactions in Rivers, Lakes and Seawater - How Do They Really Work and What Effects Do They Have on the Environment?' (April 17, 2001)
Seminar: 'Removing Selected Pollutants from the Environment by Using Molecular Imprinted Photocatalysts' (April 19, 2001)

November 12-15, 2001 û Dr. Edel Wasserman, DuPont Corporation
Seminar: 'Contrasts Between Industry and Academia in Chemistry' (November 13, 2001)

April 15-18, 2003 û Dr. David Dixon, Pacific Northwest National Laboratory
Seminar: 'Computational Thermochemistry - From the Gas Phase to Solution' (April 15, 2003)
Seminar: 'Computational Approaches to the Design of 157 nm Photoresists' (April 17, 2003)

Outreach Activities:

Educational/Outreach Activities

'PLUMEFLOW' was an educational component of the Columbia EMSI program that focused on groundwater contaminant transport. 'PLUMEFLOW' linked the research performed within EMSI with educational activities. The modules are flexible enough that they can be adapted to teaching a wide range of individuals, from K-12 students to highly specialized Ph.D. graduate students, the fundamental physical and chemical principles of groundwater contaminant transport on length scales from molecular to field level. The 'PLUMEFLOW' computer code includes a set of interactive physical and numerical models that simulate simple, idealized situations, as well as real-world case studies. The EMSI effort has been focused on the physical/numerical model connection as described in sections A and B below.

A) K-12 Sand Tank Models and Training for New York City Teachers

On August 29, 2001 EMSI hosted a workshop for the first set of K-12 teachers from the New York City School System participating in the hands on Plumeflow project. Five teachers (Roberts, Broderick, Carmody, Martin, and Iwuoha), 2 educators (Professors Sacks and Mitchell), 2 scientists (Professors Stute and Pfirman) and 1 evaluator (Lowes) attended the workshop. The teachers were first trained in the use of the hydrologic sand tank model by Professor Martin Stute. They then worked in groups with the tanks, practicing techniques and asking questions about implementation. During the following fall and winter, each teacher was provided with 4 sand tanks, which were purchased by the Environmental Molecular Sciences Institute. They developed curricula and used them in the classroom.

A second training workshop was held in October of 2002, once again led by Professor Martin Stute. The teachers who attended (Brown, Friedman, Purohit, Slutak, and Stengren) were a combination of teachers identified by previous program participants and people totally new to the program.

On June 10, 2002, 3 of the 5 original teachers came back together with the rest of the team and presented their curricula. Reports were received from:

Meghan Roberts, 8th grade Earth Science teacher at Eastside Middle School, who taught 130 students in 2002.

Julie Broderick, teaching 5th grade for the first time (had taught 1st, 2nd, and 3rd before) to a class of 26 students at Manhattan School for Children.

Ogechi Iwuoha had taught 5th grade once before and in 2002 had a class of 23 students at Mott Hall School.

All three teachers found that using the sand tanks engaged students and allowed them to expand on the science that they taught in the classroom. Julie Broderick commented that 'it is hard to find science material like this that was so open ended, that doesn't get old after one use, that you can come back to and investigate in a different way on a different day.' Her 5th grade students became interested in how the tank was built, how it functioned, how it compared to the real world, and how you can remediate contaminated groundwater. She split her students into groups that were each focused on a different set of questions, and the students then presented their analyses to the rest of the class. The students used the tanks for about 10 days over a period of 4-5 weeks. They complemented the tank work with exploration of permeability using funnels with different types of sediment. Many students brought their parents in to see the tanks and explained to them how they worked.

The other 5th grade teacher, Ogechi Iwuoha, took a more interdisciplinary approach, for example, integrating the tank work with a poem on water.

The 8th grade teacher, Megan Roberts, commented: 'We used the tanks while we were reading A Civil Action - which was part of our big project on water pollution. The kids were able to use the flow models to help them visualize what might have been going on in the town of Woburn, Mass. They added SO much to the work that we were doing.' She said that the sand tanks helped the students to understand how processes function underground, for example, how different sediments affect groundwater flow. 'I can't thank you enough for allowing our classroom to have these tanks for our class work. It has made an enormous difference and I can't tell you how appreciative I am.'

Two of the teachers from the second workshop also shared curricula they had developed for the sand tanks:

Kiran Purohit, 8th grade science teacher at Manhattan Academy of Technology.

George Stengren, high school environmental science teacher at The Heritage School in Manhattan.

Kiran Purohit used the sand tanks in conjunction with Rachel Carson's Silent Spring to look at the stories that could be explained or clarified by the model. Students examined issues as varied as economics, drought, and groundwater pollution using the tanks. They came up with various scenarios that could be modeled on the tanks, and then presented them to the rest of the class. Students, individually or in small groups, also wrote research reports on different groundwater issues.

George Stengren's class used the tanks to understand both qualitative and quantitative aspects of subsurface groundwater movement. In one investigation, they worked in small groups using green food dye to represent nitrates in order to develop standards for evaluating pollution levels. They also used the tanks to model a salt water intrusion, such as those formed from well usage in Long Island. In a third experiment, students examined how to determine how fast contamination moves through a system. The concepts and calculations introduced were somewhat challenging to the students, but the experiments inspired lively discussion and the students learned quite a bit. Stengren noted that the hands-on work with the sand tank helped students understand things much better than some commercial kits that provide more prepared samples.

All Plumeflow curricula have been published on the EMSI website at http://www.cise.columbia.edu/emsi/edout/sandtanks/curricula/ .

On June 2, 2003, EMSI sponsored a Sand Tank Science Fair at Barnard College, where teachers and students who had used the sand tanks in their classroom could share what they had learned. The students were the primary presenters of the work. George Stengren's twelfth grade students shared the comparisons between fresh and salt water that they did as part of the salt water intrusion project. Kiran Purohit's eighth graders explained the projects inspired by Silent Spring. In addition, Julie Broderick's fifth grade class, who had just started working with the tanks, attended to gain inspiration from their older colleagues. The fifth graders also shared the drawings they had done as part of their sand tank project. A pizza dinner followed the science fair, which gave the students a chance to interact with EMSI faculty members including Professor Martin Stute.

B) Extending the Sand Tank Program to New York City Park Rangers

On August 11, 2003, Professors Martin Stute and Sue Sacks and administrator Catherine Cook, all of Barnard College, met with EMSI Director

Professor Flynn and representatives from the New York City Parks Department to discuss how the sand tanks might be used in various Parks Department educational programs. Training for approximately 20 park rangers followed in September. Four sand tanks were loaned to the Parks Department for their use. The rangers have used the tanks as part of a water monitoring program in the Bronx. The Crotona Park Ranger Conservation Corps, high school students who learn about the environment through a combination of restoration, monitoring and engaging activities, have been part of a large effort to monitor the Bronx River. In the beginning of this program, they used the tanks to demonstrate ground water flow. Later in the program they set up a scenario in which the students monitored the level of contaminants that enter the local river and then use the tanks to devise and implement a remediation plan.

In addition, the Park Rangers used the tanks in a presentation to a group of AP high school teachers at a conference showing what the Rangers have to offer to these schools and in particular their AP science classes. They split the group in two and had the teachers perform chemical water tests and aquatic macro-invertebrate identification, and then compared the results. They used the ground water tanks to demonstrate how the teachers could follow up this field work with class activities. Teachers could book a field program with the Parks Department and borrow the tanks to use in the classroom in order to complement the students' field work.

C) Langmuir Scholars - Undergraduate Environmental Fellows

The goal of this program has been to attract top science and engineering students with an interest in the environment to Columbia and Barnard and provide them with special opportunities to sustain, expand, and develop their early interests in environmental sciences, technology and related disciplines. The Langmuir Scholars program provides a summer research stipend and summer housing for each student. Likewise, the Environmental Molecular Sciences Institute (EMSI) programs enrich the scholars' activities through seminars and research opportunities provided by the faculty and their research laboratories. Columbia University has committed a total of $180,000 for this program (in addition to matching funds provided for the EMSI effort itself).

In January, 2001, the first Langmuir Scholars - one each from Columbia College (CC), the Fu School of Engineering and Applied Science (SEAS), and Barnard College (BC) - were appointed. In 2002, four Langmuir Fellows were appointed in time to meet with the original group of Fellows (before they graduated) and in time to establish research ties to projects for the summer. More students were appointed in the summers of 2003 and 2004, and we plan to continue the program through at least 2005.

The Langmuir Scholars are:

Hillel Adesnik, Columbia College '02

Sinan Altiner, SEAS '04

*Jess Clancy, Columbia College '06

*Montana Childress, Barnard College '05

*Michelle Kalaw, Columbia College '06

Justin Lappen, Columbia College '02

*Kate Lundberg, SEAS '06

Jennifer Rossi, Barnard College '02

*Vera Shur, Columbia College '05

*Brian Weiss, SEAS '05

*designates current Langmuir Scholar

Following each summer, the Langmuir Scholars present their research to the Columbia community in a symposium. The schedule for the 2004 symposium follows:

Langmuir Scholars Symposium
November 30, 2004

4:00 P.M. Brian WEISS: 'Assessing water quality in Benin, West Africa: Social and technical considerations and geostatistics.'

4:20 P.M. Jess CLANCY: 'Seedling recruitment and plant ecology in tropical Malaysia'

4:40 P.M. Kathryn LUNDBERG: 'Modeling climate change impacts on Seattle's water supply'

5:00P.M. Vera SHUR: 'Direct response enabling technology for electricity meters and thermostats in California'

5:20 P.M. Michelle KALAW: 'Expression of iron export protein FPN1 in mammalian lung tissue'

Langmuir seminars by national figures in environmental science and policy were also sponsored through this effort. The undergraduate Langmuir Scholars were given the opportunity to join the speakers for dinner following each of these events, which are listed below:

December 4, 2001 - Professor Klaus Lackner, Ewing-Worzel Professor of Geophysics, Department of Earth & Environmental Engineering, Columbia University
'The Greening of Fossil Fuels'

February 28, 2002 - William Tolman, University of Minnesota
'Ligand Structural Effects on Biologically Relevant Copper(I) Dioxygen Chemistry'

March 12, 2002 - Dr. Christopher Langdon, Biological Oceanographer from Columbia University's Lamont-Doherty Earth Observatory
'A Long Term Study of the Effect of Elevated CO2 on Marine Calcification using the Biosphere 2 Coral Reef Mesocosm as a Model System'

May 7, 2002 - Dr. Arthur Ellis, Meloche-Bascom Professor of Chemistry, University of Wisconsin
'The ABCs of Nanotechnology: Atoms, Bits, and Civilization'

April 9, 2003 û Dr. Jeffrey Sachs, Columbia University
'The Kinetics of Economic Development'

March 2, 2004 û Dr. David Ho, Lamont-Doherty Earth Observatory
'SF6 Tracer Release Experiments in Tidal Hudson River'

D) Undergraduate Summer Research Programs (REU)

EMSI supported a total of 29 Research Experience for Undergraduates students over the life of the grant. Students worked directly with EMSI faculty mentors on active research projects, participating fully in the usual range of research related activities that include group meetings, seminars, and presentation of research results. The program also included a weekly lecture series by EMSI and other Columbia faculty and distinguished guest lecturers. Students were treated to events designed to integrate the EMSI REU program with programs run by the MRSEC, NSEC, and Chemistry Department such as a graduate school seminar with faculty from all four programs, and social events. Field trips to two industrial sites and a student symposium in which students presented the results of their summer research rounded out the regular program.

The following REU students were supported by EMSI:

Summer 2004

Mary Anzovino
Williams College
Mentor: Gerard Parkin, Department of Chemistry
Project: Synthetic Pathways Toward Phenolate and Thiolate Trisaryl Amines as Small Molecule Analogues of Zinc Enzymes

Vivian Chin
Barnard College
Mentor: George Flynn, Department of Chemistry
Project: Scanning Tunneling Microscopy: A Tool to Determine the Chirality of Absorbed Molecules on Graphite

Jonathan Herman

Brown University
Mentor: Ann McDermott, Department of Chemistry
Project: Crystallization of Macromolecular Proteins in a Strong Magnetic Field and its Applications in SSNMR

Maxwell Merkle
Kennesaw State University
Mentor: Louis Brus, Department of Chemistry
Project: Electrostatic Force Microscopy Study of Photoexcited Copper Oxide Nanocrystals

Toma Omonuwa
West Georgia
Mentor: Nicholas Turro, Department of Chemistry
Project: Ozonolysis of enecarbamates and a novel method for synthesis of enecarbamates

Rohita SriRamaratnam
University of Arkansas
Mentor: Kenneth Eisenthal, Department of Chemistry
Project: Steady-state Fluorescence Depolarization Studies of Serotonin.

Summer 2003

Thomas Baker
Indiana University of Pennsylvania
Mentor: George Flynn, Department of Chemistry
Project: Using Scanning Probe Microscopy to Understand Surface Chemistry at the Molecular Level: Applications in Nanotechnology and Environmental Science

Robert Bowers
Chicago State University
Mentor: David Adams, Department of Chemistry
Project: Fluorescence Studies of Intramolecular Electron-Transfer

Jennifer Guerard
Rose-Hulman Institute
Mentor: Gerard Parkin, Department of Chemistry
Project: Fluorescence Studies of Intramolecular Electron-Transfer

Pinray Huang
New College of Florida
Mentor: Louis Brus, Department of Chemistry
Project: Design and Silver Nanodisks Growth by Near Field Enhanced Photoreduction of Adsorbed [Ag+]

Rebecca Pompano
University of Richmond
Mentor: Kenneth Eisenthal, Department of Chemistry
Project: A Laser Study of Antibiotic Assisted Molecular-ion Transport through Lipid Bilayers in Real Time

Allison Tease
Claremont McKenna College
Mentor: Nicholas Turro, Department of Chemistry
Project: Spectroscopy of Biphenyl Radical Cations in Zeolites

Summer 2002

Jeffrey Carlson
University of Wyoming
Mentor: Gerard Parkin, Department of Chemistry

Project: Synthesis and Characterization of Sulfur Ligated Molybdenum and Tungsten Compounds: Progress Towards Homogeneous HDS Mimics.

Andrew Cavanagh
Fort Lewis College
Mentor: George Flynn, Department of Chemistry
Project: Influence of Lauric Acid on the Adsorption of 12-Bromododecanoic Acid at the Liquid Solid Interface as Studied by STM

Jessica Chapman
Scripps College
Mentor: Nicholas Turro, Department of Chemistry
Project: An Investigation of the Induction Capabilities of Oxazolidinones in the Enantioselective Formation of Methyldeoxybenzoin

Eric McArthur
University of Pittsburgh
Mentor: Kenneth Eisenthal, Department of Chemistry
Project: Design and Construction of a Surface Second Harmonic Spectrometer and its Application in Investigating Biological Systems

Matthew Myers
California Institute of Technology
Mentor: Louis Brus, Department of Chemistry
Project: Oxidation of Magnetite Nanoparticles

Summer 2001

Gina Brazzale
Creighton University
Mentor: Louis Brus, Department of Chemistry
Project: Thermal Diffusion of Nanoparticles on Graphite

Noah Burns
Columbia University
Mentor: Professor George Flynn, Dept. of Chemistry
Project: An STM Study of Binary Alkane Mixtures at the Liquid-Solid Interface
*Dreyfus

Marissa Solomon
University of Richmond
Mentor: Professor Nicholas Turro, Department of Chemistry
Project: The Effects of Chain Length on the Properties of the Radical End Group

Joshua Wittenberg
Columbia University
Mentor: Professor Gerard Parkin, Department of Chemistry
Project: Ansa-Bridged, bis-tetramethylcyclopentadienyl, Molybdenocene and Tungstenocene Complexes: Their Syntheses, Structures, and Reactions

Summer 2000

Shannon Biros
Grand Valley State University
Mentor: Professor Gerard Parkin, Department of Chemistry
Project: The Activity of Antimony Compounds in Polyesterification Reactions

Cheyenne Brindle
Reed College
Mentor: Professor Nicholas Turro, Department of Chemistry

Project: Carbenes: An Exploration of Supramolecular Steric Effects
*received Goldwater Scholarship, Spring 2001

Neel Joshi
Harvey Mudd College
Mentor: Professor George Flynn, Department of Chemistry
Project: Synthesis of enantiomerically Pure 2-Bromohexadecanoic Acid for Scanning Tunneling Microscopy Studies

Desiree Thayer
University of Michigan
Mentor: Professor Ann McDermott, Department of Chemistry
Project: NMR Studies of Photosynthetic Systems

Summer 1999

Charles Archer
Moorhead State University
Mentor: Professor Richard Freisner, Department of Chemistry
Project: Prediction of Protein Secondary Structure using Chemical Shift Database Statistics

Spencer Chapman
University of the District of Columbia
Mentor: Professor Nicholas Turro, Department of Chemistry
Project: The Secret Life of Zeolites: Guest Host Interactions of Carbene, Anthracene and Derivatives

Christopher Hampson
Colorado State University
Mentor: Professor George Flynn, Department of Chemistry
Exploring the Surface Morphology of Iron as it Changes During Exposure to Aqueous Solutions of Heavy Metals using Atomic Force Microscopy

Benjamin Marshall
Columbia University
Mentor: Dr. Deborah Haito, General Electric
Project: The Effect of HgO-NaCH3COO on a Au-Pd-Cu-Zn/Au-Ni-Cu-Zn Surface

A unique feature of the 2002 summer program was a mid-summer symposium on Integrative Research that brought together REU Fellows in EMSI with NSEC, MRSEC, and the Chemistry Department. Featured speakers included scientists from NIST and IBM. The program follows.

CENTER CONFERENCE on Integrative Research
Tuesday, June 25, 2002

8:00 A.M. Coffee/Continental Breakfast

8:45 A.M. Opening remarks (L. Fine/R. Breslow)

9:00 A.M. Colin Nuckolls (NSEC): 'Self-Assembly of Molecular Electronic Materials'

9:30 A.M. Robert Shull (NIST): 'SURFing the National Institute of Standards and Technology'

10:00 A.M. Irving Herman (MRSEC): 'Integrating Nanocrystals for Megagoals.'

10:30 A.M. Break

11:00 A.M. Jim O'Neill (IBM): 'Technology Innovation: A Microelectronics Industry perspective.'

11:30 A.M. George Flynn (EMSI): 'Environmental Chemistry: The View from One-billionth of an Inch.'

12:00 P.M. Closing Remarks (M. Crow, Science Policy; R. Shull, Nobel; L. Fine; J. Yardley)

12:30 P.M. LUNCH/Discussion (Havemeyer Lounge / 7th Floor)

1:30 P.M. Adjournment

In 2004, EMSI, MRSEC, NSEC, and the Chemistry Department co-sponsored a special symposium for the REU students that brought together leading scientists from Columbia University and Brookhaven National Laboratories. The program follows.

The Brookhaven National Lab and Columbia University REU Summer Symposium in 'Modern Materials and Materials Chemistry'
Thursday, July 15, 2004

8:00 A.M. Breakfast

8:20 A.M. Welcome (Richard Osgood)

8:30 A.M. Lance Cooley, Brookhaven National Laboratory
'Exploiting New Physics of Alloyed Magnesium Boride Superconductors to Reach Higher Magnetic Fields and Pioneer New Applications'

9:05 A.M. Stephen O'Brien, Columbia University
'Nanocrystals in Nanoscience'

9:40 A.M. Michael G. White, Brookhaven National Laboratory and SUNY Stony Brook
'Characterization and Reactivity of Supported Nanoparticles of Early Transition Metals and Compounds'

10:15 A.M. Jose A. Rodriguez, Brookhaven National Laboratory
'Physical and Chemical Properties of Ceria Nanoparticles and CeO2 (111) Surfaces: Effects of Zr-doping and Au Deposition'

10:50 A.M. Break

11:05 A.M. Joanna S. Fowler, Brookhaven National Laboratory
'Rapid Radiotracer Chemistry and Imaging the Human Brain'

11:40 A.M. Stanislaus S. Wong, Brookhaven National Laboratory and SUNY Stony Brook
'Synthesis and Characterization of Nanotube-Nanocrystal Heterostructures'

12:15 P.M. Colin Nuckolls, Columbia University
'Using Self-Assembly To Create Electronic Materials'

12:50 P.M. Lunch

E) High School Teacher Summer Research Program (RET)

Columbia has also had an active high school teacher recruitment plan that brings local teachers to the University for summer research activities. EMSI sponsored a total of 8 teachers over the life of the grant. In addition to lab research, the program also includes a weekly lecture series in which EMSI principal investigators have given presentations and weekly workshops on science pedagogy. Each teacher develops a lesson plan based on his or her research, which is linked to the EMSI website at http://www.cise.columbia.edu/emsi/edout/ret/participants.html .

A number of the teachers sponsored by EMSI have given posters and presentations of their research at the annual Partners in Science meetings in San Diego. Megan Roberts, who also participated in EMSI's Plumeflow program, attended the Spring 2002 NSTA conference (where she gave presentations on teaching and on her research project at Columbia) and the NSF-sponsored RET Conference in April 2002 (where she gave a presentation on the application of summer research in the classroom). In 2003, she became a Regional Instructional Supervisor and now oversees the science programs for 185 K-12 schools in Manhattan. In 2004, Todd Flomberg became a Peer Coach for the RET program and provided guidance to new program participants in adapting to the laboratory research environment.

The EMSI RET Program is coordinated in conjunction with Columbia's Summer Research Program for Secondary School Science Teachers.

These are the RET teachers supported by EMSI:

Summers 1999-2000

Anthony Mauro
Fort Hamilton High School, Brooklyn
Mentor: Professor Ken Eisenthal, Dept. of Chemistry
Project: 'Laser Studies of Molecules at Surfaces'
Online Lesson Plan: 'Devising a Set of Experiments to Test Water for Dissolved Substances' (1999)

Paul Melkonian
Satellite Academy High School, Manhattan
Mentor: Professor Peter Schlosser, Dept. of Earth and Environmental Sciences
Project: 'Air-water Exchange in the Biosphere 2 Ocean'
Online Lesson Plan: 'Water Quality Monitoring' (1999)

Summers 2000-2001

Todd Flomberg
The Nightingale-Bamford School, Manhattan (middle school)
Mentor: Professor Ken Eisenthal, Dept. of Chemistry
Project: 'Solvation Dynamics of Organic Monolayers'
Online Lesson Plans:
'How Big is a Molecule?' (2000)
'Polarity and Dissolving' (2001)

Jennifer Girard
Edward R. Murrow High School, Brooklyn
Mentor: Professor Ged Parkin, Dept. of Chemistry
Project: 'Studying the Interaction of Zinc Enzymes with Metals and Metalloids Using Small Molecule Model Compounds'
Online Lesson Plans:
'Arsenic Contamination Research' (2000)
'Acids and Bases: Their Reactions, Conductivity, Base Indicators and Neutralization Reaction (4 Lab Lessons)' (2001)

Summers 2001-2002

Megan Garrison Roberts (also participated in the Plumeflow program)
East Side Middle School, Manhattan (IS 114)
Mentor: Professor Peter Schlosser, Dept. of Earth and Environmental Sciences
Project: 'Measuring the Flow Dynamics of the Hudson River: A Deliberate Tracer Experiment'
Online Lesson Plans:
'What Impact Do Humans Have on the Environment?' (2001)
'What Impact Do Humans Have on the Environment?' (2002)

Summers 2002-2003

David Friedman (also participated in the Plumeflow program)
General Douglas MacArthur HS, Levittown, NY
Mentors: Dr. Steve Chillrud, Lamont-Doherty Earth Observatory and Professor Martin Stute, Barnard College Dept. of Chemistry & LDEO
Project: 'Traffic related particle exposure of NYC adolescents'
Online Lesson Plans:
'What is pollution and what types are there?' (2002)
'What does Erin Brockovich teach us about pollution?' (2003)

Matthew Nanes
Park West HS, Manhattan

Mentors: Professor Martin Stute, Barnard College Dept. of Chemistry & LDEO and Professor H. James Simpson, LDEO
Project: 'Arsenic mobilization in groundwater'
Online Lesson Plans:
'Investigating How Pollutants Travel through Groundwater' (2002)
'Determining the Discharge Rate of a Meandering Stream' (2003)

Summers 2003-2004

William Dugan
The High School for Math and Engineering at CCNY
Mentor: Professor Peter Schlosser, Dept. of Earth and Environmental Sciences
Project: 'Visualization of Transport and Fate of Output from Newtown Creek: A Tracer Release Experiment'
Online Lesson Plans:
'Testing water quality in the laboratory and the field' (2003)
'Testing water quality in the laboratory and the field II' (2004)

F) Scientific Meetings

Over the lifetime of the program, outcomes and results of EMSI-based educational and outreach activities were presented at 3 national meetings and 1 international conference, and at a series of invited lectures. These are listed below.

(a) National ACS Meeting, August 27, 2001, in Chicago, Illinois
'Lessons from History and History Lessons. A Case Studies Exploration of Environmental Impacts,' Leonard W. Fine.

(b) National Educators Workshop: 15th Annual Conference, October 17-20, 2001, at the University of Maryland, College Park
'Materials and Nanotechnology in Engineering the Biosphere,' Leonard W. Fine and Morton Friedman.

(c) GE Lecture, Antwerp, Belgium, February 2, 2002.
'Paradigms Lost and Paradigms Found. Materials for New Designs, and Designing New Materials in the Changing World of Engineering Plastics,' Leonard W. Fine.

(d) National ACS Meeting, April 8, 2002, Orlando, FL
'Undergraduate Research in Chemistry at Columbia,' Leonard Fine and Bhawani Venkataraman.

(e) The SWEENY Lectures, Lehman College, SUNY, Bronx, NY, November, 2002
'The TECHNOSPHERE and the BIOSPHERE - Environmental Studies at the Interface Between Teaching and Research,' Leonard W. Fine.

Journal Publications

Elsa Yan and Kenneth Eisenthal, "Probing the Interface of Microscopic Clay Particles in Aqueous Solution by Second Harmonic Generation", Journal of Physical Chemistry B, p. 6056, vol. 103, (1999). Published

HyeRim Lee, Tatyana Polenova and Ann McDermott, "Lineshape Fitting of Deuterium Magic Angle Spinning Spectra of Paramagnetic Compounds in Slow and Fast Limit Motion Regimes", Journal of the American Chemical Society, p. 6884, vol. 121, (1999). Published

HyeRim Lee, Paul Ortiz de Montellano, Ann McDermott, "Motion of Substrates bound to Cytochrome P450", Biochemistry, p. 10808, vol. 38, (1999). Published

Takashi Hirano, Wei Li, Lloyd Abrams, Paul J. Krusic, M. Francesca Ottaviani, and Nicholas J. Turro, "A Reversible Oxygenation Reaction of a Supramolecularly Persistent Diphenylmethyl Radical Adsorbed on a MFI Zeolite", Journal of the American Chemical Society, p. 7170, vol. 121, (1999). Published

T. Hirano, W. Li, L. Abrams, P. J. Krusic, M. F. Ottaviani, and N. J. Turro, "Supramolecular Steric Effects as a Means of Making Reactive Carbon Radicals Persistent; Quantitative Characterization of the External Surface of MFI Zeolites through a Persistent Radical Probe and a Langmuir Adsorption Isotherm", Journal of Organic Chemistry, p. 1319, vol. 65, (2000). Published

B. D. Dunietz, M. D. Beachy, Y. Cao, D. Whittington, S. Lippard, and R. A. Friesner,, "Large Scale Ab Initio Quantum Chemical Calculation of the Intermediates in the Methane Monooxygenase Catalytic Cycle", JACS, p. 2828, vol. 122, (2000). Published

S. Jockusch, T. Hirano, Z. Liu, and N.J. Turro, "A Spectroscopic Study of Diphenylmethyl Radicals and Diphenylmethyl Carbocations Stabilized by Zeolites", J. Phys. Chem. B, p. 1212, vol. 104, (2000). Published

G. Lem and N.J. Turro, "Radical Pair Recombination Stereoselectivity as a Probe of Magnetic Isotope and Magnetic Field Effects", Chem. Commun, p. 293, vol. , (2000). Published

T. Hirano, W. Li, L. Abrams, P.J. Krusic, M.F. Ottaviani, and N.J. Turro, "Supramolecular Steric Effects as the Means of Making Reactive Carbon Radicals Persistent. Quantitative Characterization of the External Surface of MFI Zeolites through a Persistent Radical Probe and a Langmuir Adsorption Isotherm", J. Org. Chem, p. 1319, vol. 65, (2000). Published

W. Li, X.-G. Lei, G. Lem, A.E. McDermott, and N.J. Turro, "Oxygen and Structural Effects on Silicalite 29Si Spin-Lattice Relaxation Studied by High Resolution 29Si Solid-State NMR", Chem. Mater, p. 731, vol. 12, (2000). Published

H. Lee, T. Polenova, R. H. Beer and A. E. McDermott, "Lineshape Fitting of Deuterium Magic Angle Spinning Spectra of Paramagnetic Compounds in Slow and Fast Limit Motion", J. Am. Chem. Soc., p. 6884, vol. 121, (1999). Published

H. Lee, P. R. Ortiz de Montellano and A. E. McDermott, "Deuterium Magic Angle Spinning Studies of Substrates Bound to Cytochrome", P450 Biochemistry, p. 10808, vol. 38, (1999). Published

D.G. Churchill, B. M. Bridgewater, and G. Parkin, "Modeling Aspects of Hydrodesulfurization at Molybdenum: Carbon-Sulfur Bond Cleavage of Thiophenes by Ansa Molybdenocene Complexes", J. Am. Chem. Soc, p. 178, vol. 122, (2000). Published

C. Kimblin, B. M. Bridgewater, T. Hascall, and G. Parkin, "The Synthesis and Structural Characterization of Bis(mercaptoimidazolyl)hydroborato Complexes of Lithium, Thallium and Zinc", J. Chem. Soc., Dalton Trans, p. 891, vol. , (2000). Published

J. I. Dadap, J. Shan, K. B. Eisenthal, and T. F. Heinz, "Second-harmonic Rayleigh scattering from a sphere of centrosymmetric material", Phys. Rev. Lett, p. 4045, vol. 83, (1999). Published

N.J. Turro, "From Boiling Stones to Smart Crystals: Supramolecular and Magnetic Isotope Control of Radical-Radical Reactions in Zeolites", Acc. Chem. Res., p. 637, vol. 33, (2000). Published

M.F. Ottaviani, P. Favuzza, M. Bigazzi, N.J. Turro and D.A. Tomalia, "A TEM and EPR Investigation of the Binding of Uranyl Ions to Starburst Dendrimers: Potential Use of Dendrimers as Uranyl Ion Sponges", Langmuir, p. 7368, vol. 16, (2000). Published

N.J. Turro, X.-G. Lei, W. Li, Z. Liu, A. McDermott, M.F. Ottaviani, and L. Abrams, "Photochemical and Magnetic Resonance Investigations of the Supramolecular Structure and Dynamics of Molecules and Reactive Radicals on the External and Internal Surface of MFI Zeolites", J. Am. Chem. Soc., p. 11649, vol. 122, (2000). Published

M. Kleinman, J. Flory, D.A. Tomalia and N. J. Turro, "PAMAM Dendrimers as pH Sensitive Release Systems", J. Phys. Chem B, p. 11472, vol. 104, (2000). Published

M. Warrier, N.J. Turro and V. Ramamurthy, "Heavy Cation Effect on Intersystem Crossing between Triplet and Singlet Phenylacyl and Benzyl Radical Pair within Zeolites", Tetrahedron Letts., p. 7163, vol. 41, (2000). Published

S. Uppili, V. Marti, A. Nikolaus, W. Adam, P. S. Engel, N. J. Turro and V. Ramamurthy, "Heavy-Cation-Induced Phosphorescence of Alkanones in Zeolites as Hosts: Induced S1(n,p*) to T1(n,p*) Intersystem Crossing and S0 to T1 (n,p*) Absorption", J. Am. Chem. Soc., p. 11025, vol. 122, (2000). Published

S.R. Qiu, H.-F. Lai, M. J. Roberson, M. L. Hunt, C. Amrhein, L.C. Giancarlo, G. W. Flynn, and J. A. Yarmoff, "A Surface Chemistry Investigation of the Removal of Contaminants in Aqueous Solution by Iron", Langmuir, p. 2230, vol. 16, (2000). Published

Deborah Colodner, Leonard Fine, William Harris and Bhawani Venkataraman-, "The Columbia University Biosphere 2 Center. A Place for Integrative Studies in Chemical Research and Chemical
Education in Defense of Planet Earth", Journal of Chemical Education, p. 144, vol. 78, (2001). Published

L.C. Giancarlo and G. W. Flynn, "Raising Flags: Applications of Chemical Marker Groups to Study Self-Assembly, Chiralty, and Orientation of Interfacial Films by Scanning Tunneling Microscopy", Accounts of Chemical Research, p. 491, vol. 33, (2000). Published

D.G. Yablon, L.C. Giancarlo, and G.W. Flynn, "Manipulating Self-Assembly with Achiral Molecules: An STM Study of Chiral Segregation by Achiral Adsorbate", Journal of Physical Chemistry B, p. 7627, vol. 104, (2000). Published

Stanilaus S. Wong and Louis E. Brus,, "Narrow Mie Optical Cavity Resonances From Individual 100nm Hematite Crystallites", J. Phys. Chem., p. 599, vol. B105,, (2001). Published

K. Adib, N. Camillone III, J.P. Fitts, K.T. Rim, G.W. Flynn, S.A. Joyce, and R.M. Osgood, Jr.,, "CCl4 Chemistry on the Magnetite Selvedge of Single-Crystal
Hematite: Competitive Surface Reactions", Surface Science, p. 127, vol. 497, (2002). Published

N. Camillone III, K. Adib, J.P. Fitts, K.T. Rim, G.W. Flynn, S.A. Joyce, and R.M. Osgood, Jr., "Surface-Termination-Dependence of the Reactivity of Single
Crystal Hematite with CCl4", Surface Science, p. 267, vol. 511, (2002). Published

Gherman, Benjamin F., Barry D. Dunietz, Douglas A. Whittington, Stephen J. Lippard, and Richard A. Friesner, "Activation of the C-H Bond of Methane by Intermediate Q of Methane Monooxygenase: A Theoretical Study", J. Am Chem. Soc., p. 3836, vol. 123, (2001). Published

Brian M. Bridgewater and Gerard Parkin,, "Lead poisoning and the inactivation of 5-aminolevulinate
dehydratase as modeled by the tris(2-mercapto-1-
phenylimidazolyl)hydroborato lead complex, {[Tm-Ph]Pb}[Cl04]", J. Am. Chem. Soc., p. 7140, vol. 122, (2000). Published

Clare Kimblin, David G. Churchill, Brian M. Bridgewater, Jennifer N. Girard, Duncan Quarless, and Gerard Parkin,
"Tris(mercaptoimidazolyl)hydroborato Complexes of Cobalt and
Iron, [TmPh]2M (M = Fe, Co): Structural Comparisons with their
Tris(pyrazolyl)hydroborato Counterparts", Polyhedron, p. 1891, vol. 20, (2001). Published

N.J. Turro, X.-G. Lei, S. Niu, Z. Liu, S. Jockusch, and M.F. Ottaviani, "An EPR Investigation of Persistent Radicals from the Photolysis of p,pÆ-Dialkyl-Substituted Phenyl Benzyl Ketones Adsorbed on MFI Zeolites", Organic Letts., p. 3991, vol. 2, (2000). Published

N.J. Turro, X. Lei, W. Li, Z. Liu and M.F. Ottaviani, "Adsorption of Cyclic Ketones on the External and Internal Surfaces of a Faujasite Zeolite (CaX). A Solid-State 2H NMR, 13C NMR, FT-IR, and and EPR Investigation", J. Am. Chem. Soc., p. 12571, vol. 122, (2000). Published

M.F. Ottaviani, X.-G. Lei, Z. Liu, and N.J. Turro, "Supramolecular Structure and Dynamics of Organic Molecules
Adsorbed on the External Surface of MFI Zeolites. A Direct and
Indirect Computational EPR Analysis", J. Phys. Chem. B, p. 7954, vol. 105, (2001). Published

Lee, Hyerim, Paul R. Ortiz de Montellano and Ann E. McDermott, "Deuterium Magic Angle Spinning Studies of Substrates Bound to Cytochrome P450", Biochem, p. , vol. , (1999). Accepted

E. Y. Yan, Y. Liu, K.B. Eisenthal, "In-situ Studies of Molecular Transfer between Microparticles by Second Harmonic Generation'", J. Phys. Chem. B, p. 8531, vol. 105, (2001). Published

S. R. Qiu, H. F. Lai, M. J. Roberson, M. L. Hunt, C. Amrhein, L.C. Giancarlo, G.W. Flynn, and J. A. Yarmoff

, "A Surface Chemistry Investigation of the Removal of Contaminants in Aqueous Solution by Iron", Langmuir, p. 2230, vol. 16, (2000). Published

D. G. Yablon, Jinsong Guo, David Knapp, Hongbin Fang, and George W. Flynn, "Scanning Tunneling Microscopy Investigation of a Chirally Pure Molecule at the Liquid-solid Interface: Unambiguous Topographic Markers", J. Phys. Chem. B, p. 4313, vol. 105, (2001). Published

N.J. Turro, "Supramolecular organic photochemistry: Contol of covalent bond formation through noncovalent supramolecular interactions and magnetic effects", PNAS, p. 4805, vol. 99, (2002). Published

N.J. Turro, X. Lei, S. Jockusch, W. Li, Z. Liu, L. Abrams, M.F. Ottaviani, "EPR Invesitgation of Persistent Radicals Produced fromthe Photolysis of Dibenzyl Ketones Adsorbed of ZSM-5 Zeolites", The Journal of Organic Chemistry, p. 2606, vol. 67, (2002). Published

T. Hirano, W. Lei, L. Abrams, P.J. Krusic, M.F. Ottaviani, N.J. Turro, "Reversible Oxygenation of a Diphenylmethyl Radical Rendered Supramolecularly Persistent", J. American Chemistry Society, p. 12399, vol. 122, (1999). Published

G. Lem, N.J. Turro, "Radical pair recombination stereoselectivity as a probe of magnetic isotope and magnetic field effects.", Chemical Communications, p. 293, vol. 4, (2000). Published

T. Wada, M. Shikimi, Y. Inoue, G. Lem, N.J. Turro, "First Photosenesitized Enantiodifferentiating Isomerization by Optically Active Sensitizer Immobilized in Zeolite Supercages", The Royal Society of Chemistry, p. 1864, vol. , (2001). Published

Richard A. Friesner, and Barry D. Dunietz, "Large Scale Ab Initio Quantum Chemical Calculations on Biological Systems", Accounts of Chemical Research, p. 351, vol. 34, (2001). Published

Victor Guallar, Benjamin F. Gherman, Stephen J. Lippard, and Richard A. Friesner, "Quantum chemical studies of methane monooxygenase: comparison with P450", Current Opinion in Chemical Biology, p. 236, vol. 6, (2002). Published

Enrique R. Batista and Richard A. Friesner, "A Self-Consistent Charge Embedding Methodology for Ab Initio
Quantum Chemical Cluster Modeling of Ionic Solids and
Surfaces: Application to the (001) Surface of Hematite (_-
Fe2O3),", Journal of Physical Chemistry, p. , vol. , ( ). Accepted

K. Adib, D.R. Mullins, G. Totir, N. Camillone III, J.P. Fitts, K.T. Rim, G.W. Flynn and R.M. Osgood, Jr, "Dissociative Adsorption of CCl4 on the Fe3O4 (111)-(2x2)
Selvedge of a-Fe2O3 (0001)", Surface Science, p. 113, vol. 524, (2002). Published

S. Jockusch, Z. Liu, M.F. Ottaviani, and N.J. Turro, "Time-Resolved CW-EPR Spectroscopy of Powdered Samples:
Electron Spin Polarization of Nitroxyl Radical Adsorbed on NaY
Zeolite, Generated by the Quenching of Excited Triplet Ketones", J. Phys. Chem. B., p. 7477, vol. 105, (2001). Published

T. Wada, M. Shikimi, Y. Inoue, G. Lem, and N.J. Turro, "First Photosensitized Enantiodifferentiating Isomerization by Optically Active Sensitizer Immobilized in Zeolite Supercages", Chem. Commun., p. 1864, vol. , (2001). Published

N.J. Turro, "Supramolecular Organic Photochemistry. Control of Covalent
Bond Formation through Non-Covalent Supramolecular
Interactions and Magnetic Effects", Proc. NatÆl, Acad. Sci., p. 4805, vol. 99, (2002). Published

N.J. Turro, X.-G. Lei, S. Jockusch, W. Li, Z. Liu, L. Abrams, and M.F. Ottaviani, "An EPR Investigation of Persistent Radicals Produced from the
Photolysis of Dibenzyl Ketones Adsorbed on ZSM-5 Zeolites", J. Org. Chem, p. 2606, vol. 67, (2002). Published

T. M?ller, D.G. Yablon, R. Karchner, D. Knapp, M.H. Kleinman, H. Fang, C.J. Durning, D.A. Tomalia, N.J. Turro and G.W. Flynn, "AFM Studies of High Generation PAMAM Dendrimers at the Liquid/Solid Interface", Langmuir, p. 7452, vol. 18, (2002). Published

N.J. Turro, "From Molecular Chemistry to Supramolecular Chemistry to Superdupermolecular Chemistry. Controlling Covalent Bond Formation through Non-Covalent and Magnetic Interactions", Chem. Comm, p. 2279, vol. , (2002). Published

J. Shailaja, P. H. Lakshminarasimhan, A. R. Pradhan, R. B Sunoj, S. Jockusch, S. Karthikeyan, S. Uppili, J. Chandrasekhar, N. J. Turro, and V. Ramamurthy, "Alkali Ion-Controlled Excited-State Ordering of Acetophenones Included in Zeolites: Emission, Solid-State NMR, and Computational Studies", J. Phys. Chem. A, p. 3187, vol. 107, (2003). Published

N.J. Turro, S. Jockusch, and X.-G. Lei, "Supramolecular Effects on the Dynamics of Radicals in MFI Zeolites: A Direct EPR Investigation", J. Org. Chem, p. 5779, vol. 67, (2002). Published

N. J. Turro, S. Jockusch, and X.-G. Lei, "Supramolecular Effects on the Dynamics of Radicals in MFI Zeolites: A Direct EPR Investigation", Journal of Organic Chemistry, p. 5779, vol. 67, (2002). Published

N. J. Turro, "From Molecular Chemistry to Supramolecular Chemistry to Superduper Molecular Chemistry. Controlling Covalent Bond Formation through Non-Covalent and Magnetic Interactions", Chemical Communications, p. 2279, vol. , (2002). Published

J. Shailaja, P. H. Lakshminarasimhan, A. R. Pradhan, R. B. Sunoj, S. Jockusch, S. Karthikeyan, S. Uppili, J. Chandrasekhar, N. J. Turro, and V. Ramamurthy, "Alkali Ion-Controlled Excited-State Ordering of Acetophenones Included in Zeolites: Emission, Solid-State NMR, and Computational Studies", Journal of Physical Chemistry A, p. 3187, vol. 107, (2003). Published

J. Sivaguru, S. Jockusch, N. J. Turro, and V. Ramamurthy, "Photoisomerization of 2,3-Diphenlycyclopropane-1-Carboxylic Acid Derivatives", Photochemical and Photobiological Sciences, p. 1101, vol. 2, (2003). Published

G. G. Totir, G. Y. Lee, and R. M. Osgood, Jr., "Photoinduced-Reaction Dynamics of Halogenated Alkanes on Iron-Oxide Surfaces: CH3I", Journal of Physical Chemistry, p. , vol. , (   ). Submitted

G. Y. Lee, G. G. Totir, G. W. Flynn, and R. M. Osgood, "A TPD Study of CBr2Cl2 Surface Chemistry on the Fe3O4(111)-(2x2) Selvedge of -Fe2O3(0001)", Surface Science Letters, p. , vol. , (   ). Submitted

J. I. Dadap, J. Shan, and T. F. Heinz, "Theory of Second-Harmonic Generation from a Sphere of Centrosymmetric Material: Small Particle Limit", Journal of the Optical Society of America B, p. 1328, vol. 21, (2004). Published

J. P. Fitts, X. Shang, G. W. Flynn, T. F. Heinz, and K. B. Eisenthal, "Electrostatic Surface Charge at Aqueous/_-Al2O3 Single-Crystal Interfaces as Probed by Optical Second-Harmonic Generation", Journal of Physical Chemistry B, p. , vol. , (   ). Accepted

J. P. Fitts, M. L. Machesky, D. J. Wesolowski, X. Shang, J. D. Kubicki, G. W. Flynn, T. F. Heinz, and K. B. Eisenthal, "Second-Harmonic Generation and Theoretical Studies at the Aqueous/_-TiO2 Interface", Chemical Physics Letters, p. , vol. , (   ). Submitted

Dalia G. Yablon, David Wintgens, and George W. Flynn, "Odd/Even Effect in Self-Assembly of Chiral Molecules at the Liquid-Solid Interface: An STM Investigation of Coadsorbate Control of Self-Assembly", Journal of Physical Chemistry B, p. 5470, vol. 106, (2002). Published

David Wintgens, Dalia G. Yablon, and George W. Flynn, "Packing of HO(CH2)14COOH and HO(CH2)15COOH on Graphite at the Liquid-Solid Interface Observed by Scanning Tunneling Microscopy: Methylene Unit Direction of Self-Assembly Structures", Journal of Physical Chemistry B, p. 173, vol. 107, (2003). Published

Thomas Mueller, Dalia G. Yablon, Ryan Karchner, David Knapp, Mark H. Kleinman, Hongbin Fang, Christopher J. Durning, Donald A. Tomalia, Nicholas J. Turro, and George W. Flynn, "AFM Studies of High-Generation PAMAM Dendrimers at the Liquid/Solid Interface", Langmuir, p. 7452, vol. 18, (2002). Published

Kwang Taeg Rim, Jeffrey P. Fitts, Thomas Mueller, Kaveh Adib, Nicholas Camillone III, Richard M. Osgood, S. A. Joyce, George W. Flynn, "CCl4 chemistry on the reduced selvedge of a alpha-Fe2O3(0001) surface: a scanning tunneling microscopy study", Surface Science, p. 59, vol. 541, (2003). Published

Kwang Taeg Rim, Thomas Mueller, Jeffrey P. Fitts, Kaveh Adib, Nicholas Camillone III, Richard M. Osgood, Enrique R. Batista, Richard A. Friesner, S. A. Joyce, and George W. Flynn, "Scanning Tunneling Microscopy and Theoretical Study of Competitive Reactions in the Dissociative Chemisorption of CCl4 on Iron Oxide Surfaces", Journal of Physical Chemistry B, p. 16753, vol. 108, (2004). Published

Books or Other One-time Publications

Dalia G. Yablon, Hongbin Fang, Leanna C. Giancarlo,
and George W. Flynn, "'Raising Flags: Chemical Marker Group Probes of Self-assembly and Chirality at Liquid-solid Interfaces'", (2002). Book, Published
Editor(s): Janice Hicks
Collection: The Physical Chemistry of Chirality
Bibliography: The Physical Chemistry of Chirality, ACS Symposium
Series, 810, pp205-224, Ed. Janice Hicks, American
Chemical Society, Washington, DC, 2002

Web/Internet Site

URL(s):
http://www.cise.columbia.edu/emsi/
Description:

Other Specific Products

Contributions

Contributions within Discipline:

One contribution of our EMSI work within our discipline is in resolving the long-standing controversy of the location of zero charge for hematite/water interfaces. We have also demonstrated that a new and powerful method (Second Harmonic Generation) can be used to measure the transfer of molecules between microscopic particulates in water. The transfer between particles can not be directly studied by other methods.

EMSI supported research has been recognized by the discipline of Chemistry through a feature research article in Chemical & Engineering News (summer 2000). This journal is widely distributed among chemists and researchers involved in environment studies.

The general body of research produced by EMSI PI Nicholas Turro was recognized by his selection to receive the Gibbs Medal by the Chicago Section of the American Chemical Society in May 2000. He also received invitations to present EMSI supported research at the Gordon Conference on Interfaces, the Gordon Conference on Physical Organic Chemistry and the Gordon Conference on Supramolecular Chemistry.

EMSI research has been successful in identifying a number of phases of iron oxide surfaces using Scanning Tunneling Microscopy. The rich complexity of these surfaces is responsible for a variety of chemical transformations that take place when organic pollutants are adsorbed on such surfaces. Reactions of CCl4- and other organic species are being studied with STM and a variety of surface science techniques.

This work is providing a detailed, molecular-level chemical and structural characterization of these reactions with a specific surface termination of hematite. This work fills gaps in the general understanding of halocarbonûmetal oxide surface chemistry. Our studies have identified various chemical pathways for the degradation of carbon tetrachloride on iron oxide surfaces and should lead to the identification and characterization of specific reaction sites.

Contributions to Other Disciplines:

Our EMSI work on transition metal oxides of direct environmental relevance is also contributing to our knowledge of nanoscale effects in the electrical and magnetic properties of these same transition metal oxides, which is a subject of deep current interest in microelectronics materials science. Correlated electron motion is far more important in these oxides than in most other materials, and simple models often fail to predict properties as discussed above. It is a rich, poorly understood, and inviting area in which to work. This work also directly supports the NSF MRSEC effort on thin films composed of oxide nanoparticles.

We are providing kinetic data and surface charge data to be used in models of metal oxide structure and to describe the role of molecular species transport between soil particles in the spreading of various chemical species.

The basic research work being done under the EMSI program is of value in achieving a description of important aspects of soil chemistry and potentially assisting in pollution cleanup efforts.

EMSI work has contributed to providing fundamental knowledge of the inorganic chemistry that is required to solve environmental pollutant issues. These studies have included demonstrating that zero valent iron complexes are capable of abstracting chlorine from carbon tetrachloride.

Contributions to Human Resource Development:

Contributions to Human Resource Development:
See Section 4, Education/Outreach Activities above.

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

The research reported in the paper entitled íºTris(2-mercapto-1-phenylimidazolyl)hydroborato Complexes of Lead, {[TmPh]Pb}[ClO4] and [TmPh]2Pb: Relevance to Lead Poisoning and the Inactivation of âÑ-Aminolevulinate Dehydrataseí¿ (Brian M. Bridgewater and Gerard Parkin, J. Am. Chem. Soc. 2000, 122, 7140-7141) is of particular relevance the most commonly encountered toxic metal pollutant in the environment. As such it provides an important contribution to public health issues.

The website (http://turmac13.chem.columbia.edu/) contains a Power Point program describing the connection between mining in the classical Greek period (600-300 BC), current environment pollution problems and chemical and chemical engineering attempts to solve these pollution problems. A web site for General Chemistry C1404y, Spring 1999 was created as a vehicle for discussing environmental issues related to Chemistry. In particular the environmental challenges created by centuries of mining were highlighted. This site was linked to articles selected by Professor Turro and published in Chemical & Engineering News and in the New York Times. The URL for this web site is: http://www.columbia.edu/itc/chemistry/chem-c1404/.

Categories for which nothing is reported:

Any Product

Contributions: To Any Resources for Research and Education

EMSI Research Activities

Major Research Activities

Columbia University's traditional strengths in the chemical and geological sciences were united to form the multi-investigator Environmental Molecular Sciences Institute (EMSI) in 1998. Columbia's EMSI consisted of 7 senior investigators in a number of academic departments (Chemistry, Chemical Engineering, Applied Physics, Electrical Engineering, Environmental Sciences (at Barnard College), Earth and Environmental Science (DEES)) with the Columbia Earth Institute and the Lamont-Doherty Earth Observatory (L-DEO). This effort primarily addressed fundamental chemical questions associated with subsurface contaminants, particularly those on porous or particulate substrates. The focus of the research was aimed at achieving a molecular level understanding of the microscopic creation and loss of interfacial chemical sources and sinks of contaminant species. Work in this area was performed on molecular, microscopic and macroscopic scales. Training of scientists to work across these length scales in both theory and experiment spread over multiple academic and intellectual disciplines is critical in developing techniques that will lead to the evolution of strategies linking molecular behavior to geochemical observations.

The Institute's activities were divided into three Research Areas corresponding to the different length scales of importance to environmental science: atomic (a few angstroms); microscopic (0.01 - 10 µm); and macroscopic (≥ 1 km); and one Education/Outreach Area. Research Area A on Molecular-Scale Processes on Mineral Surfaces and in Pores was led by Richard Osgood and focused on structure and dynamics at gas/solid interfaces. Research Area B on Fundamental Chemical Reaction and Transport Processes in Microscopic Porous Media was headed by Nicholas Turro. This Area focused on molecular and supramolecular processes such as equilibria and kinetics, as well as transport in aqueous pseudophases and liquid/solid porous media. Finally, Research Area C on Macroscopic Chemical Transport and Dispersal, headed by Peter Schlosser (L-DEO), concentrated on the large-scale transport properties of environmental tracer molecules. The entire program was strongly collaborative with and built on facilities and staff at DOE's Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL). At each stage of the experimental process, collaborative theoretical modeling studies were conducted at both Columbia and PNNL. Columbia's major research center in the geological sciences, the Lamont-Doherty Earth Observatory (L-DEO), was a major contributor to this effort through its extensive staff and facilities. The program encompassed a basic experimental and theoretical molecular core, modeling and measurements of species transport, and microscopic studies of reactive migration in porous media. It was, of necessity, highly interdisciplinary, including faculty from five academic departments and extensive collaborations with the Chemical Structure and Dynamics; the Theory, Modeling, Simulation; and the Environmental Dynamics and Simulation Groups at PNNL. In addition to receiving NSF and DOE funds for the research, the EMSI also obtained matching funds from Columbia for instrumentation, for the education/outreach program, and for graduate and undergraduate fellowships.

A particularly successful feature of the EMSI program, which has now been copied by both the MRSEC and NSEC centers at Columbia, was the work of the "Bridging Post-doctoral Fellows." Based on a proposal written by EMSI Director Professor Flynn in 1999, the Camille and Henry Dreyfus Foundation awarded the EMSI program at Columbia a two year post-doctoral fellowship for environmental studies in the Chemical Sciences. A second Dreyfus Foundation award was made in 2002. In addition the EMSI program used an equivalent amount of its matching funds from Columbia University to finance a second such fellowship each year of the program (the EMSI Langmuir Post-doctoral Fellowship). The first Langmuir Fellowship was awarded to Dr. Jeffery Fitts; a second such fellowship was awarded to Dr. Brian Mailloux (Ph.D. Princeton, Geociences). The fellows did an excellent job of integrating the research activities of several groups within the EMSI program. They worked jointly with the Eisenthal, Flynn, Heinz, Osgood, Turro, and Schlosser research groups to unite their efforts in iron oxide chemistry and transport in porous material on both a micro and a macro scale. Fellows met regularly (about once per month) on Columbia's Lamont-Doherty Earth Observatory campus with the EMSI Executive Committee (Flynn, Osgood, Pfirman, Turro, and Schlosser) as a group to review progress and to seek alternative routes to the solution of any scientific problems that may have arisen. In addition each of the fellows attended regular group meetings of the individual principal investigators. Each had an office both on the Columbia main campus and at the Lamont-Doherty Earth Observatory. Communication among groups with widely divergent approaches to environmental problems was significantly improved and the integration of the scientific efforts in these groups noticeably enhanced.

I. Research Area A: Molecular Scale Processes on Mineral Surfaces

A) Application and Development of Theoretical Tools: (PI's Bruce Berne and Richard Friesner)

Calculations for large iron oxide clusters were successfully converged. The convergence of the ionization potential of these clusters was examined as a function of cluster size and shape. Quite large clusters were required to achieve convergence (on the order of 100 atoms). Our Poisson-Boltzmann continuum solvation code was modified to handle the solid-liquid interface. Modeling pollutants adsorbed on iron oxide surfaces was attacked directly.

B) UHV Surface Probes of Iron Oxide: (PI Richard Osgood)

Research efforts in this part of the EMSI program were focused on molecular-level studies of the interactions and reactions of environmentally relevant molecules, specifically halogenated hydrocarbons, on clean, well-characterized surfaces of iron oxide. These studies provided molecular-level reaction mechanism and structural information regarding the chemistry relevant to environmental processes as diverse as electron-transfer reactions on metal-oxide-containing mineral surfaces and photochemistry of organics absorbed on particulates. Our efforts focused on obtaining detailed data of value to researchers involved in modeling the interactions of molecules on environmental surfaces at the atomic level, as well as those modeling chemistry on the kilometer scale in the earth's crust and atmosphere.

Multitechnique ultrahigh vacuum (UHV) surface science studies of the surface structure, thermal chemistry and photoinitiated chemistry of halogenated hydrocarbons (HHC's) on several iron oxide surfaces were performed. The complement of experimental techniques used included low energy electron diffraction (LEED), Auger electron spectroscopy (AES), scanning tunneling microscopy (STM), secondary ion mass spectrometry (SIMS), mass-resolved time-of-flight (TOF) photofragment angular distribution measurements, synchrotron soft x-ray photoelectron spectroscopy (SXPS) and temperature programmed reaction and desorption (TPR/D) measurements.

C) Diffusion and Reactivity on Surfaces: (PI Irving Herman)

The Herman group has characterized and analyzed the four basic binary iron oxide nanoparticles: $Fe_{1-x}O$ (wustite), Fe_3O_4 (magnetite), γ-Fe_2O_3 (maghemite), and α-Fe_2O_3 (hematite), and the assembly of these particles. Small particles and nanoparticles of these were synthesized by other groups on campus and shared with the Herman group. The optical and spectral properties of these oxides were investigated in order to make precise use of them in future environmental applications. Raman scattering characterization and analysis of these particles was used to identify elementary excitations within the particles.

D) Scanning Tunneling Microscopy of Environmentally Relevant Surfaces: (PI George Flynn)

Ultimately, most problems in sub-surface contamination usually involve chemical reactions taking place at interfaces. The structure and dynamics of both physisorbed and chemisorbed species at solid interfaces, often in the presence of water, thus become of great significance in determining the fate of sub-surface contaminants. At Columbia, a state-of-the-art temperature tunable UHV STM was used to investigate the microscopic structure of oxide surfaces. A knowledge of the structure and behavior of these surfaces before they are exposed to any contaminant or liquid solvent is crucial in obtaining a molecular level picture of the environmental impact of sub-surface chemistry and transport.

Ambient or air based STM instrumentation was also used to investigate the changes in surface morphology that take place when a piece of iron foil is exposed to a solution containing impurities such as selenium, chromium, and uranium ions. While the UHV experiments described above provided information concerning the structure and reactivity of model oxide surfaces under controlled conditions, the ambient, air based STM allowed us to look at near real world sample conditions. Direct probes of the liquid-solid interface were possible with this instrumentation.

E) Optical Probes of Liquid-Solid Interfaces (PI's Kenneth Eisenthal and Tony Heinz)

Optical probe work in the EMSI program involved the development of two spectroscopic techniques for examining interfaces between two dense media, such as those commonly formed between water and mineral surfaces under natural conditions. The approach pursued by the Columbia EMSI relied on the use of nonlinear optical techniques based on the second-order nonlinear response. These methods, which exploit fundamental symmetry properties, are known to be sensitive to single molecular monolayers at buried interfaces between centrosymmetric materials, such as most liquids and commonly found solids. The focus of this optical probe work was the oxides of Fe, Al and Si because of their importance in soil chemistry as sites of adsorption and chemical reaction of ionic and neutral aqueous species. The interfaces formed between water and the (012) and (001) surfaces of hematite and corundum single crystals were investigated using optical second harmonic generation (SHG) as an interface probe.

II. Research Area B: Fundamental Chemical Reaction and Transport Processes in Microscopic Porous Media

A) Molecular Probes of Adsorption in Porous Materials: (PI Nicholas Turro)

Photochemical and spectroscopic methods were employed to determine the structure and dynamics of adsorbed species on model porous solids (zeolites) and ionic polymers (dendrimers). This research provided insight into the nature and mechanism of adsorption at interfaces and should be useful in the design of porous solid systems and water soluble polymers that can be used for environmental benefaction, remediation and stabilization programs. The photochemistry of organic molecules adsorbed on zeolite systems also serves as a model for surface assisted redox chemistry and molecular transport of material through small pore, oxide laden soils exposed to sunlight.

B) Synthesis and Characterization of Oxide Nanocrystals: (PI Louis Brus)

This EMSI work focused on the magnetite phase (Fe_3O_4) of iron oxide. Magnetite (more than hematite) is thought to be the responsible catalytic and reactive iron oxide in ground water chemical processes. Much of the iron in the earth's surface layers is present as magnetite; in oxidizing environments it slowly oxidizes, first to maghemite and finally to hematite. These efforts were aimed at the characterization of surface reactions on 10nm particles of magnetite under aqueous conditions at ambient temperature.

C) Inorganic Synthesis and Characterization of Environmentally Relevant Materials: (PI Ged Parkin)

As part of the effort to understand the interaction of pollutants with a variety of surfaces (*e.g.,* iron and iron oxides) the EMSI program has pursued an investigation of the synthesis and characterization of small inorganic molecules. The techniques used in these studies involve inert atmosphere syntheses and product characterization using NMR spectroscopy and single crystal X-ray diffraction.

III. Research Area C: Macroscopic Chemical Transport and Dispersal

A) Macroscopic Chemical Transport and Dispersal: (PIs Peter Schlosser and James Simpson)

High concentrations of dissolved arsenic in ground water at many locations have important public health implications. As part of the EMSI program, Columbia faculty and students have participated in several field sampling efforts, including one in Winthrop, ME, a former landfill classified as a Superfund site approximately 15 years ago. United Technologies Corporation (UTC) operates a large groundwater pump-and-treat facility at Winthrop, designed to remove toxic organic compounds (eg dimethyl formamide), which also accomplishes the removal of the high levels of dissolved As present there. Groundwater samples were collected at a number of locations at the site, and chemical analyses including $^3H/^3He$ dating and tracer species (NaCl, NaBr and SF_6) were performed. As part of the tracer experiments, substantial quantities of "Oxygen Release Compound" (ORC, which is primarily magnesium peroxide) were injected by subcontractors of UTC in an attempt to oxidize ground waters moving past this "barrier" towards the single groundwater extraction well. The experimental design was intended to cause oxidation of soluble Fe(II) to insoluble Fe(III), resulting in precipitation of nearly all the dissolved Fe, which would co-precipitate or sorb dissolved As and, thus, greatly reduce transport of dissolved arsenic beneath the landfill.

Major Research Findings

I. Research Area A: Molecular Scale Processes on Mineral Surfaces

A) Application and Development of Theoretical Tools: (PIs Bruce Berne and Richard Friesner)

A new self-consistent embedding technique to model ionic solids has been applied to compute the work function of hematite. The computed value for the work function is in good agreement (within a few tenths of an electron volt) with the best experimental estimates, considerably closer to the experimental value than that of Scheffler and coworkers (whose results deviate from the best experimental estimates by approximately 1eV). Efforts to study the chemistry of carbon tetrachloride on magnetite were successful. Results for the binding of CCl_2 in various surface sites, which are in good qualitative agreement with the experimental results, were obtained.

B) UHV Surface Probes of Iron Oxide: (PI Richard Osgood)

1. Thermal Chemistry:

Temperature program desorption studies were used to characterize the surface chemistry which occurs between CCl_4 and the Fe_3O_4(111) selvedge (overlayer) of single crystal α-Fe_2O_3 (0001). Six separate desorption events were clearly observed and four desorbing species have been identified: CCl_4, $OCCl_2$, C_2Cl_4, and $FeCl_2$. These indicate that $OCCl_2$, C_2Cl_4 and $CC1_4$ are produced in reactions involving the same precursor, CCl_2. Three reaction paths compete for the CCl_2 precursor: oxygen atom abstraction (for $OCCl_2$), molecular recombinative desorption (for CCl_4) and associative desorption (for C_2Cl_4). During the TPR/D temperature ramp, the branching ratio was observed to depend upon temperature and the availability of reactive sites. The data are consistent with a rich site-dependent chemistry.

Synchrotron x-ray photoemission spectroscopy studies showed a chemistry on the Fe_3O_4 (111)-(2×2) selvedge of natural hematite consistent with the above results. These studies were done on the Oak Ridge beamline (Dave Mullins) at the NSLS, Brookhaven National Lab. The important aspect of the SXPS measurements is that they are able to observe specific reaction products directly, while they remain adsorbed on the surface. In addition, SXPS provides oxidation state information. In particular, we have found that CCl_4 dissociates on the Fe_3O_4 surface at 100 K producing chemisorbed Cl and adsorbed CCl_2. Companion TPD results showed that the large majority of the dissociatively adsorbed CCl_2 fragments extract lattice oxygen and desorb as phosgene at >275 K. However, the SXPS spectra showed no evidence for the formation of surface-bound phosgene at 100 K, indicating that its formation involves at least two steps. The first step, dissociation of CCl_4, is spontaneous at 100 K, whereas the second, oxygen atom abstraction to form phosgene, requires thermal excitation. Cl chemisorption yielded two separate species, the mono- and dichloride termination of surface iron sites. The identification of these two surface terminations is based on the coverage dependence and the surface temperature history of their Cl $2p_{3/2}$ peak intensity. For example, heating to >450 K allows the monochloride to transform into iron dichloride, indicating Cl adatom mobility at these temperatures.

Room temperature Auger Electron Spectroscopy measurements were also carried out in collaboration with Steve Joyce at PNNL (now at LANL). These have shown the important result that the reactivity of the hematite surface is critically dependent on the nature of the termination. In contrast to the high reactivity of the Fe_3O_4 (111) surface, certain FeO and α-Fe_2O_3 surface terminations do not react with CCl_4. Specifically, ultrahigh vacuum Auger electron spectrometric measurements were used to measure the uptake of chlorine following the room temperature exposure of single crystal hematite to CCl_4. The surface chemistry of two specific surface phases formed on the basal plane of α-Fe_2O_3were compared: the Fe_3O_4(111)-(2X2) "selvedge" and the α-Fe_2O_3/FeO "biphase." For Fe_3O_4(111)-(2X2) saturation levels of Cl, estimated to be ~ 75 % of a monolayer, were attained at relatively low CCl_4 exposures. Carbon uptake was well below that expected for simple stoichiometric dissociative chemisorption, consistent with desorption of organic products during the surface reaction. Low energy electron diffraction measurements suggested that at least two types of α-Fe_2O_3/FeO biphase structures can be formed depending upon surface preparation procedures. For either of these biphases, no significant Cl or C uptake was observed. The marked difference between the reactivity of the Fe_3O_4 and biphase surfaces suggests that the active site for the dissociative adsorption of CCl_4 on Fe_3O_4(111)-(2x2) is comprised of both an iron cation and an oxygen anion with a surface-normal oriented dangling bond that is uncapped by iron cations. Electron stimulated and thermal desorption of Cl from the saturated Fe_3O_4(111)-(2x2) selvedge was also observed. The surface reactions of CCl_4 with the α-Fe_2O_3/FeO biphase structure have also been investigated at 100 K. CCl_4 dissociatively adsorbs on this surface as well, indicating that the dissociation of CCl_4 on the iron-oxide surfaces does not necessarily depend on the availability of both iron cations and oxygen anions on the surface.

2. Coadsorbate Studies – Water and Hydrocarbons:

The sequential adsorption of D_2O and CCl_4 on single crystal iron oxide surfaces was investigated using temperature programmed desorption (TPD). α-Fe_2O_3 natural single crystals were subjected to sputter-anneal cycles in UHV, producing a surface selvedge of Fe_3O_4 (111)-2x2, which was exposed to various coverages of D_2O, followed by subsequent exposure of the resulting surface to CCl_4. Preliminary TPD studies of adsorbed D_2O indicated a rich surface chemistry, with multiple desorption events extending to temperatures as high as ~ 800 K, consistent with the dissociative adsorption of D_2O on the Fe_3O_4(111) surface. Previous TPD and XPS results described above had suggested that in the absence of D_2O, CCl_4 dissociatively adsorbed on Fe_3O_4(111), producing chemisorbed Cl and CCl_2, which upon subsequent heating of the surface abstracted lattice iron and oxygen atoms to desorb as $FeCl_2$ and $OCCl_2$, respectively. The presence of adsorbed D_2O was observed to substantially suppress the formation of $FeCl_2$ and $OCCl_2$, suggesting that D_2O fragments block the reactive surface sites.

3. UV Photochemistry:

The adsorption, thermal chemistry and photoreaction dynamics of methyl iodide on the (2×2) magnetite termination of natural single-crystal hematite were investigated by time-of-flight quadrupole mass spectrometry (TOF-QMS), temperature programmed desorption (TPD) and Auger electron spectroscopy (AES). The methyl-iodide thermal desorption spectra, taken after dosing the (2×2) surface at 100 K, show a multiple-peak coverage-dependent behavior, consistent with the presence of several distinct adsorbed phases, along with defect-mediated dissociative chemisorption in the first monolayer. At >1 ML, methyl iodide forms a metastable physisorbed second layer, which desorbs at 148 K, but at higher coverage converts to a layer, which desorbs at 170 K. In the presence of low-fluence-pulse irradiation at 248 nm, angle-resolved TOF-QMS measurements show that 1.6 eV and 0.3 eV CH_3 fragments are ejected from the adsorbate surface; these fragments originate from direct photodissociation and dissociative photoinduced electron transfer, respectively. The angular distribution of each of these energetic photoejected fragments have characteristic angular distributions, peaked at ~0° with respect to the surface normal. These results and the coverage–dependent relative intensities suggest that the predominant orientation in the first monolayer of the adsorbed CH_3I is normal to the crystal plane.

C) Diffusion and Reactivity on Surfaces: (PI Irving Herman)

1. Spectroscopy

Wustite and maghemite nanoparticles were obtained from Professor O'Brien's group in Applied Physics. The wustite particles were 12 nm in diameter and dissolved in hexane. The maghemite particles were 12 nm in diameter, capped by oleic acid, and dissolved in octane. All particles were deposited both on a glass cover slide and on a silicon substrate. Raman spectroscopy was performed with the 488 nm line of an argon-ion laser and the 647.1 nm line of a krypton-ion laser. In all cases no Raman signal was detected from the samples. A broad luminescence occurred for both excitation sources but was most prevalent in the argon laser studies with the particles on glass. Still, the luminescence did not overwhelm the Raman signal since the silicon substrate Raman signal was detected for most of the investigations on silicon. All of these studies were done at room temperature. Raman spectra of the particles on the silicon substrate were also attempted at low temperatures (-170 C). The low temperatures neither diminished the luminescence nor enhanced the (missing) iron oxide Raman signal. Previous work has reported Raman spectra from all four basic binary iron oxides, most often using a He-Ne laser (632.8 nm); however, the number of studies in this area have been limited. The effort described here as well as that in other EMSI Columbia labs (Brus) has been unable to duplicate the published results.

2. Assembly

A uniform dc electric field was used (to attract the fraction of maghemite (γ-Fe_2O_3) nanoparticles that are charged) to form films of controllable and equal thickness on both electrodes. Maghemite nanoparticles were prepared with oleic acid capping ligands. Solutions of these dots (usually ~6 nm diameter) with densities 10^{12} - 10^{13} dots/cc were prepared in hexane. Two electrodes, usually rectangular sections of Si wafers, coated over 0.8 × 1.4 cm with10 nm Ti and then ~150 nm Au, and separated by ~1.2 mm, were submerged in a beaker with this solution. DC voltages up to 500 V were applied across the electrodes at room temperature in the dark, with solvent added as needed to counter any evaporation. DC current was monitored during runs, and the deposits on the electrodes were examined afterwards.

Uniform, apparently identical films formed on both electrodes, which suggests equal densities of positively and negatively charged particles. No deposit was formed without a voltage being applied. Visible microscopy showed that the film was rough when it was grown rapidly, but the roughness decreases when the film was grown at a slower pace. The thickness of the film formed in a 50 V bias experiment was 0.141 micron (20 minute deposition) and the roughness was measured to be 0.0162 micron, which is about 11% of the thickness. The initial deposition rate was ~ (0.0024 nm/s) V(in volts) n(in 4.0×10^{12} dots/cc), per electrode. After drying, these films did not dissolve in hexane as do those formed by dry casting. From conductivity measurements, ~11.4% of the nanocrystals are charged, half positively and half negatively. Over 4 dots were deposited for each elementary charge collected.

D) Scanning Tunneling Microscopy of Environmentally Relevant Surfaces (PI George Flynn)

1. UHV-STM Studies of CCl_4 at Fe-oxide/UHV Interfaces

Recently, the reactions of CCl_4 on magnetite and biphase selvedges produced on an α-Fe_2O_3(0001) single crystal in UHV have been characterized with Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy (AES). (See section IB above) The results of these studies indicate that CCl_4 reacts with the magnetite selvedge to produce surface-bound CCl_2 intermediates and Fe-Cl species. XPS results suggest that this reaction occurs spontaneously at temperatures as low as 100K. As all carbon-containing reaction products desorb below 300 K, dosing CCl_4 on the Fe_3O_4(111) selvedge at room temperature leaves only the Fe-Cl species on the surface. In addition, TPD and AES results indicate that this reaction is too extensive (~75% of surface area) to be limited to defect sites only, and thus, must occur at regular surface sites. Finally, AES studies show no chlorine uptake on the biphase selvedge upon dosing CCl_4 at room temperature, thereby indicating no reaction (except for a possible reversible chemisorption), where it is assumed (based on LEED measurements) that this surface is comprised of wustite and hematite domains. These results along with information regarding the surface structure provided in the literature were used to explain the observed reactivity in terms of unique structural attributes of the magnetite surface However, in order to identify the reactive sites and determine why neither the remaining ~20-25% of the (nominal) magnetite selvedge nor biphase terminated α-Fe_2O_3(0001) react with CCl_4 requires atomically resolved images of these surfaces before and after CCl_4 exposure.

As part of the EMSI program, the degradation of CCl_4 on the reduced selvedge of a natural single crystal α-Fe_2O_3(0001) surface was studied using Scanning Tunneling Microscopy. Based on the images obtained before dosing CCl_4 vapor, approximately 80–90% of the reduced surface exhibits a Fe_3O_4(111)-2×2 termination, while the remaining 10–20% is terminated by a 1×1 structure probably arising from the close-packed oxygen plane of a continuous underlying Fe_3O_4(111) selvedge. In agreement with recently reported TPD and AES studies, (see section IB above) STM images obtained after dosing and flashing the surface to 600 K show reaction products only on the Fe_3O_4(111)-2×2 terminated areas of the surface. The same TPD and AES studies indicate that the additional features seen in STM images upon dosing must arise from chlorine species produced by CCl_4 degradation. In agreement with recent XPS measurements, (see section IB above) two distinct chlorine adsorption sites were identified, the position atop lattice protrusions and three-fold hollow sites. High-resolution STM images show marked electronic and/or geometric differences between the two chlorine species. This site specific chemistry together with the site specificity in dissociative Cl_2 adsorption (as observed in separate STM experiments) strongly suggests the imaged surface consists of a $Fe_3O_4(111)\text{-}2 \times 2$ surface exhibiting an unreconstructed bulk termination exposing ¼ monolayer of iron atoms over a hexagonal close-packed oxygen layer. In addition, the I/V characteristics of the unreacted substrate are in agreement with theoretical predictions for this iron-terminated surface. The observation of a three-fold hollow site for chlorine adsorption upon CCl_4 but not Cl_2 dosing is in agreement with previous suggestions that the single uncapped oxygen atom per unit cell available in this termination is abstracted during phosgene formation. The availability of both oxygen and iron species appears to be important in driving the reaction that produces $OCCl_2$ from CCl_4 adsorption on a clean iron oxide surface.

E) Optical Probes of Liquid-Solid Interfaces: (PIs Kenneth Eisenthal and Tony Heinz)

Understanding environmental problems at a fundamental level requires us to probe the nature of mineral surfaces and their reactions in an aqueous environment. The Columbia EMSI program has attacked this problem at several levels. In this segment of the work, we focused on investigations of well-characterized single-crystal surfaces (of high symmetry and amenable to comparison with theory) that are probed directly by in-situ optical techniques. These measurements can be compared with UHV studies in which an aqueous environment is simulated by the deposition of condensed layers of water molecules. On the other hand, single-crystal surfaces can be compared with the multitude of traditional studies on high-surface area colloids. Although these materials lack the defined crystallographic geometry that is advantageous for fundamental modeling, they have the advantage of being amenable to various experimental techniques and, most importantly, correspond to the materials found in the environment.

The particular focus of this part of the EMSI program concerns charging effects at aqueous mineral interfaces The charging behavior of metal (hydr)oxide colloid surfaces plays an important role in flocculation, dissolution and sorption processes. A fundamental understanding of these processes is relevant to chemical models of both natural and industrial systems. The wide variation in charge-related properties derived from bench-scale studies of aqueous colloidal suspensions suggests that oxide particle surfaces have complex structures and compositions that are highly dependent on sample history and environment. However, the push to develop predictive structure-reactivity relationships necessitates a molecular-level representation of the amphoteric surface groups that control the charge-state of a colloidal particle. High quality single-crystal substrates and thin films are attractive models for colloid surfaces because they are amenable to molecular-level probes and provide the means to use crystallographic orientation to control the variation of surface structure. This model-system approach has been successfully used to investigate the crystallographic dependence of adsorbate geometries, reactions sites, and hydrated surface structures. The applicability of this molecular-level information to colloidal systems relies in large part on the assumption that active surface groups on single crystal substrates and oxide colloids have similar local structure and reactivity. This assumption, however, remains largely untested due to the paucity of experimentally determined properties of single crystal substrates that are directly comparable to results from studies of colloidal systems.

Optical second-harmonic generation (SHG) is uniquely suited for measuring surface charge properties of well-defined crystallographic surfaces. SHG, a second- order nonlinear optical process, is forbidden in centrosymmetric media. Therefore, SHG from the interface formed between water and any centrosymmetric solid only responds strongly to the spatial arrangement and electronic properties of water molecules and surface atoms in the narrow interfacial region where the inversion center is broken. This situation implies a strong dependence of SHG on the average orientation of water dipoles aligned in the presence of static electric fields associated with a charged surface. SHG associated with this process can be related to the surface potential in a quantitative fashion.

1. Investigations of αα-Al_2O_3 Single-Crystal Interfaces

An important model environmental system is aluminum oxide. It plays a central role in soil, particularly in clays, in which it and closely related compounds are primary constituents. In this investigation, we have emphasized the capability of the SHG technique to explore the relative chemistry of different well-defined crystallographic faces of a given material. This is a direct consequence of the ability of SHG to probe single interfaces, without the requirement of high-surface area dispersions.

The SHG results show that (001) and (012) single-crystal surfaces of corundum (α-Al_2O_3) exhibit significantly different values for the point of zero charge (pzc). The measured pzc is at a pH of 4.1 for the (001) surface, while the pzc for (012) is 5.2. This result suggests that each crystallographic surface possesses a unique set of potential-determining surface groups. Based on a simple model of acid/base equilibria, the calculated p.z.c value for the (001) surface is ~ 6. In contrast, the p.z.c. value predicted for the (012) surface, which is presumably terminated by an equal number of all three types of surface functional groups, is ~ 8. These model predictions are consistent with the SHG determined pzc values in that the p.z.c. of the (001) surface occurs at a lower pH than the pzc value of the (012) surface. However, the predicted p.z.c values are shifted ~2.5 pH units higher than the experimentally determined values. This discrepancy may result from the use of a model of the acid/base equilibrium which draws on data for oxo and hydroxo complexes in bulk solution.

2. Investigations of αα-TiO_2 Single-Crystal Interfaces

A second material system that we have investigated is single crystal rutile. TiO_2 is of particular interest in an environmental context because of its demonstrated properties as a photocatalyst. In this context it has been demonstrated to decompose halogenated compounds and other toxins. Additionally, TiO_2 is of importance in solar energy conversion as implemented in the Graetzel cell.

In this study, we have investigated the charging behavior of the α-TiO_2 single-crystal aqueous interface. This work was carried out in collaboration with David J. Wesolowski at Oak Ridge National Laboratory who provided us with a well characterized sample and with theorists Michael L. Machesky at the Illinois State Water Survey and Jim Kubicki at Penn State University (Department of Geosciences).

The pH of zero net surface charge (pH_{pzc}) of the (110) surface of a rutile crystal was characterized using second-harmonic generation spectroscopy. Charge development at the surface was determined by monitoring the SHG response during a series of pH titrations conducted at three distinct concentrations of the non-specifically adsorbing electrolyte $NaNO_3$. The measured pH_{pzc} was compared with a pH_{pzc} using a theoretical approach based on the revised MUltiSIte Complexation (MUSIC) model of surface oxygen protonation. The MUSIC model input parameters are based on relaxed surface bond lengths of a hydrated surface that were derived from *ab initio* calculations. The agreement between model ($pH_{pzc} = 4.76$) and experiment ($pH_{pzc} = 4.8 \pm 0.3$) establishes the incorporation of independently derived structural parameters into models of oxide surface acidity as a viable approach to predict oxide surface reactivity. It should be noted that the calculations were not adjusted to agree with the SHG results.

II. Research Area B: Fundamental Chemical Reaction and Transport Processes in Microscopic Porous Media

A) Molecular Probes of Adsorption in Porous Metal Oxides: (PI Nicholas Turro)

A major theme of Columbia's EMSI research program is "the connection between surface assisted redox chemistry and the nature of molecular transport that involves reactions and constricted flow of material through small pore, oxide laden soils." For example, in the course of modeling environmental transport of impurities, it is of interest to understand in detail the extent to which a co-adsorbate might enhance a degradation reaction rate or whether exposure to sun causes a species to oxidize faster. This theme has been addressed through investigations of the adsorption and photochemistry of organic molecules on metal oxide models of soil (zeolites, silica, alumina). Soils near the surface of the earth are most likely to be conveyed over large length scales through particle transport, and pollutants on surface soil experience significant exposure to sunlight. Investigations of the photochemical reactions of pollutants adsorbed on metal oxides, therefore, provide information on the transport and environmental photochemical reactivity of pollutants adsorbed on soil.

We have demonstrated for the first time that time resolved chemically induced dynamic electron polarization (CIDEP) can be measured for radicals adsorbed in porous solid zeolites. In particular, CIDEP was generated in a faujasite zeolite (NaY) as the result of the interaction of a stable free radical (4-oxo-TEMPO) and the triplet state of benzophenone. The kinetics of triplet quenching inside the zeolite were studied by diffuse reflection laser flash photolysis.

The EPR of nitroxide was used to elucidate the supramolecular structure and dynamics of molecules adsorbed on the external surface of zeolites. Quantitative distance relationships were established between nitroxide probe molecules adsorbed on the holes of the external surface.

The first photosensitized chirality sensitive reaction that could be accomplished in a cyclic manner was observed for molecules adsorbed on faujasites. The results demonstrated that chirally modified zeolites not only serve as a supramolecular photosensitizing media, but also enhance the original chiral differentiating ability of a chiral photosensitizer.

EPR was used to investigate directly the structure and dynamics of free radicals generated by photolysis of molecules adsorbed on zeolites. A model rationalizing the relationship between radical structure and radical persistence was proposed.

B) Synthesis and Characterization of Oxide Nanocrystals: (PI Louis Brus)

Magnetite nanoparticles were synthesized using a chemical co-precipitation method: $FeCl_2 + 2\ FeCl_3 + 8\ NH_4OH$ (or NaOH) $\rightarrow Fe_3O_4$. The reaction must be done with a strict molar ratio of Fe (II) / Fe (III) = 0.5 and at a pH of 11-12. The resulting magnetite particles are around 10 nm in diameter and are highly crystalline, as evidenced by TEM and electron diffraction images. If tetramethylammonium hydroxide (TMAOH) is used instead of NH_4OH or NaOH, a stable aqueous colloid is formed at a pH of ~13. TMAOH serves not only as the basic reactant, but also caps the particles and leads to an electric double layer stabilization in aqueous media. The oxidation of magnetite to maghemite is a significant process in the environment. Due to their identical crystal structure, these two phases show only minor differences in their x-ray diffraction, electron diffraction and X-ray photoelectron spectra. However, the two phases have very distinct bulk Raman spectra, and this may provide a ready diagnostic to determine the phase of the particles.

C) Inorganic Synthesis and Characterization of Environmentally Relevant Materials: (PI Ged Parkin)

"Zero valent iron" plays an important role in detoxifying waste streams by destroying alkyl halides. To understand this process, it is imperative to understand the mechanism of how simple zero valent iron compounds react with alkyl halides. Simple zero-valent iron compounds are not common, but two examples that were initially investigated as part of the EMSI project are the trimethyl phosphine and trimethylphosphite derivatives, "$Fe(PMe_3)_4$" and $Fe[P(OMe)_3]_5$. Importantly for these studies, both "$Fe(PMe_3)_4$" and $Fe[P(OMe)_3]_5$ are reactive towards CCl_4. Thus, $Fe[P(OMe)_3]_5$ reacts with CCl_4 to give $Fe[P(OMe)_3]_3Cl_2$. This observation is significant because it demonstrates that a zero valent iron center has the ability to react with CCl_4 to form a compound that has iron–chlorine bonds. "$Fe(PMe_3)_4$" is also reactive towards CCl_4, but the reaction is considerably more complex because it yields $[(Me_3P)_2CH_2]^{2+}[FeCl_4]^{2-}$. Thus, in this case, all the ligands originally attached to iron have been displaced by chlorine. Zero valent iron compounds are very reactive and so we have employed additional ligands to stabilize such species. For example, we have constructed a ligand with a "tubular" cavity by attaching three mercaptoimidazole groups to the 1-, 3-, and 5-positions of a benzene ring.

Aspects of lead pollution have also been studied. One of the major reasons for lead toxicity is due to the ability of lead to replace zinc in 5-aminolevulinate dehydratase (ALAD). This exchange reaction has been studied in a synthetic analogue system by using the *tris*(2-mercapto-1-phenylimidazolyl)borate ligand to provide a coordination motif which mimics the three cysteine residues that bind the metal at the active site of ALAD.

Sulfur impurities in fuels are major contributors to atmospheric pollution and the existence of acid rain. The method used to remove sulfur-containing species is hydrodesulfurization (HDS) which uses a molybdenum based catalyst. We have studied aspects of hydrodesulfurization by investigating the reactivity of molybdenocene hydride compounds towards thiophene and have observed the first example of c–S bond cleavage by a molybdenum compound.

III. Research Area C: Macroscopic Chemical Transport and Dispersal

A) Macroscopic Chemical Transport and Dispersal: (PIs Peter Schlosser and James Simpson)

1. SF_6 and CFCs in soil

Data obtained as part of the EMSI project show that there are significant SF_6 excesses in soil air reflecting the average excesses of atmospheric SF_6 above clean air levels. The data can be used to determine the footprint around emission centers that are characterized by SF_6 excesses. In these areas SF_6 can be used as an inert tracer for transport of soil air. The CFC data generally show slight enrichment compared to atmospheric concentrations. This is most likely related to adsorption of CFCs on soil.

2. CCl_4 in soil air

Significant degradation of CCl_4 in soil air was observed at all sites sampled. However, large differences were found in the degree to which CCl_4 is degraded at the individual sites. In order to understand the processes responsible for CCl_4 degradation, further study will be required.

3. Laboratory experiments on adsorption and degradation of CFCs and CCl_4

The focus of this project, which was performed in collaboration with Professor Turro's group, was the study of molecular adsorption on model soil materials. The objective was to be able to quantify the loss of halocarbons from groundwater to soil. Specifically, this work includes investigations of microporous aluminosilicate materials such as MFI and faujasite (FAU) zeolites, mesoporous materials such as silica gels, and nonporous particulate matter (SiO_2, Al_2O_3, Fe_2O_3 and humic acids). The MFI class of zeolites have channels with diameters of ~5 Å and the FAU zeolites have supercages with pores of ~8 Å and internal diameters of ~13 Å. A Langmuir adsorption approach was used to evaluate the binding affinity and maximum amount adsorbed onto each geosorbent. These experiments showed that halocarbons can bind in appreciable amounts to the internal volumes of zeolites and silica gels. Although these types of materials are present in small quantities in many geographical regions, their presence may drastically alter the adsorption of small halocarbons. The amount of these nonspecific microporous sinks and the internal volume of soil samples should be taken into account when using small molecules as groundwater tracers.

4. Arsenic Related Work

Groundwaters at the Winthrop site in Maine are strongly reducing and quite high in dissolved arsenic in the aquifer beneath the landfill and in several large plumes of groundwater transported away from the site. Based on the first tracer injection experiment, the mean transport velocity within about 20 meters of the pumping extraction well was found to be of the order of 1 to 2 meters per day, far in excess of likely velocities in the absence of pumping. The rate of transport appears to be extremely heterogeneous within the aquifer, with dominant flows occuring in highly transmissive zones that are not uniform with depth or spatial location at the site. Clearly, it would not have been feasible to accurately estimate critical aquifer parameters relevant to chemical transport behavior without the use of chemically inert tracers. There has not been significant lowering of dissolved arsenic or iron concentrations “downstream” of the line of oxygen release compound (ORC) injection more than six months after initial addition of ORC. Persistently high arsenic concentrations were found in samples that had substantial amounts of our chemically inert tracers present, and thus must have been derived in part from the zone of injection for the ORC. Laboratory measurements of chemical oxygen demand of the water and particle phases from the site indicate that the particles probably dominate control of redox conditions of water in the subsurface at Winthrop. Details of the interactions of groundwater and particle phase geochemistry will require further study. It seems reasonable to conclude, based on the studies to date, that it can be quite difficult to significantly modify redox conditions of even modest volumes of an aquifer for the purposes of altering mobilization behavior of toxic metals such as arsenic.

Further laboratory measurements were continued at L-DEO for environmental isotopes in groundwater samples collected in 1999-2000 from the Ganges-Brahmaputra Delta in Bangladesh. Additional samples were collected during January 2001, in conjunction with installation of a network of eight monitoring wells having different depths in a region that has a large range of dissolved arsenic concentrations in domestic supply wells within a very small area. Another network of monitoring wells was installed several months later at a second site characterized by consistently high dissolved arsenic concentrations in nearly all of the shallow wells used for domestic water supplies by the local population. Both of these groups of monitoring wells will be followed in detail over a period of several years, well after the conclusion of the EMSI program. Our strategy in the field work in Bangladesh, as well as Winthrop, ME, has been to couple new transport information derived from environmental isotope measurements with chemical parameters in the groundwater to help elucidate processes that lead to mobilization of dissolved arsenic and other redox sensitive metals.

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Name: WANG, YINGMIN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: YANG, JEFFREY
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CHO, SO-HYE
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: ZHANG, JUNLIAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: GRAVES, CHRISTOPHER
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: ZHU, XINJIANG
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: LANIER, COURTNEY
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: LIBERA, JOSEPH
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: SAVARA, ADITYA
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: LAW, HIU YING
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: RAPHULU, M.C.
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CHRISTENSEN, STEVEN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: GREENE, MARK
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: QU, FENG
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: WHITNEY, ALYSON
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CHEN, LE
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: QUEZADA, BRIAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: GADZIKWA, TENDAI
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: SARATOVSKY, IAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: DAHL, AMY
Worked for more than 160 Hours: Yes
Contribution to Project:

Undergraduate Student

Name: CHEUNG, CHRISTINE
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: WALKER, GRAHAM
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: HUNTER, DeMARCUS
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: HUSTON, JEREMY
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: FUNDERBUNK, APRYLE
Worked for more than 160 Hours: No
Contribution to Project:

Name: LUGO, BRET
Worked for more than 160 Hours: No
Contribution to Project:

Name: McKAY, JONATHAN
Worked for more than 160 Hours: No
Contribution to Project:

Name: KLINGENSMITH, LIANE
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: DAKLARAS, ANGELO
Worked for more than 160 Hours: No
Contribution to Project:

Name: MILLER, AARON
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: HSIEH, ABRAHAM
Worked for more than 160 Hours: No
Contribution to Project:

Name: MOYA, MONICA
Worked for more than 160 Hours: No
Contribution to Project:

Name: OKTEN, HATICE
Worked for more than 160 Hours: No

Contribution to Project:

Name: KIM, JUNGYUN
Worked for more than 160 Hours: No
Contribution to Project:

Name: TU, WEN
Worked for more than 160 Hours: No
Contribution to Project:

Name: SCHWARTZ, CRAIG
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CRIST, SARAH
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: DUKES, FAITH
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CALDERWOOD, SHARON
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CAO, SHITONG
Worked for more than 160 Hours: No
Contribution to Project:

Name: WU, DI
Worked for more than 160 Hours: No
Contribution to Project:

Name: WALTHER, NOLAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: SCHMERBERG, CLAIRE
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: GRANDE, WILL
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: LORD, RICHARD
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: HIYAMA, YAEKO
Worked for more than 160 Hours: No
Contribution to Project:

Name: LAITAR, DAVID
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: DHILLON, SATWANT
Worked for more than 160 Hours: No
Contribution to Project:

Technician, Programmer

Other Participant

Name: HUCUL, DENNIS
Worked for more than 160 Hours: No
Contribution to Project:
Dennis Hucul, Dow Chemical Company, is an industrial mentor for Charles Parkinson.

Name: REDING, MATTHEW
Worked for more than 160 Hours: No
Contribution to Project:
Matthew T. Reding, Pharmacia & Upjohn, is an industrial mentor for Erik Gustafson.

Name: KUPERMAN, ALEX
Worked for more than 160 Hours: No
Contribution to Project:
Alex Kuperman, Dow Chemical Company, is an industrial mentor for Robert Paddock.

Name: ROSEN, BRUCE
Worked for more than 160 Hours: No
Contribution to Project:
Bruce Rosen, BP Amoco Chemicals, is an industrial mentor to Greg Morris.

Name: JACKSON, S. DAVID
Worked for more than 160 Hours: No
Contribution to Project:
S. David Jackson, ICI Synetix, is an industrial mentor for Lei Fu.

Name: SLONE, ROBERT
Worked for more than 160 Hours: No
Contribution to Project:
Robert Slone, Rohm & Haas, is an industrial mentor for Melissa Merlau.

Name: SIKKENGA, DAVID
Worked for more than 160 Hours: No
Contribution to Project:
David Sikkenga, BP Amoco Chemicals, is an industrial mentor for Chen Huang.

Name: STURCHIO, NEIL

Worked for more than 160 Hours: No

Contribution to Project:

Neil Sturchio, Argonne National Laboratory, is a laboratory collaborator in the IEC.

Name: FENTER, PAUL

Worked for more than 160 Hours: No

Contribution to Project:

Paul Fenter, Argonne National Laboratory, is a laboratory collaborator in the IEC.

Name: CHAMBERS, SCOTT

Worked for more than 160 Hours: No

Contribution to Project:

Dr. Scott Chambers, Pacific Northwest National Laboratory, is a laboratory collaborator in the IEC.

Name: RAY, G. JOSEPH

Worked for more than 160 Hours: No

Contribution to Project:

Dr. G. Joseph Ray (retired-BP Amoco Chemicals) is an industrial mentor for Yoo Joong Kim.

Name: LESTER, GEORGE

Worked for more than 160 Hours: No

Contribution to Project:

Dr. George Lester, G. Lester Inc., is an industrial mentor for Pablo Pasten.

Name: LAU, ANTONIO

Worked for more than 160 Hours: No

Contribution to Project:

Antonio Lau, BP Amoco Chemicals, is an industrial mentor for Mwende Munyasya.

Name: PRATT, STEVE

Worked for more than 160 Hours: No

Contribution to Project:

Steve Pratt, Argonne National Laboratory, is a laboratory collaborator in the IEC.

Name: THORSTEINSON, ERL

Worked for more than 160 Hours: No

Contribution to Project:

Erl Thorsteinson, Union Carbide Corp., is an industrial mentor for Jason Pless.

Name: SMITH, JACK

Worked for more than 160 Hours: No

Contribution to Project:

Jack Smith, Union Carbide Corp, is an industrial mentor for Oliver Warschkow.

Name: BARE, SIMON

Worked for more than 160 Hours: No

Contribution to Project:

Simon Bare, UOP Research, is an industrial mentor for Li Liu.

Name: DISKO, MARK

Worked for more than 160 Hours: No

Contribution to Project:
Mark Disko, Exxon Research, is an industrial mentor for Lisen Cheng.

Name: BOGDAN, PAULA
Worked for more than 160 Hours: No
Contribution to Project:
Paula Bogdan, UOP Research, is an industrial mentor for David Pedersen.

Name: BROACH, ROBERT
Worked for more than 160 Hours: No
Contribution to Project:
Robert Broach, UOP Research, is an industrial mentor for Chang-Yong Kim.

Name: LI, YUEJIN
Worked for more than 160 Hours: No
Contribution to Project:
Yuejin Li, Engelhard Corp., is an industrial mentor for J.-H. Lee.

Name: JOHNSON, RUSSELL
Worked for more than 160 Hours: No
Contribution to Project:
Russ Johnson, Honeywell Research, is an industrial mentor for Alex Agrios.

Name: LUPTON, STEVEN
Worked for more than 160 Hours: No
Contribution to Project:
Steve Lupton, Honeywell Research, is an industrial mentor for Mike Marsolek.

Name: GAI, PRATIBHA
Worked for more than 160 Hours: No
Contribution to Project:
Pratibha Gai, DuPont Research, is an industrial mentor for Natasha Erdman.

Name: BOWMAN, ROBERT
Worked for more than 160 Hours: No
Contribution to Project:
Robert Bowman, Dow Chemical, is an industrial mentor for Trent Guidry.

Name: ZHOU, ROBERT
Worked for more than 160 Hours: No
Contribution to Project:
Robert Zhou, UOP Research, is an industrial mentor for Scott McMillan.

Name: BHASIN, MADAN
Worked for more than 160 Hours: No
Contribution to Project:
Madan Bhasin, Union Carbide, is an industrial mentor for Ben Ritchey.

Name: LIU, D.J.
Worked for more than 160 Hours: No
Contribution to Project:
D.J. Liu, Honeywell Research, is an industrial mentor for Hyung-Seuk Oh.

Name: DAVIS, JOHN
Worked for more than 160 Hours: No
Contribution to Project:
John Davis, Dow Chemical, is an industrial mentor for Alex Schwarz.

Name: ETTINGER, DEON
Worked for more than 160 Hours: No
Contribution to Project:
Deon Ettinger, Program Leader, Science Education and Technology, Argonne National Laboratory, is involved with the Materials World Module of the IEC.

Name: KRUPER, JACK
Worked for more than 160 Hours: No
Contribution to Project:
Scientist, Dow Chemical Company

Name: BARDIN, BILLY
Worked for more than 160 Hours: No
Contribution to Project:

Name: HENAO LOPEZ, JUAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: VASQUEZ, SEBASTIAN
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CORDOBA, LUIS
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: NEMETH, LASZLO
Worked for more than 160 Hours: No
Contribution to Project:
UOP LLC

Name: MILLER, JEFFREY
Worked for more than 160 Hours: No
Contribution to Project:
BP Chemical Company

Name: KADUK, JAMES
Worked for more than 160 Hours: No
Contribution to Project:

Name: HERSAM, MARK
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: GEIGER, FRANZ
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: CHANG, ROBERT P.
Worked for more than 160 Hours: Yes
Contribution to Project:

Robert Chang is the program director for the Materials World Module of the IEC.

Name: ZAJAC, GERRY
Worked for more than 160 Hours: No
Contribution to Project:

Name: SINKLER, WHARTON
Worked for more than 160 Hours: No
Contribution to Project:

Research Experience for Undergraduates

Name: DOMSKI, GREGORY
Worked for more than 160 Hours: No
Contribution to Project:

Years of schooling completed: Freshman
Home Institution: Same as Research Site
Home Institution if Other:
Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree
Fiscal year(s) REU Participant supported: 2002
REU Funding: REU supplement

Name: SIGWING, ANDREA
Worked for more than 160 Hours: Yes
Contribution to Project:

Years of schooling completed: Freshman
Home Institution: Same as Research Site
Home Institution if Other:
Home Institution Highest Degree Granted(in fields supported by NSF): Doctoral Degree
Fiscal year(s) REU Participant supported: 2002
REU Funding: REU supplement

Organizational Partners

National Water Research Instit, Canada

DuPont Chemicals

Air Products and Chemicals Inc

UOP Research

Honeywell Research Center

Union Carbide Corporation

BP Amoco

Dow Chemical Company

ICI Synetix

Engelhard Corporation

Argonne National Laboratory

Pacific Northwest National Laboratory

Rohm and Haas Company

Exxon Mobil

Pharmacia

Notre Dame Radiation Laboratory

University of Notre Dame
Prof. Edward Maginn

University of Leipzig (Germany)
Prof. Jorg Karger

Other Collaborators or Contacts

Dr. WeiJie Ji; Pr. Sonia Flores, Univ. of Salta, Argentina; Michael Hu, Ercan ALp; Pr. K.C. Mundim, Federal U. of Bahia, Salvador, BA, Brazil;

Argonne National Laboratory: Dr. Neil Sturchio; Dr. Paul Fenter; Dr. Alexander Trifunac; Dr. Tiajana Rajh; Dr. Marion Thurnauer; Deon Ettinger, Science Education and Technology; APS.

Brookhaven National Laboratory; NIST.

Dr. Scott Chambers, Pacific Northwest National Laboratory; Jeffrey Miller, BP Amoco Chemicals; Joerg Zegenhagen, ESRF, France; Prof. R.A. van Santen (Eindhoven University); Dr. Hongwei Du, Northwestern University; Dr. Michael Boyne, Northwestern University; Dr. John Low, UOP Research; Dr. Laszlo Nemeth, UOP LLC; Dr. David Goodspeed, New Trier High School; Professor K.-Dieter Asmus, Notre Dame Radiation Laboratory, Notre Dame, IN.

Gregor Zlokarnik, Aurora Biosciences Corporation; BP Amoco; Engelhard; Dow Chemical Company; Dr. Marrija Bonifacic, Ruder Boskovic Institute;

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:
The size and scope of the Institute for Environmental Catalysis (21 faculty, 43 postdoctoral students, 53 graduate students, and 27 undergraduate students; 11 projects) provide a range of training and development opportunities. Graduate and postdoctoral students learn the

details of laboratory techniques and/or computational methods required for their project as they would in any research laboratory. However, since most of the projects are multidisciplinary, students are required to learn a wider variety of synthetic, characterization, and computational methods. They learn how to work in a team, and they are exposed to the industrial research culture. In some cases postdoctoral students are given supervisory responsibilities that provide excellent preparation for eventually becoming a principal investigator in either academia or industry. Students and faculty become familiar with the fields of chemistry, catalysis, materials synthesis and characterization, biology and biochemistry, and chemical engineering since aspects of all these fields are represented in the IEC projects.

Outreach Activities:

The outreach activities are described in the section 'Activities'.

Journal Publications

W.M.H. Sachtler, Haiying Chen, Timur V. Voskoboinikov, "Reduction of NO over Fe/ZSM-5 Catalysts: Effect of Different Alkanes", Catalysis Today, Special Issue of Miami congress, p. 483, vol. 54, (1999). Accepted

Wolfgang M. H. Sachtler, Timur V. Voskoboinikov and Haiying Chen, "Characterization of Fe/ZSM-5 by Isotopic Exchange with (18)0(2)", J. Molec. Catal., p. 155, vol. 155, (2000). Published

W. M. H. Sachtler, H. Y. Chen and T. Voskoboinikov, "Reaction Intermediates in the SCR of NOx over Fe/ZSM-5", J. Catal., p. 91, vol. 186, (1999). Accepted

W. M. H. Sachtler, R. A. van Santen and El M. El Malki, "Introduction of Zn, Ga and Fe into HZSM-5 Cavities by Sublimation: Identification of Catalytic Sites", J. Phys. Chem. B., p. 4611, vol. 103, (1999). Accepted

El M. El Malki, R. A. van Santen and W. M. H. Sachtler, "Isothermal Oscillations of N2O Decomposition over Fe/ZSM-5 Catalysts: Effect of H2O Vapor", Microporous and Mesoporous Materials, p. 235, vol. 35-36, (2000). Published

Haiying Chen, Xiang Wang and Wolfgang M. H. Sachtler, "Reduction of NOx over various Fe/Zeolite Catalysts", Appl. Catal. A, (General), p. 159, vol. 194-195, (2000). Submitted

Payne, J.C.; ter Horst, M.A.; Godwin, H.A., "oLead-Fingers: Pb(ll)-Binding to Structural Zinc-Binding Domains Determined Directly by Monitoring Lead-Thiolate Charge Transfer BandsoPayne", J. Am. Chem. Soc., p. , vol. , ( ). Accepted

S. Leytner and J.T. Hupp, "Evaluation of the Energetics of Electron Trap States at the Nanocrystalline Titanium Dioxide/Aqueous Solution Interface via Time-Resolved Photoacoustic Spectroscopy", Journal of Physical Chemistry B, p. 231, vol. 330, (2000). Submitted

Pasten, P.; Hurum, D.; Gaillard, J.F., "Structures of Bacterially Produced Manganese Oxides", Advanced Photon Source - User Activity Report, p. 189, vol. 1, (2000). Published

Hurum, D; Pasten, P.; and Gaillard, J.F., "Reaction of Colloidal and Bacterial MnO2 with Iron (II)", Advanced Photon Source - User Activity Report, p. 182, vol. 1, (2000). Published

Xiang Wang, Haiying Chen, W.M.H. Sachtler, "Catalytic Reduction of NOx by Hydrocarbons over Co/ZSM-5 Catalysts Prepared with Different Methods", Applied Catalysis B, Environmental, p. L227, vol. 26, (2000). Published

Timur V. Voskoboinikov, Hai-Ying Chen, W.M.H. Sachtler, "Isotopic (18)O2 Exchange over Fe-containing ZSM-5", J. Molecular Catalysis, p. , vol. , ( ). in press

Hai-Ying Chen, Xiang Wang, W.M.H. Sachtler, "Reduction of NOx over Zeolite MFI Supported Iron Catalysts: Nature Active Sites", Physical Chemistry, Chemical Physics, p. 3083, vol. 2, (2000). Published

El-M. El-Malki, David Werst, Peter E. Doan, and W.M.H. Sachtler, "Coordination of CO(2+) Cations Inside Cavities of Zeolite MFI with Lattice Oxygen and Adsorbed Ligands", Journal of Physical Chemistry B, p. 5924, vol. 104, (2000). Published

Hai-Ying Chen, El-Mekki El-Malki, Xiang Wang, and W.M.H. Sachtler, "Identification of Active Sites and Adsorption Complexes in Fe/MFI Catalysts for NOx Reduction", J. Molecular Catalysis A, p. 159, vol. 162, (2000). Published

Xiang Wang, Hai-Ying Chen, W.M.H. Sachtler, "Selective Reduction of NOx with Hydrocarbons over Co/MFI Prepared by Sublimation of CoBr2 and Other Methods", Appl. Catal. B, p. 47, vol. 19, (2000). Published

Xiang Wang, W.M.H. Sachtler, "Comparison of Fe/MFI and Co/MFI Catalysts for Selective Reduction of NOx; Site Characterization and Reaction Mechanism", J. Catal., p. , vol. , ( ). Submitted

A. Yezerets, Y. Zheng, P.W. Park, M.C. Kung, and H.H. Kung, "Bifunctional Nature of SnO2/ Al2O3 Catalysts in the Selective Reduction of NOx", Proc. 12th intern. Congress Catal., Stud. Surf. Sci. Catal., p. 629, vol. 130, (2000). Accepted

M.L. Merlau; W.J. Grande; S.T. Nguyen; J.T. Hupp, "Enhanced Stability of Manganese (III) Porphyrin Epoxidation Catalysts Through Supramolecular Complexation", J. Mol. Catal. A: Chemical, p. 79-84, vol. 156, (2000). Published

M.L. Merlau; M.P. Mejia; S.T. Nguyen; J.T. Hupp, "A Tailorable Artificial Enzyme for Olefin Epoxidation", Science, p. , vol. , (2000). manuscript in preparation

P. Fenter; L. Cheng; S. Rihs; M. Machesky; M.J. Bedzyk; and N.C. Sturchio, "Probing the Double-Layer Structure at the Rutile-Water Interface with X-Ray Standing Waves", J. Colloid and Interface Science, p. , vol. , ( ). in press

L. Cheng; N.C. Sturchio; M.J. Bedzyk, "The Local Atomic-Scale Structure of Cobalt Incorporated at the Calcite Surface: An X-Ray Standing Wave and SEXAFS Study", Phys. Rev. B, p. 4877, vol. 61, (2000). Published

D.E. Ellis and D. Guenzburger, "Discrete Variational Method and its Applications to Large Molecules and Solids", Adv. Quantum Chem., p. 51, vol. 34, (1999). Published

K.C. Mundim and D.E. Ellis, "Stochastic Classical Molecular Dynamics Coupled to Density Functional Theory: Applications to LMolecular Systems", J. of Physics, p. 199, vol. 29, (1999). Published

P.L. Cao, D.E. Ellis, V.P. Dravid, "First Principles Study of Initial Stage Ni Thin Film Growth on a TiO2(110) Surface", J. of Mat. Res., p. 3684, vol. 14, (1999). Published

El. M. El-Malki, R.A.van Santen, Wolfgang M.H. Sachtler, "Active Sites in Fe/MFI Catalysts for NOx Reduction and Oscillating N2O Decomposition", Journal of Catalysis, p. 212, vol. 196, (200). Published

X. Wang, Hai-Ying Chen, W.M.H. Sachtler, "Mechanisms of the Selective Reduction of NOx over Co/MFI: Comparison with Fe/MFI", J. Catalysis, p. 281, vol. 197, (2001). Published

Zhixian Gao, Qi Sun, W.M.H. Sachtler, "Adsorption Complexes of O2 on Fe/MFI and their Role in the Catalytic Reduction of NOx", Appl. Catal. B, p. 9, vol. 33, (2000). in press

Qi Sun, Zhixian Gao, and W.M.H. Sachtler, "SCR of NOx with Ammonia over Fe/MFI: Reaction Mechanism Based on Isotopic Labeling", J. Catal., p. , vol. , ( ). in press

Zhixian Gao, Qi Sun, Hai-Ying Chen, Xiang Wang, and W.M.H. Sachtler, "Characterization and Catalytic Testing of Au/MFI Prepared by Sublimation of AuCl3 onto HMFI", Catal. Lett., p. , vol. , ( ). in press

Zhixian Gao, Hack-Sung Kim, Qi Sun, Peter C. Stair, and W.M.H. Sachtler, "UV-Raman Characterization of Iron Peroxo Adsorbates on Fe/MFI Catalyst with High Activity for NOx Reduction", J. Phys. Chem. B., p. 6186, vol. 105, (2001). Accepted

B. Wen, Q. Sun and W.M.H. Sachtler, "Function of Pd(o)(n) Clusters, Pd (2+) (oxo)-ions and PdO Clusters in the Catalytic Reduction of NO with Methane over Pd/MFI Catalysts", J. Catal., p. , vol. , ( ). Submitted

B. Wen, Q. Sun and W.M.H. Sachtler, "H/D Exchange of CH4 as a Catalytic Probe for the Presence of TMo Clusters in the Steady State of NOx Reduction with Methane", Appl. Catal., p. , vol. , (2002). Submitted

L. Cheng, N.C. Sturchio, M.J. Bedzyk, "Impurity Structure in a Molecular Ionic Crystal: Atomic Scale X-Ray Study of CaCo3:Mn2+", Phys. Rev. B., p. , vol. , (63). Accepted

P. Fenter, L. Cheng, S. Rihs, M. Machesky, M.J. Bedzyk and N.C. Sturchio, "Electrical Double-Layer Structure at the Rutile-Water Interface as Observed in-situ with Small-Period X-ray Standing Waves", J. Colloid and Interface Science, p. 154, vol. 225, (2000). Published

Broadbelt, L.J. and Snurr, R.Q., "Applications of Molecular Modeling in Heterogeneous Catalysis Research", Appl. Catal. A, p. 23, vol. 200, (2000). Published

Gaillard, J.-F., Webb, S.M., and Quintana, J.P.G., "Quick X-ray Absorption Spectroscopy for Determining Metal Speciation in Environmental Samples", Journal of Synchrotron Radiation, p. 928, vol. 8, (2001). Published

Merlau, M.L., Mejia, M.P., Nguyen, S.T., and Hupp, J.T., "Artifical Enzymes Formed Via Directed Assembly of Molecular Square-Encapsulated Epoxidation Catalysts", Nature, p. , vol. , (2001). Submitted

Morris, G.A., Zhou, H., Stern, C.L. and Nguyen, S.T., "A General High-Yield Route to Zinc(II) Salens: Application to the Synthesis of Pyridine-Modified Zinc(II) Salen Complexes", Inorg. Chem., p. 3222-3227, vol. 40, (2001). Published

Morris, G.A., Nguyen, S.T. and Hupp, J.T., "Enhanced Activity of (salen) Mn(III) Epoxidation Catalysts Through Supramolecular Complexation", J.Mol. Catal. A: Chem., p. 15, vol. 174, (2001). in press

Morris, G.A. and Nguyen, S.T., "A General Route to Pyridine-Modified Salicylaldehydes via Suzki Coupling", Tetrahedron Lett., p. 2093, vol. 42, (2001). Published

Pless, J., Ko, D. and Poeppelmeier, K.R., "Single Crystal Growth of Magnesium Orthovanadate Mg3((VO4)2)", Crystal Growth and Design, p. , vol. , ( ). Submitted

J.-H. Lee, A. Yezerets, M.C. Kung and H.H. Kung, "Hydrocarbon Reaction Pathway in Selective NO Reduction over a Bifunctional SnO2/Al2O3 Catalyst", Chemical Communications, p. 1404, vol. , (2001). Accepted

X. Dang, A.M. Massari, and J.T. Hupp, "Electrochemically Modulated Diffraction: A New Strategy for the Determination of Conduction-Band-Edge Energies for Nanocrystalline Thin-Film Semiconduction Electrodes", Electrochemical and Solid State Letters, p. 555, vol. 31, (2000). Published

X. Dang, K.J. Stevenson and J.T. Hupp, "Monitoring Molecular Adsorption on High-Area Titanium Dioxide via Modulated Diffraction of Visible Light", Langmuiur, p. 3109, vol. 17, (2001). in press - published online

B.C. Tzeng, R.C. Bailey, X. Dang, G.A. Mines, K.A. Walters and J.T. Hupp, "Photonic Lattices as Diffraction Based Chemical Sensors", Electrochemical Society (Sensors Division) Proceedings, p. 511, vol. , (2001). Submitted

N. Erdman, O. Warschkow, D.E. Ellis and L.D. Marks, "Solution of p(2x2) NiO(111) Surface Structure Using Direct Methods Applied to X-ray Diffraction Data", Surface Science, p. 1, vol. 470, (2000). Published

C.-X. Guo, O. Warschkow, D.E. Ellis, V.P. Dravid, and E.C. Dickey, "Oxide-Oxide Interfaces: Atomistic and Density Functional Study of Cubic ZrO2(100)|| NiO(111)", J. Am. Ceram. Soc., p. , vol. , ( ). to be published

Pedersen, David B. and Weitz, Eric, "Photolysis of Intrasilicalite I2: Spectroscopy and Dynamics", Journal of Chemical Physics, p. , vol. , (2002). Accepted

Paddock, R.L.; Nguyen, S.T., "Chemical CO2 Fixation: Cr(III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO2 and Epoxide", J. American Chemical Society, p. 11498, vol. 123, (2001). Published

Wang, S., Chen, H.Y., Sachtler, Wolfgang M.H., "Mechanism of Selective Reduction of NOx over CO/MFI: Comparision with Fe/MFI", J. Catalysis, p. 281, vol. 197, (2001). Published

Wen, B., Sun, Q., Sachtler, Wolfgang M.H., "H/D Exchange of Methane over Transition Metal/MFI Catalysts", Appl. Catal. A, p. 11, vol. 229(1), (2002). Published

Wen, B., Sachtler, W.M.H., "Synergism of Cobalt and Palladium in MFI Zeolites of Relevance to NOx Reduction with Methane", Phys. Chem. B, p. 1983, vol. 106, (2002). Published

Jia, J., Sun, Q., Wen, B., Sachtler, W.M.H., "Identification of Highly Active Iron Sites in N2O-Activated Fe/MFI", Catal. Lett., p. 7-11, vol. 82, (2002). Submitted

Sun, Q., Gao, Z-G., Wen, B., Sachtler, Wolfgang M.H., "Spectroscopic Evidence for a Nitrite Intermediate in the Catalytic Reduction of NOx with Ammonia on Fe/MFI", Cat. Lett., p. 1-5, vol. 78, (2002). Published

Schwartz, V., Prins, R., Wang, X., Sachtler, W.M.H., "Characterization of EXAFS of CO/MFI Catalysts Prepared by Sublimation", J. Phys. Chem. B, p. 7520, vol. 106, (2002). Published

Wen, B., Jia, J., Sachtler, Wolfgang M.H., "Chemical Anchoring of Palladium by Fe-oxo ions in Zeolite ZSM-5", J. Phys. Chem. B, p. 7520, vol. 106, (2002). Published

Fu, L., Johnson, D. Lynn, Zheng, J.G., Dravid, Vinayak P., "Microwave Plasma Synthesis of Nanostructured gamma-Al2O3 Powders", Journal of Nano Letters, p. , vol. , ( ). Submitted

Whitely, M., Bangera, M.G., Bumgarner, R.E., Parsek, M.R., Teitzel, G.M., Lory, S., Greenberg, E.P., "Gene Expressions in Pseudomonas aeruginosa Biofilms", Nature, p. 860, vol. 413, (2001). Published

Costello, C.K., Kung, M.C., Oh, H-S., Wang, Y., Kung, H.H., "Nature of the Active Site for CO Oxidation on Highly Active Au/gamma-Al2O3", App. Catal. A:General, p. 159, vol. 232, (2002). Published

Oh, H-S., Yang, J.H., Costello, C.K., Wang, Y., Bare, S.R., Kung, H.H. and Kung, M.C., "Selective Catalytic Oxidation of CO: Effect of Chloride on Supported Au Catalysts", J. Catal., p. 375, vol. 210, (2002). Published

Zhang, J., Williams, M.E., Keefe, M.H., Morris, G.A., Nguyen, S.T., Hupp, J.T., "Molecular Sieving and Thin-film Transport by Molecular Materials Featuring Large (> 20 Angstrom Diameter) Component Cavities", Electrochemical and Solid State Letters, p. E25, vol. 5, (2002). Published

Hupp, J.T., and Nguyen, S.T., "Functional Nanostructured Molecular Materials", Interface, p. 28-32, vol. 10(3), (2001). Published

Taillefert, M., MacGregor, B., Gaillard, J.-F., Lienemann, C.-P., Perret, D., and Stahl, D.A., "Evidence for a Dynamic Cycle between Mn and Co in the Water Column of a Stratified Lake", Environmental Science and Technology, p. 468, vol. 36, (2002). Published

Hentzer, M.; Teitzel, G.M; Balzer, G.J.; Heydorn, A., Molin, S.; Givskov, M.; Parsek, M.R., "Alginate Overproduction Affects Pseudomonas aeruginosa Biofilm Structure and Function", J. Bacteriol., p. 395, vol. 183(18), (2001). Published

Outten, C.E.; O'Halloran, T.V., "Femtomolar Sensitivity of Metalloregulatory Proteins Controlling Zinc Homeostasis", Science, p. 2488, vol. 292, (2001). Published

Outten, F.W.; Huffman, D.; Hale, J.; O'Halloran, T.V., "The Independent cue and cus Systems Confer Copper Tolerance During Aerobic and Anaerobic Growth in Eschericia coli", J. Biol. Chem., p. 30670, vol. 376, (2001). Published

Outten, C.E.; Tobin, D.A.; Penner-Hahn, J.E.; O'Halloran, T.V., "Characterization of the Metal Receptor Sites in E. coli Zur, An Ultrasensitive Zn(II) Metalloregulatory Protein", Biochemistry, p. 10417, vol. 40, (2001). Published

Hitomi, Y.; Outten, C.E.; O'Halloran, T.V., "Extreme Zinc-Binding Thermodynamics of the Metal Sensor/Regulator Protein, ZntR", J. Amer. Chem. Soc., p. 8614, vol. 123, (2000). Published

Wang, X.; Norquist, A.; Pless, J.; Stern, C.; Vander Griend, D.A.; Poeppelmeier, K.R., "Crystal Growth and Co-Substitution in (Mg(1-x) Fe(x))(Mo(2-x)V(x))O7 (0.13x0.47) with (V/Mo)=O Oxo Double Bonds", J. Alloys Compd., p. , vol. , (2002). Accepted

Erdman, N.; Poeppelmeier, K.R.; Marks, L., "Oxide Surface Chemistry: TiO2 Surface of SrTiO3", Nature, p. , vol. , (2002). Submitted

Huffman, D.L.; Huyett, J.; Outten, F.W.; Doan, P.E.; Hoffman, B.M.; O'Halloran, T.V.;, "ENDOR Spectroscopy of Cu(II)-PcoC and the Multicopper Oxidase Function of PcoA, Two Essential Components of the pco Copper Resistance Operon in Escherichia coli", Biochemistry, p. , vol. , (2002). Submitted

Kung, H.H. and Kung, M.C., "Alumina-Supported Catalysts for NO Reduction in an Oxidizing Atmosphere", J. Chin. Inst. Chem. Eng., p. , vol. , (2002). Accepted

Claudio, E.S.; Magyar, J.S.; Godwin, H.A., "Fundamental Coordination Chemistry, Environmental Chemistry, and Biochemistry of Lead(II)", Prog. Inorg. Chem., p. , vol. , (2002). in press

Chopp, D.L.; Kirisits, M.J.; Moran, B.; Parsek, M.R., "A Mathematical Model of Quorum Sensing in a Growing Pseudomonas aeruginosa Biofilm", J. Industrial Microbiology and Biotechnology, p. , vol. , (2002). Submitted

Rittmann, B.E.; Schwarz, A.O.; Eberl, H.; Morgenroth, E.; Wanner, O., "Results of the Multi-Species Benchmark Problems", Report of the Biofilm Modeling Working Group, International Water Association, London, p. , vol. , (2002). in press

Morgenroth, E.; Eberl, H.; Noguera, D.; Piciorneanu, C.; Rittmann, B.E.; Schwarz, A.O.; van Loosdrecht, M.L.M.; Wanner, O., "Results of the First Benchmark Problem", Report of the Biofilm Modeling Working Group, International Water Association, London, p. , vol. , (2002). in press

Rittmann, B.E. and Schwarz, A.O., "Modeling Multi-Species Biofilms using Pseudo-Analytical Solutions for a Steady State Biofilm", Report of the Biofilm Modeling Working Group, International Water Association, London, p. , vol. , (2002). in press

Rittmann, B.E., "Using X-Ray Absorption to Understand Microbial Transformations of Metals", SES II Symposium, Argonne National Laboratory, p. , vol. , (2002). Extended Abstract in press

Bonifacic, M.; Asmus, K-D.; Gray, K.A., "On the Reaction of 2,4,5-Trichlorophenol with Hydroxyl Radicals: New Information on Transients and their Properties", Journal of Physical Chemistry, p. , vol. , (2002). Submitted

Kim, C.-Y.; Bedzyk, M.J.; Nelson, E.J.; Wojcik, J.C.; Berman, L.E., "Site-Specific Valence Band Photoemission Study of Alpha-Fe2O3", Phys. Rev. B, p. 085115-1, vol. 66, (2002). Published

Czaplewski, K.F.; Reitz, T.L.; Kim, Y.J.; Snurr, R.Q., "One-dimensional Zeolites as Hydrocarbon Traps", Micropor. Mesopor. Materials, p. , vol. , (2002). Submitted

McMillan, S.A.; Broadbelt, L.J.; Snurr, R.Q., "Density Functional Theory Investigation of Cobalt Siting in Ferrierite", J. Phys. Chem. B, p. 10864, vol. 106(42), (2002). Published

Q. Sun, Wolfgang M.H. Sachtler, "Mn/MFI Catalyzed Reduction of NOx with Alkanes", Appl. Cataly. B, p. 393, vol. 42, (2003). Published

B. Wen, Wolfgang M.H. Sachtler, "Enhanced Catalytic Performance of Co/MFI by Hydrothermal Treatment", Catal. Lett, p. 393-401, vol. 86, (2003). Published

B. Wen, Younghoon Yeom, Eric Weitz, Wolfgang M.H. Sachtler, "NOx Reduction from Diesel Emissions over a Non-Transition Metal Zeolite Catalyst: Catalytic Tests and MS-TP Analysis", Applied Catalysis, B, Environmental, p. 125-131, vol. 48, (2004). Published

Younghoon Yeom, Bin Wen, Wolfgang M.H. Sachtler, Eric Weitz, "NOx Reducation from Diesel Emissions over a Non-Transition Metal Zeolite Catalyst: A Mechanistic Study Using FTIR Spectroscopy", Journal of Physical Chemistry B, p. 5386-5404, vol. 108, (2004). Published

Hay-Ying Chen, Qi Sun, Bin Wen, Younghoon Yeom, Eric Weitz, Wolfgang M.H. Sachtler, "Reduction over Zeolite-based Catalysts of Nitrogen Oxides in Emissions Containing Excess Oxygen: Unraveling the Reaction Mechanism", Catalysis Today, p. 1-10, vol. 96, (2004). Published

Meijun Li, Juan Henao, Younghoon Yeom, Eric Weitz, Wolfgang M.H. Sachtler, "Low Activation Energy Pathway for the Catalyzed Reduction of Nitrogen Oxides to N2 by Ammonia", Catalysis Letters, p. 5-9, vol. 98, (2004). Published

Bin Wen, Younghoon Yeom, Eric Weitz, Wolfgang M.H. Sachtler, "Mechanism of Nitrogen Oxide Reduction with Acetaldehyde in Simulated Diesel Emissions over Zeolite-based Catalysts", Abstract for ICC in Paris,, p. , vol. , (2004).

Younghoon Yeom, Juan Henao, Meijun Li, Wolfgang M.H. Sachtler and Eric Weitz, "The Role of NO in the Mechanism of NOx Reduction with Ammonia over a BaNa-Y Catalyst", Journal of Catalysis, p. , vol. , ( ). Submitted

Meijun Li, Younghoon Yeom, Eric Weitz and Wolfgang M.H. Sachtler, "Mechanism of Catalyzed NOx Reduction in Diesel Engine Exhaust", Abstract (Invited Keynote Lecturer), 19th North American Congress on Catalysis, p. , vol. , (2004).

Mayfair C. Kung and Harold H. Kung, "Selective Lean NOx Reduction over Metal Oxides", Topics in Catalysis, p. 105, vol. 28, (2004). Published

Angelina Kozlova, Hiu-Ying Law, Mayfair C. Kung and Harold H. Kung, "Nitrogen Production Efficiency for Acetaldehyde and Propionadehyde in Lean NOx Reducation over Anatase Titania", Catal. Lett., p. 211, vol. 95, (2004). Published

C.K. Costello, J. Guzman, J.H. Yang, Y.M. Wang, M.C. Kung, B.C. Gates, and H.H. Kung, "Activation of Au/y-Al2O2 Catalysts for CO Oxidation: Characterization by X-ray Absorption Near Edge Structure and Temperature Programmed Reduction", J. Phys. Chem. B, p. 12529, vol. 108(33), (2004). Published

Mayfair C. Kung, Colleen K. Costello, Harold H. Kung, "CO Oxidation over Supported Au Catalysts", Catalysis, p. 425, vol. 17, (2003). Published

H.H. Kung, M.C. Kung, and C.K. Costello, "Supported Au Catalysts for Low Temperature CO Oxidation", J. Catal., p. 425, vol. 216, (2003). Published

C.K. Costello, J.H. Yang, H-Y. Law, Y. Wang, J-N. Lin, L.D. Marks, M.C. Kung and H.H. Kung, "On the Potential Role of Hydroxyl Groups in CO Oxidation over Au/Al2O2", Appl. Catal. A General, p. 15-24, vol. 243(1), (2003). Published

C.K. Costello, H-S. Oh, J.H. Yang, Y.M. Wang, S.R. Bare, H.H. Kung, M.C. Kung, "Selective Catalytic Oxidation of CO in H2 over Au/Al2O3", Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry, p. 669, vol. 47(2), (2002). Published

M.E. Greene, A.N. Chiaramonti, S.T. Christensen, L.X. Cao, M.J. Bedzyk and M.C. Hersam, "Controlled Nanoscale Morphology of Hematite(0001) Surfaces Grown by Chemical Vapor Transport", Adv. Mater., p. , vol. , (2004). Submitted

D.L. Johnson, Vinayak P. Dravid, F. Qu, L. Fu, "Direct Evidence of Oxidized Gold on Supported Gold Catalysts", J. Phys. Chem., p. , vol. , (2004). Submitted

O. Geier, R.Q. Snurr, F. Stallmach, J. Karger, "Boundary Effects of Molecular Diffusion in Nanoporous Materials: A Pulsed Field Gradient Nuclear Magnetic Resonance Study", J. Chem. Phys., p. , vol. , ( ). in press

Haubein, N.C., McMillan, S.A., and Broadbelt, L.J., "Many-Body Optimization Using Quantum Mechanical Monte Carlo", Journal of Chemical Information and Computer Science, p. 68-74, vol. 43(1), (2003). Published

McMillan, S.A., Snurr, R.Q., and Broadbelt, L.J., "Interaction of Divalent Metal Cations with Ferrierite", Microporous and Mesoporous Materials, p. , vol. , (2003). Accepted

McMillan, S.A., Broadbelt, L.J. and Snurr, R.Q., "Ab Initio Stochastic Optimization of Conformational and Many-Body Degrees of Freedom", Journal of Chemical Information and Computer Science, p. , vol. , (2003). Accepted

McMillan, S.A., Broadbelt, L.J. and Snurr, R.Q., "Effect of Local Framework Heterogeneity on NO Adsorption in Cobalt-Ferrierite", J. Catal., p. 117, vol. 219, (2003). Published

McMillan, S.A., Snurr, R.Q., and Broadbelt, L.J., "Origin and Characteristics of Preferential Adsorption on Different Sites in Cobalt-Exchanged Ferrierite", J. Phys. Chem. B, p. , vol. , (2003). Accepted

McMillan, S.A., Broadbelt, L.J., and Snurr, R.Q., "Theoretical Modeling of Zeolite Catalysis: Nitrogen Oxide over Metal-Exchanged Zeolites", Environmental Catalysis, p. , vol. , (2003). Submitted

Hurum, D.C., Agrios, A.C., Crist, S.E., Gray, K.A., Rajh, T., Thurnauer, M.C., "Probing Reaction Mechanisms in Mixed Phase TiO2 by EPR", J. Electron Spect., p. , vol. , ( ). Submitted

Hurum, D.C., Gray, K.A., Rajh, T., Thurnauer, M.c., "Recombination Pathways in the Degussa P25 Formation of TiO2: Surface versus Lattice Mechanisms", J. Phys. Chem. B, p. , vol. , ( ). in press

Hurum, D.C., Gray, K.A., Rajh, T., Thurnauer, M.C., "Photo-initiated Reactions of 2,4,6 TCP on Degussa P25 Formulation TiO2: Wavelength Sensitive Decomposition", J. Phys. Chem. B, p. 16483, vol. 108, (2004). Published

Hurum, D.C., Agrios, A.G., Gray, K.A., Rajh, T., Thurnauer, M.C., "Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO2 Using EPR", J. Phys. Chem. B, p. 4545, vol. 107, (2003). Published

A. Agrios, K. Gray, E. Weitz, "Narrow-Band Irradiation of Homologous Series of Chlorophenols on TiO2: Charge Transfer Complex Formation and Reactivity", Langmuir, p. 5911, vol. 20, (2004). Published

A. Agrios, K.A. Gray, E. Weitz, "Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO2 under Sub-bandgap Illumination", Langmuir, p. 1402, vol. 19, (2003). Published

S.I. Chang, K.A. Gray,, "Qualitative and Quantitative Analysis of the Extracellular DNA from Pseudomonas aeruginosa Biofilms by Pyrolysis/GC/MS", Applied and Analytical Pyrolysis, p. , vol. , (2004). Accepted

S.I. Chang, K.A. Gray, M. Parsek, "Chemical Characterization of the Extracellular Polymeric Substances from Pseudomonas aeruginosa Biofilms", Environ. Sci. Technol., p. , vol. , (2004). Submitted

A.N. Chiaramonti, J.D. Pless, L. Liu, J.P. Smit, C.H. Lanier, K.R. Poeppelmeier, P.C. Stair, and L.D. Marks, "Optical Floating Zone Growth of Single Crystal Hematite from a CaFe4O2 Based Solvent", Journal of Crystal Growth and Design, p. 749, vol. 4, (2004). Published

A.N. Chiaramonti and L.D. Marks, "Impurity Stabilized Surface Phase on Ion Bombarded Hematite(0001)", Surface Science, p. , vol. , (2004). Submitted

L. Cheng, P. Fenter, M.J. Bedzyk, N.C. Sturchio,, "Fourier-Expansion Solution of Atom Distributions in a Crystal Using X-Ray Standing Waves", Phys. Rev. Lett., p. 255503-1, vol. 90, (2003). Published

J.S. Okasinski, D.A. Walko, C-Y. Kim, M.J. Bedzyk, "X-ray Standing Wave Imaging of the 1/3 ML Sn/Ge(111) Surface", Phys. Rev. B., p. 041401(R), vol. 69, (2004). Published

Z. Zhang, P. Fenter, L. Cheng, N.C. Sturchio, M.J. Bedzyk, M. Machesky, D.J. Wesolowski, "Model-independent X-ray Imaging of Adsorbed Cations at the Crystal-Water Interface", Surf. Sci. Lett., p. L95, vol. 554, (2004). Published

Z. Zhang, P. Fenter, L. Cheng, N.C. Sturchio, M.J. Bedzyk, M. Predota, A. Bandura, J. Kubicki, S.N. Lovov, P.T. Cummings, A.A. Chialvo, M.K. Ridley, P. Benezeth, L. Anovitz, D.A. Palmer, M.L. Machesky, D.J. Wesolowski, "Ion Adsorption at the Rutile-Water Interface: Linking Molecular and Macroscopic Properties", Langmuir, p. 4954, vol. 20, (2004). Published

J.A. Libera, R.W. Gurney, S.T. Nguyen, J.T. Hupp, C. Liu, R. Conley, and M.J. Bedzyk, "X-ray Nanoscale Profiling of Layer-by-Layer Assembled Metal/Organo-Phosphonate Films", Langmuir, p. 8022, vol. 20, (2004). Published

S. Rihs, N.C. Sturchio, K. Orlandini, L. Cheng, H. Teng, P. Fenter and M.J. Bedzyk, "Interaction of Uranyl with Calcite Under Alkaline Conditions", Enviro. Sci. & Technol., p. , vol. , (2004). in press

C.-Y. Kim, A.A. Escuadro, M.J. Bedzyk, L. Liu, and P.C. Stair, "X-ray Scattering Study of Stoichiometric Recovery of the alphaFe2O3(0001) Surface", Surf. Sci., p. , vol. , (2004). in press

A.A. Escuadro, D.M. Goodner, J.S. Okasinski, and M.J. Bedzyk, "X-ray Standing Wave Imaging of the Sn/Si(111) (Square root of 3) X (Square root of 3) Surface", Phys. Rev. B, p. , vol. , (2004). in press

C.Y. Kim and M.J. Bedzyk, "The Electronic Structure Study of the V/alpha-Fe2O3(0001) System", Phys. Rev. B, p. , vol. , ( ). Submitted

D.M. Goodner, D.L. Marasco, A.A. Escuadro, L. Cao, M.J. Bedzyk, "X-ray Standing Wave Investigation of (2x1) Phases of Barium and Strontium on Si(001)", Phys. Rev. B, p. , vol. , (2004). to be submitted

J.A. Libera, R.W. Gurney, C.P. Schwarz, H. Jin, T-L. Lee, S.T. Nguyen, J.T. Hupp, and M.J. Bedzyk, "Comparative X-Ray Standing Wave Analysis of Metal-Phosphonate Multilayer Films of Dodecane and Porphyrin Molecular Square", J. Phys. Chem. B, p. , vol. , (2004). Submitted

Wang, Y., Marks, L.D., "Surface Evolution of Rutile TiO2 Under Oxidation Condition", Surface Science, p. , vol. , (2004). Submitted

O. Warschkow, Y. Wang, A. Subramanian, M. Asta, D.E. Ellis, L.D. Marks, "Ordered Oxygen Vacancy Structure on the TiO2(100) Surface", Phys. Rev., p. , vol. , (2004). in draft

Alyson V. Whitney, Benjamin D. Myers, and Richard P. Van Duyne, "Sub-100nm Triangular Nanopores Fabricated with the Reactive Ion Etching Variant of Nanosphere Lithography and Angle-Resolved Nanosphere Lithography", Nano Letters, p. 1507-1511, vol. 4 (8), (2004). Published

Edulji, S.K.; Nguyen, S.T., "Catalytic Olefin Cyclopropanation Using -oxo-Bis(salen)Iron(III) Complexes", Organometalics, p. 3374-3381, vol. 22, (2003). Published

Paddock, R.L.; Hiyama, Y.; McKay, J.; Nguyen, S.T., "Co(III) Porphyrin/DMAP: An Efficient Catalyst for the Synthesis of Cyclic Carbonates from CO2 and Epoxides", Tetrahedron Lett., p. 2023-2026, vol. 45, (2003). Published

Jing, H.; Edulji, Smita K.; Gibbs, J.M.; Stern, C.L.; Zhou, H.; Nguyen, S.T., "(Salen) Tin Complexes: Syntheses, Characterization, Crystal Structures, and Catalytic Activity in the Formation of Propylene Carbonate from CO2 and Propylene Oxide", Inorg. Chem., p. 4315-4327, vol. 43(14), (2004). Published

Keefe, M.H.; O'Donnell, J.L.; Bailey, R.C.; Nguyen, S.T.; Hupp, J.T., "Permeable, Microporous Polymeric Membrane Materials Constructed from Discrete Molecular Squares", Adv. Mater., p. 1936-1939, vol. 15, (2003). Published

Edulji, S.K.; Nguyen, S.T., "Substrate Scope in the Olefin Cycloproponation Reaction Catalyzed by -ixo-bis[(salen)iron(III)] Complexes", Pure Appl. Chem., p. 67-72, vol. 76(3), (2004). Published

Graves, C.R.; Merlau, M.L.; Morris, G.A.; Sun, S.-S.; Nguyen, S.T.; Hupp, J.T., "Analysis and Purification of Supramolecular Complexes Using Gel-Permeation Chromatography", Inorg. Chem., p. 2013-2017, vol. 43(14), (2004). Published

Paddock, R.L.; Nguyen, S.T., "Chiral CoIII(Salen) Catalyst for the Synthesis of Cyclic Carbonates", Chem. Commun., p. 1622-1623, vol. , (2004). Published

Jin, H.; Kinser, C.R.; Bertin, P.A.; Kramer, D.E.; Libera, J.A.; Hersam, M.C.; Nguyen, S.T.; Bedzyk, M.J., "X-ray Studies of Self-Assembled Organic Monolayers Grown on Hydrogen-Terminated Si(111)", Langmuir, p. 6252-6285, vol. 20(15), (2204). Published

Snurr, R.Q.; Hupp, J.T.; Nguyen, S.T., "Propsects for Nanoporous Metal-Organic Materials in Advanced Separations Processes", AIChE, p. 1090-1095, vol. , (2004). Published

Libera, J.A.; Gurney, R.W.; Nguyen, S.T.; Hupp, J.T.; Liu, C.; Conley, R.; Bedzyk, M.J., "X-ray Nanoscale Profiling of Layer-by-Layer Assembled Metal/Organo-Phosphate Films", Langmuir, p. 8022-8029, vol. 20(19), (2004). Published

Merlau, M.L.; Sun, S.-S.; Nguyen, S.T.; Hupp, J.T., "Anthracene-Induced Turnover Enhancement in the Manganese(III) Porphryin-Catalyzed Epoxidation of Olefins", Inorg. Chem., p. , vol. , (2004). Accepted

Cho, S.-H.; Nguyen, S.T.; Hupp, J.T., "Manganese Porphyrin Multilayer Films Assembled on ITO Electrodes via Zirconium Phosphonate Chemistry: Chemical and Electrochemical Catalytic Activity", Topics in Catalysis, p. , vol. 31, (2004). Accepted

Andrea B. Voges, Hind A. Al-Abadleh, Michael J. Musorrafiti, Paul A. Bertin, and Franz M. Geiger, "Carboxylic Acid- and Ester-Functionalized Silane Scaffolds on Glass Studied by Broadband Sum Frequency Generation", J. Phys. Chem. B., p. , vol. , (2004). in press

Hind A. Al-Abadleh, Andrea B. Voges, Paul A. Bertin, SonBinh T. Nguyen, and Franz M. Geiger, "Chromium(VI) Binding to Functionalized Silica/Water Interfaces Studied by Nonlinear Optical Spectroscopy", J. Am. Chem. Soc., p. 11126, vol. 126, (2004). Published

Christopher T. Konek, Michael J. Musorrafiti, Hind A. Al-Abadleh, Paul A. Bertin, SonBinh T. Nguyen, and Franz M. Geiger, "Interfacial Acidities, Charge Densities, Potentials, and Energies of Carboxylic Acid Functionalized Silica/Water Interfaces Determined by Second Haromic Generation", J. Am. Chem. Soc., p. 11754, vol. 126, (2004). Published

Patricia Metthe Todebush, Janet Maher, and Franz M. Geiger, "Soil Science Experiment: I. Sedimentation Time Measurements of Soil Particles by Light Scattering; II. Determination of Chromium, Lead and Iron Concentrations in Soil Samples via ICP", J. Chem. Ed., p. , vol. , (2004). in press

Pless, J.D.; Erdman, N.; Ko, D.,; Marks, L.D.; Stair, P.C.; Poeppelmeier, K.R., "Single-Crystal Growth of Magnesium Orthovanadate, Mg-3(VO4)(2), by the Optical Floating Zone Technique", Crystal Growth and Design, p. 615-619, vol. 3(4), (2003). Published

Erdman, N.; Poeppelmeier, K.R.; Asta, M.; Warschkow, O.; Ellis, D.E.; Marks, L.D., "The Structure and Chemistry of the TiO2-rich Surface of SrTiO3(001)", Nature, p. 55, vol. 419, (2002). Published

Erdman, N.; Poeppelmeier, K.R.; Asta, M.; Warschkow, O.; Ellis, D.E.; Marks, L.D.;, "Surface Structures of SrTi03(001): A TiO2-rich Reconstruction with a c(4x2) Cell", J. Am. Chem. Soc., p. 10050, vol. 125(33), (2002). Published

Pless, J.D.; Bardin, B.B.; Kim, H.-S.; Ko, D.; Smith, M.T.; Hammond, R.R.; Stair, P.C., "Catalytic Oxidative Dehydrogenation of Propane over Mg-V/Mo Oxides", Journal of Catalysis, p. 419, vol. 223(2), (2004). Published

Wang, X.D.; Pless, J.D.; Van der Griend, D.A.; Stair, P.C.; Poeppelmeier, K.R., "Vanadium and Molybdenum Disorder in M2.5VMoO8 (M=Mg, Mn, and Zn) Determined with Neutron Powder Diffraction and Phase Formation Studies of Mg2.5+xV1+2xMo1-2xO8", Journal of Alloys and Compounds, p. 87, vol. 379, (2004). Published

D.L. Chopp, M.J. Kirisits, B. Moran, M. Parsek, "The Dependence of Quorum Sensing on the Depth of a Growing Biofilm", Bulletin of Mathematical Biology, p. 1053-1079, vol. 65, (2003). Published

G.M. Teitzel and M.R. Parsek, "Heavy Metal Resistance of Biofilm and Planktonic Pseudomonas aeruginosa.", Appl. Environ. Microbiol. , p. 2313-2320, vol. 69, (2003). Published

Books or Other One-time Publications

D.E. Ellis and K.C. Mundim, "Electroceramics: Modeling of Grain Boundaries, Interfaces and Defects", (2000). Book, in press
Collection: Encyclo. of Materials: Science and Technology
Bibliography: Elsevier, Amsterdam

D.E. Ellis, K.C. Mundim,, "An Embedded Cluster Approach to Computational Materials Science", (1999). Book, Published
Editor(s): P. Vincenzini, Techna, Faenza

Collection: (Proc. of 9th CIMTEC Congress)
Bibliography: Techna, Faenza

D.E. Ellis, K.C. Mundim, V.P. Dravid, J.W. Rylander, "Hybrid Classical and Quantum Modeling of Defects, Interfaces, and Surfaces", (1999). Book, Published
Editor(s): A. Pechenik, R.K. Kalia, and P. Vashista
Collection: Computer-Adied Design of High Temperature Materials
Bibliography: Oxford University Press

Hai-Ying Chen, El M. El Malki, Xiang Wang, and W.M.H. Sachtler, "Mono- and Multinuclear Oxo-Cations in Zeolite Cavities", (2001). Book, Published
Editor(s): G. Centi, B. Wichterlova, A.T. Bell
Collection: Catalysis by Unique Metal Ion Structures in Solid Matrices: From Science to Application
Bibliography: NATO Science Series II Mathematics, Physics and Chemistry; Kluwer Academic Publishers, Dordrecht, The Netherlands (Vol 13)

McMillan, S.A., Broadbelt, L.J., and Snurr, R.Q., "Structure and Ultraviolet/Visible Spectra of Cobalt-Exchanged Ferrierite: A Computational Study", (2000). Book, Published
Bibliography: Proceedings of FOMMS, Keystone, CO.

Colleen K. Costello, "Aspects of CO Oxidation over Supported Gold Catalysts and Characterization of the Active Site", (2003). Thesis, Published
Bibliography: Ph.D. Thesis, Chemical and Biological Engineering, Northwestern University

A. Agrios, K. Gray, "Beyond Photocatalytic Environmental Remediation: Novel TiO2 Materials and Applications", (2004). Book, in press
Editor(s): V. Grassian ed. (Marcel Dekker)
Bibliography: Environmental Catalysis

M. Starkey, M. Parsek, K. Gray, S.I. Chang, "A Sticky Business: The EPS Matrix of Bacterial Biofilms", (2003). Book, Published
Editor(s): M. Ghannoum and G.A. O'Toole, eds.
Bibliography: ASM Press

Scott A. McMillan, "Modeling Nitrogen Oxide Catalysis Over Cobalt-Exchanged Zeolites: The Role of Cobalt-Zeolite Coordination Environment", (2003). Thesis, Ph.D. Thesis
Bibliography: Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208

M.J. Bedzyk and L. Cheng, "X-ray Standing Wave Studies of Minerals and Mineral Surfaces: Principles and Applications", (2002). Publication, Published
Editor(s): P.A. Fenter, M.L. Rivers, N.C. Sturchio, S.R. Sutton
Bibliography: Mineralogical Society of America, Washington, DC; Vol. 49, p.221

D.A. Walko, O. Sakata, P.F. Lyman, T.-L. Lee, B.P. Tinkham, J.S. Okasinski, Z. Zhang and M.J. Bedzyk, "Surface and Interface Studies at

APS Endstation 51D-C", (2004). Publication, Published
Editor(s): T. Warwick, J. Arthur, H.A. Padmore and J. Stohr
Collection: Synchrotron Radiation Instrumentation: Eighth International Conference
Bibliography: AIP Conference Proceedings 705, American Institute of Physics, New York

M.J. Bedzyk, P. Fenter, Z. Zhang, L. Cheng, J.S. Okasinski, N.C. Sturchio, "X-ray Standing Wave Imaging", (2004). Publication, Published
Collection: Synchrotron Radiation News (Technical Review)
Bibliography: Vol. 17, No. 3, p.5-10.

M.J. Bedzyk, "Scattering: X-ray Standing Wave Techniques", (2004). Publication, in press
Editor(s): F. Bassani, J. Liedl, P. Wyder
Bibliography: Elsevier

Andrea B. Voges, Hind A. Al-Abadleh, and Franz M. Geiger, "Applications of Non-Linear Optical Techniques for Studying Heterogeneous Systems Relevant in the Natural Environment", (2004). Review, Invited Book Chapter, Accepted
Editor(s): V. Grassian
Bibliography: Environmental Catalysis

J. H. Hoover and F.M. Geiger, "Progress Report - Red Valley Land Use Planning Committee", (2004). Progress Report, Published
Bibliography: USA

F.M. Geiger, "Article, Toxic Metal and Atmospheric Research", (2004). Featured Newspaper Article, Published
Bibliography: The New Reader

F. M. Geiger, "Investigative Report on the Navajo Project", (2005). Report/Newspaper Article, Accepted
Collection: Los Angeles Times Newspaper
Bibliography: Los Angeles, California

Erdman, Natasha, "Structure, Morphology and Chemistry of Catalytic Transition Metal Oxides", (2002). Thesis, Published
Bibliography: Department of Materials Science and Engineering
Northwestern University
Evanston, IL

Pless, Jason D., "Oxidative Dehydrogenation of Propane over Magnesium Vanadates and Molybdates", (2003). Thesis, Published
Bibliography: Department of Chemistry
Northwestern University
Evanston, IL

Web/Internet Site

URL(s):
http://www.iec.northwestern.edu/
Description:
www.iec.northwestern.edu (main web site for the IEC and gives detailed information on related projects, faculty members, etc.)

Other Specific Products

Product Type:

Other inventions

Product Description:

An innovative vapor condensation nanophase particle synthesis system, inaugurated under AFOSR funding, has been completed. Both resistive and arc heating are incorporated. A two-stage jet ensures high recovery rates and atmospheric isolation downstream from the evaporator. An optional aerosol reactor can be inserted between the synthesis chamber and the collector. Two patents already have been issued on the system (prior to NSF support).

Sharing Information:

Novel catalyst or materials synthesis

Product Type:

Method for Measuring

Product Description:

Developed a method for measuring in situ the diffuse double layer structure that exists at the liquid/solid interface and effects surface chemistry. We are also developing the use of XSW surface analysis for less-than-perfect (normal) single crystal surfaces, i.e., TiO2 and Fe2O3.

Sharing Information:

These methods will be implemented as collaborative research.

Product Type:

Software (or netware)

Product Description:

We developed a reactive transport code to examine the effects of coupling one-dimensional steady-state groundwater flow with equilibrium- and kinetic-based reactions to understand how microbial communities bioprotect themselves from metal toxicity using gradients.

Sharing Information:

Will be shared as a means of collaborative research efforts.

Product Type:

Data or databases

Product Description:

A 250-page document that presents the research background, the results obtained so far, and a plan of future investigation for the completion of the Ph.D. thesis of Pablo Pasten.

Sharing Information:

As a means of collaborative research efforts.

Product Type:

Physical collection (samples, etc.)

Product Description:

Nanophase gamma-alumina

Sharing Information:

As a means of collaborative research.

Product Type:

Physical collection (samples, etc.)

Product Description:

Well characterized TS-1 samples for our use in future catalytic and adsorption studies.

Sharing Information:

As a means of collaborative research.

Product Type:

Patent Disclosures

Product Description:

"Enhancement of Epoxidation Catalysts Through Lewis Acid Additives", Merlau, M.L.; Grande, W.J.; Morris, G.A.; Nguyen, S.T.; Hupp, J.T. NU Patent Disclosure# 98090; Provisional Patent filed 4/99.

"Commercial-Scale Synthesis of p-Type Transparent Conductors", Shahriari, D.Y.; Barnabe, A.; Mason, T.O.; Poeppelmeier, K.R.
U.S. Provisional Patent 60/281,211(2001).

"Chemical CO2 Fixation: Salen Complexes as Highly Efficient Catalysts for the Coupling of CO2 and Epoxides", Paddock, R.L. and Nguyen, S.T.
NU Patent Disclosure# 21048; Provisional Patent filed 8/01.

"One-Dimensional Zeolites as Hydrocarbon Traps for Cold-Start Automotive Emissions", Czaplewski, K.F.; Reitz, T.L.; Snurr, R.Q.
NU Patent Disclosure# 21070; Provisional Patent filed 1/02.

Sharing Information:

Patent disclosure.

Product Type:

Teaching aids

Product Description:

This research project has produced a stand-alone Materials World Module (MWM) unit entitled "Environmental Catalysis". The module is highly engaging and involves two weeks of hands-on activities, problem solving and internet research on the topic of catalysis. The curriculum gives secondary school students a good understanding of how kinetic processes take place in chemical reactions that can be applied to catalysis, photochemistry and the protection of our natural environment. Students analyze different types of catalytic systems, including homogeneous and heterogeneous catalysis, thermocatalysis, and photocatalysis. In their study, they explore concepts such as catalytic selectivity, poisoining, condition optimization, and waste minimization, which they apply in the design and construction of a unique catalytic deodorizing device.

Sharing Information:

As part of the IEC Materials World Module, several materials were developed as educational aids for secondary school students:
1. Scientific Experiment/demonstration for Catalyzing with Platinum Black (Brief Summary of Exercise: To observe the effect of a catalyst);
2. Scientific experiment: Our Dependence on Catalysts (Concept: Catalysts allow us to use less energy and fewer raw materials and to produce less harmful waste in the manufacturing of products. Thus, catalysts are essential to protecting and preserving the environment.);
3. Scientific experiment: Searching for Catalysts (Concept: Catalysts are used in a wide variety of areas, including industrial processes, pollution treatment, and natural processes.);
4. Scientific experiment: Homogeneous and Heterogeneous Acid Catalysts (Concept: There are a number of safety and environmental benefits to using heterogeneous acid catalysts rather than homogeneous acid catalysts.);
5. Scientific experiment: Using a Metal Catalyst to Degrade an Air Pollutant: Catastrophe or Catalysts (Note: Exhaust gases from the combustion chambers of the engine flow out of the exhaust manifold toward the catalytic converter. The reacted gaseous products then flow out of the catalytic converter and proceed through the resonantor, the exhaust pipe, muffler, and eventually out of the tailpipe; Concept: Heterogeneous metal catalysts can be used to clean polluted air by catalyzing the conversion of pollutants into safer substances.);
6. Group exercise: Conceptual Design for Environmental Catalysis (Goal is to think of an original solution to an environmental problem, researched by the class, and to outline conceptually how you (the students) would design, construct, test, evaluate and design your prototype.);
7. Environmental Catalysis Activities: a) Catalyst Poisoning and Catalyst Inactivation; b) Incomplete Combustion of Fossil Fuels; c) Photocatalysis; d) Using Photocalysis to Degrade a Water Pollutant; e) Titanium Dioxide;

Product Type:

Scientific Presentations

Product Description:

SCIENTIFIC PRESENTATIONS

8th IEC Semi-Annual Scientific Meeting, September 2002,
Northwestern University, Evanston, IL

Oral Presentations:
? Peter C. Stair, IEC Overview and MSCO Highlights
? SonBinh T. Nguyen, Chemical Processing Highlights
? Jason Pless, K. R. Poeppelmeier, Peter C. Stair, ?Single Crystal Growth of Magnesium Orthovanadate and Surface Studies?
? Natasha Erdman, L. D. Marks, K.R. Poeppelmeier, ?Perovskite Surface Chemistry: Structure and Morphology of SrTiO3?
? Harold H. Kung, Kimberly A. Gray, Emissions Treatment Highlights

? Oliver Warschkow, D. Ellis, ?Surface Structures of SrTiO3(001) ? The Theoretical Perspective?
? Bin Wen, Wolfgang M.H. Sachtler, ?Enhanced Activity and Selectivity of Co/ZSM-5 for NO Reduction with CH4 After Water Vapor Pretreatment?
? Jean-François Gaillard, Natural Environment Hightlights
? Gail Teitzel, Matthew Parsek, ?Biofilm and Free-Swimming Resistance of Pseudomonas aeruginosa to Heavy Metals?
? Sung IL Chang, Kimberly A. Gray, ?The Role of Extracellular Polymeric Substances in Reducing Metal Stress; The Chemical Characterization of Pseudomonas aeruginosa Biofilms?

Poster Presentations:
? Chang-Yong Kim, A.A. Escuadro, Michael J. Bedzyk, Li Liu, Peter C. Stair, ?Stoichiometric Change of ά-Fe2O3(0001) Surfaces: X-ray Scattering and XPS Study?
? Scott A. McMillan, Linda J. Broadbelt, Randall Q. Snurr, ?Effect of Local Framework Heterogeneity on NO Adsorption on Cobalt-Ferrierite?
? Maria C. Curet-Arana, SonBinh T. Nguyen, Linda J. Broadbelt, Randall Q. Snurr, ?Novel Epoxidation Catalysts: Manganese Porphryins Encapsulated within Molecular Squares?
? Oliver Warschkow, Natasha Erdman, M. Asta, Kenneth R. Poeppelmeier, Laurence D. Marks, Donald E. Ellis, ?Surface Structures of SrTiO3(001) ? The Theoretical Perspective?
? Nathan P. Guisinger, R. Basu, Mark C. Hersam, ?Atomic Level Characterization and Control of Organosilicon Surface Chemistry using Scanning Tunneling Microscopy?
? Terry E. Heil, Susa Stone, Amy L.. Dahl, Edward Peltier, Jean-François Gaillard, ?Quantitative Fluorescence Imaging of an Arsenic Hyper-Accumulating Fern?
? Amy L. Dahl, Jean-François Gaillard, ?A Suite of Analytical Techniques for Probing Metal-microbe Interactions?
? Amanda Mifflin, Katie A. Gerth, Brian M. Weiss, Franz M. Geiger (speaker), ?In situ Laser Studies of Chromium Interaction with Quartz-Water Interfaces?
?Andrea B. Voges, Jasmy A. Methipara, Franz M. Geiger (speaker), ?Heterogeneous NOx Chemistry in the Atmosphere?
? Alexander Agrios, Kimberly A. Gray, ?Photocatalytic Transformation of 2,4,5-Trichlorophenol on TiO2 under Sub-Bandgap Illumination?
? Jason D. Pless, Natasha Erdman, Billy Bardin, Dongguen Ko, Laurence D. Marks, Peter C. Stair, Kenneth Poeppelmeier, ?Catalytic Studies for the Oxidative Dehydrogenation of Propane over Mixed Metal Oxides?
? Ann N. Chiaramonti, Natasha Erdman, Peter C. Stair, Laurence D. Marks, ?Investigation of the ά-Fe2O3 (0001) Surface Structure Using TEM?
? Wen-Mei Xue, Alexander Kozlov, Mayfair C. Kung, Harold H. Kung, SonBinh T. Nguyen, Jeffery T. Miller, ?Lewis-based Accelerated Trans-Epoxidation Reaction?
? Colleen K. Costello, Jeffery H. Yang, Hyung-Seuk Oh, Mayfair C. Kung, Harold H. Kung, ?Deuterium Isotope Effect in CO Oxidation over Au/γAl2O3?
? Robert L. Paddock, SonBinh T. Nguyen, ?Catalysts for Chemical CO2 Fixation?
? Christopher R. Graves, Gregory A. Morris, Melissa L. Merlau, SonBinh T. Nguyen, Joseph T. Hupp, ?The Analysis and Purification of Molecular Squares Using Gel-Permeation Chromatography?
? Richard W. Gurney, Peerasak Paoprasert, Matthew Wightman, SonBinh T. Nguyen, Joseph T. Hupp, ?Sensing Strategies Based Upon Porphyrin/Rhenium Molecular Square Films?
? Younghoon Yeom, Eric Weitz, ?An FT-IR Study of the Role of Acetaldehyde Adsorbed in Cation Exchanged Zeolite Y in the Catalytic Reduction of NOx?

9th IEC Semi-Annual Scientific Meeting, March 2003
Northwestern University, Evanston, IL

Oral Presentations:
? Peter C. Stair, IEC Overview and MSCO Highlights
? Chen Huang, Linda J. Broadbelt, Randall Q. Snurr, ?Effects of Solvent on the Liquid Phase Oxidation of Olefins with Titanium Silicate-1?
? Chang-Yong Kim, Michael J. Bedzyk, ?X-ray Scattering Study of Stochiometry Recovery of ά-Fe2O3(0001) Surfaces?
? Michael Marsolek, Bruce E. Rittmann, Matthew Parsek, ?The Need for Photobiocatalysis: Biodegradation of 2,4,5-Trichlorophenol and Application to Actual Photocatalytic Effluent?
? Richard W. Gurney, SonBinh T. Nguyen, Joseph T. Hupp, ?Towards Catalytic Membrane Reactors: Molecular Thin-Films for Single-Site Epoxidation Catalysis?
? Colleen K. Costello, Mayfair C. Kung, Harold H. Kung, ?Nature of the Active Site for CO Oxidation over Au/γAl2O3?
? Hack-Sung Kim, Peter C. Stair, ?The Formation of 3 x 3 Tunnel Structured Todorokite Nanoparticles by Microbial Catalysis?

Poster Presentations:
? Lixin Cao, Mark C. Hersam, Michael J. Bedzyk, ?Atomic-Scale Scanning Tunneling Microscopy of Oxide Surfaces?

? Scott A. McMillan, Linda J. Broadbelt, Randall Q. Snurr, ?The Influence of Cobalt-Zeolite Environment on NOx Reduction Catalysis?
? Chen E. Huang, Linda J. Broadbelt, Randall Q. Snurr, Mayfair C. Kung, ?Effects of Solvent on the Liquid Phase Oxidation of Olefins with Titanium Silicate-1?
? Oliver Warschkow, Natasha Erdman, Kenneth R. Poeppelmeier, Mark Asta, Donald E. Ellis, Laurence D. Marks ?Surface Structures of SrTiO3(001)?
? Peter Wightman, Ian Saratovsky, Jean-François Gaillard, ?Biogenic Manganese Oxides: Formation, Characterization, and Reactivity?
? Andrea B. Voges, Jasmy A. Methipara, Franz M. Geiger (speaker), ?Vibrational Sum Frequency Spectra of Environmentally Relevant Surfaces?
? Amanda Mifflin, Katie A. Gerth, Brian M. Weiss, Franz M. Geiger (speaker), ?Investigations of Chromate Interaction with Quartz/Water Interfaces Using Second Harmonic Generation?
? Deanna Hurum, Alexander Agrios, Kimberly A. Gray, Marion C. Thurnauer, Tijana Rahj, ?Recombination Processes in Degussa P25 TiO2?
? Sarah Crist, Deanna Hurum, Alexander Agrios, Kimberly A. Gray, ?Differing Catalytic Activity of Size Fractions of Degussa P25?
? Junlian Zhang, Joseph T. Hupp, ?Directed Assembly Supramolecular Materials Featuring Nanoporous Cavity as Efficient and Selective Catalysts?
? Colleen K. Costello, Hyung-Seuk Oh, Mayfair C. Kung, Harold H. Kung, Yingmin Wang, Laurence D. Marks, ?Nature of Active Sites on Au/γAl2O3 for CO and Selective Oxidation?
? Hiu-Ying Law, Alexandra Kozlova, Mayfair C. Kung, Harold H. Kung, ?Low Temperature NOx Reduction by Acetaldehydge over TiO2?
? Wen-Mei Xue, Mayfair C. Kung, Harold H. Kung, SonBinh T. Nguyen. ?Deoxygenation of Epoxides by Methyltrioxorhenium(VII)?
? So-Hye Cho, SonBinh T. Nguyen, Joseph T. Hupp, ?Mn(Salen) Epoxidation Catalysts Heterogenized on Metal Oxide Supports?
? Ann Chiaramonti, Jason D. Pless, Peter C. Stair, Kenneth R. Poeppelmeier, Laurence D. Marks, ?Growth of Single Crystal ά-Fe2O3 from High Temperature Solutions?
? Gail Teitzel, Matthew R. Parsek, ?Response of Pseudomonas aeruginosa to Heavy Metals?
? Mary Jo Kirisits, Michael D. Marsolek, Bruce E. Rittmann, Matthew R. Parsek, ?Two-dimensional DNA Array ? Technique Development?
? Alex Schwarz, ByoungIn Sang, Bruce E. Rittmann, Jean-François Gaillard, Matthew R. Parsek, ?Biogeochemical Modeling?
? Jason D. Pless, Jared P. Smit, Courtney H. Lanier, Laurence D. Marks, Peter C. Stair, Kenneth R. Poeppelmeier, ?Catalytic Studies for the Oxidative Dehydrogenation of Propane over Mixed Metal Oxides?
? Jifei Jia, Krishnan Pillai, Wolfgang M.H. Sachtler, ?One-step Oxidation of Benzene to Phenol with Nitrous Oxide over Fe/MFI Catalysts?
? Bin Wen, Younghoon Yeom, Wolfgang M.H. Sachtler, Eric Weitz, ?NOx Reduction with Acetaldehyde over Non-Transition Metal Zeolite Catalysts: Tests and MS-TPO Analysis?
? Chao Zhang, Peter C. Stair, ?Coke Formation in MTG Process?
? Li Liu, Peter C. Stair, ?The Partial Oxidation of Methyl Radicals on ά-Fe2O3 (0001) Surfaces?
? Minseok Kim, Peter C. Stair, ?Selectivity and Activity ? How to Control??
? Younghoon Yeom, Eric Weitz, Bin Wen, Wolfgang M.H. Sachtler, ?NOx Reduction with Acetaldehyde over Non-Transition Metal Zeolite Catalyst: A Mechanistic Study Using FTIR Spectroscopy?
IEC Annual Scientific Meeting, March 2004
Northwestern University, Evanston, IL

Oral Presentations
? Peter C. Stair, IEC Overview and MSCO Highlights
? Maria Curet-Arana, Linda J. Broadbelt, Randall Q. Snurr, ?Epoxidation Reactions Catalyzed by Manganese Porphyrins: Understanding the Reaction Mechanism?
? Li Liu, Peter C. Stair, ?The Methyl Radical Chemistry on Single Crystal ά-Fe2O3 (0001) Surfaces?
? Guang Xiong, Peter C. Stair, ?Oxidative Dehydrogenation of Cyclohexane over Vanadium Oxide Catalyst Supported on Nanoporous Alumina Membrane?
? So-Hye Cho, SonBinh T. Nguyen, Joseph T. Hupp, ?Catechol Functionalized Salen Transition Metal Complexes Heterogenized on Metal Oxide Supports?
? Younghoon Yeom, Eric Weitz, Bin Wen, Wolfgang M.H. Sachtler, ?NOx Reduction from Diesel Emissions over a Non-Transition Metal Zeolite Catalyst: A Mechanistic Study Using FTIR Spectroscopy?
? Feng Qu, Vinayak P. Dravid, D. Lynn Johnson, ?Physical Synthesis of Heterogeneous Catalysts Using JENDA (Jet-Enhanced Nano-particle Deposition Apparatus)?

Poster Presentations:
? Chang-Yong Kim, Anthony Escuadro, Michael J. Bedzyk, ?XPS and XSW Studies of Vanadium Oxide Films Supported on ά-Fe2O3(0001)?
? Simon E. Albo, Linda J, Broadbelt, Randall Q. Snurr, ?Multiscale Modeling of Selective Catalytic Oxidation in Nanostructured Membranes?
? Chen E. Huang, Shaji Chempath, Linda J. Broadbelt, Mayfair C. Kung, Randall Q. Snurr, ?Effects of Solvent on the Liquid Phase Oxidation of Olefins with Titanium Silicate-1?

? Ian Saratovsky, Kenneth Poeppelmeier, Peter Wightman, Jean-François Gaillard, ?Synthesis and Structure of Manganese Oxides?
? Christopher Konek, Franz M. Geiger (speaker), ?Arsenic in the Environment: Interactions with Environmentally Relevant Surfaces?
? Catherine Schmidt, Xianghuai Wang, Eric Weitz, Franz Geiger, ?Indoor Air Pollution Remediation with Titanium Dioxide: Investigations of Thermal and Photochemical Behavior?
? Deanna Hurum, Sarah Crist, Kimberly A. Gray, Marion C. Thurnauer, Tijana Rahj, ?Effect of Nitrogen Containing Compounds on TiO2 Activity?
? Wen-Mei Xue, Mayfair C. Kung, Harold H. Kung, SonBinh T. Nguyen, Jeffery T. Miller, ?Deoxygenation of Epoxides by Methyltrioxorhenium(VII)?
? Hiu-Ying Law, Mayfair C. Kung, Harold H. Kung, ?Low Temperature NOx Reduction by Acetaldehyde over TiO2?
? Jeffrey H. Yang, Colleen Costello, Yingmin Wang, Laurence D. Marks, Mayfair C. Kung, Harold H. Kung, ?Nature of the Active Site for CO Oxidation over Au/γAl2O3 ?
? Smita Edulji, SonBinh T. Nguyen, ?Catalytic Epoxidation and Cyclopropanation using Fe(salen) Complexes?
? Courtney Lanier, Laurence Marks, Kenneth Poeppelmeier, ?Investigation of the SrTiO2 and Mg3V2O8 Surface Structures Under Reducing Conditions?
? Ann Chiaramonti, Jason D. Pless, Courtney Lanier, Jared Smit, Laurence D. Marks, Kenneth Poeppelmeier, Peter C. Stair, ?Low Pressure Single Step Growth of Single Crystal ά-Fe2O3 from High Temperature Solution?
? Jared P .Smit, Peter C. Stair, Kenneth Poeppelmeier, ?Catalytic Studies for the Dehydrogenation of Propane over Mixed Metal Oxides?
? Qi Zhao, Jodi O?Donnell, Joseph T. Hupp, Randall Q. Snurr, ?Porosity of Powder and Polycrystalline Bipyridine Re(CO)3CI Molecular Square Studied Through N2 Isotherm and NMR Techniques?
? Alyson Whitney, Richard Van Duyne, ?Sub-100 nm Triangular Nanowells Fabricated with the Reaction Ion Etching Variant of Nanosphere Lithography and Angle-Resolved Nanosphere Lithography?
? Xinjiang Zhu, Eric Weitz, Joseph T. Hupp, ?Tantalum Containing Oxynitride Compounds?

Additional Presentations:
? McMillan, S.A., Broadbelt, L.J. and Snurr, R.Q. ?Structure and Ultraviolet/Visible Spectra of Cobalt-Exchanged Ferrierite: A Computational Study?, poster presentation at Catalysis Club of Chicago Spring Symposium, Naperville, IL, May, 2000.
? McMillan, S.A., Broadbelt, L.J. and Snurr, R.Q. ?Structure and Ultraviolet/Visible Spectra of Cobalt-Exchanged Ferrierite: A Computational Study?, poster presentation at Foundations of Molecular Modeling and Simulation 2000, Keystone, CO, July, 2000.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?Structure and Spectra of Cobalt-Exchanged Ferrierite from Computational Chemistry?, UOP Engineering Science Skill Center, Des Plaines, IL, September, 2000.
? Snurr, R.Q. (speaker), McMillan, S.A., Clark, L.J. and Broadbelt, L.J. ?Computational Investigations of Zeolite Catalysis?, 221st National Meeting of the American Chemical Society, San Diego, CA, April, 2001.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?A Quantum Chemical Investigation of Cobalt Siting in Ferrierite?, poster presentation at Catalysis Club of Chicago Spring Symposium, Naperville, IL, May, 2001.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?Computational Investigation of NOx on Cobalt-Exchanged Ferrierite?, 17th North American Catalysis Society Meeting, Toronto, ON, June, 2001.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?Ab Initio Investigation of Cobalt Siting in Zeolites?, 222nd National Meeting of the American Chemical Society, Chicago, IL, August, 2001.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?Ab Initio Investigation of Cobalt Siting in Zeolites?, poster presentation at Center for Catalysis and Surface Science Annual Scientific Meeting, Evanston, IL, September, 2001.
? McMillan, S.A. (speaker), Broadbelt, L.J. and Snurr, R.Q. ?A Quantum Chemical Investigation of Cobalt Siting in Ferrierite?, Annual Meeting of the American Institute of Chemical Engineers, Reno, NV, November, 2001.
? Franz M. Geiger (speaker), ?Environmentally Relevant Surfaces and Interfaces Studied in situ and in Real Time Using Nonlinear Optics", January 2002:
- Institute for Industrial Catalysis, Northwestern University.
- Dept. of Civil Engineering, Northwestern University.
- Calvin College, MI.
- Hope College, MI.

? McMillan, S.A. (speaker), Snurr, R.Q., and Broadbelt, L.J. ?The Influence of Cobalt-Zeolite Environment on NOx Reduction Catalysis?, poster presentation at Catalysis Club of Chicago Spring Symposium, Evanston, IL, May, 2002.
? Lixin Cao (speaker), Mark C. Hersam, Michael J. Bedzyk, ?Self-Organized Nanometer Scale Structural Modulation Domains in Ultra-Thin Pseudomorphic RBa2Cu3O7 Films?, Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, October 2002.
? Oliver Warschkow (speaker), Donald E. Ellis, ?Surface Structures of Strontium Titanate(001) ? Towards a Model of Perovskite Surface Reconstruction?, Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, November 2002.
? McMillan, S.A. (speaker), Snurr, R.Q. and Broadbelt, L.J., ?The Influence of Cobalt-Zeolite Environment on NOx Reduction Catalysis?, Annual Meeting of the American Institute of Chemical Engineers, Indianapolis, IN, November, 2002.

? Curet-Arana, M.C. (speaker), Snurr, R.Q., and Broadbelt, L.J. ?Novel Epoxidation Catalysts: Manganese Porphyrins Encapsulated within Molecular Squares?, poster presentation at Catalysis Club of Chicago Spring Symposium, Evanston, IL, May, 2002.
? Snurr, R.Q. (speaker), Sanborn, M.J., Sarkisov, L., Curet-Arana, M.C. and Broadbelt, L.J. ?Catalysis and Transport in Nanoporous Materials?, Great Lakes ACS Meeting, Minneapolis, MN, June, 2002.
? Curet-Arana, M.C. (speaker), Snurr, R.Q. and Broadbelt, L.J., ?Novel Epoxidation Catalysts: Manganese Porphyrins Encapsulated within Molecular Squares?, Annual Meeting of the American Institute of Chemical Engineers, Indianapolis, IN, November, 2002.
? McMillan, S.A. (speaker), Snurr, R.Q. and Broadbelt, L.J., ?A Density Functional Theory Investigation of Metal Siting in Ferrierite?, Annual Meeting of the American Institute of Chemical Engineers, Indianapolis, IN, November, 2002.
? Peter Wightman (speaker), Jean-François Gaillard, ?The Effects of Biosorption on Mineral Solubilities?, Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, February 2003.
? McMillan, S.A. (speaker), Snurr, R.Q. and Broadbelt, L.J. ?Origin and Characteristics of Preferential Molecular Adsorption on Different Metal-Zeolite Sites?, poster presentation at Catalysis Club of Chicago Spring Symposium, Evanston, IL, May, 2003.
? L.J. Broadbelt, R.Q. Snurr, S.A., McMillan, D.Majumder, and M. C. Curet-Arana, ?Multiscale Modeling in Catalysis?, Department of Chemical Engineering, The Ohio State University, May 15, 2003.
? L.J. Broadbelt, R.Q. Snurr, S.A., McMillan, D.Majumder, and M. C. Curet-Arana, ?Multiscale Modeling in Catalysis?, ACS Colloid and Surface Science Symposium, Georgia Tech, June 15, 2003.
? McMillan, S.A. (speaker), Snurr, R.Q. and Broadbelt, L.J. ?Effect of Local Framework Heterogeneity on the Catalytic Activity of Cobalt-Ferrierite?, 18th North American Catalysis Society Meeting, Cancun, Mexico, June, 2003.
? McMillan, S.M., Snurr, R.Q. and Broadbelt, L.J. (speaker), ?Origin and Characteristics of Preferential Molecular Adsorption on Different Metal-Zeolite Sites?, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November, 2003.
? L.J. Broadbelt (speaker), R.Q. Snurr, S.A., McMillan, D.Majumder, and M. C. Curet-Arana, ?Multiscale Modeling in Catalysis?, Department of Chemical Engineering, The Ohio State University, May 15, 2003.
? Curet-Arana, M.C. (speaker), Gurney, R.W., Nguyen, S.T., Snurr, R.Q. and Broadbelt, L.J. ?Epoxidation Reactions Catalyzed by Manganese Porphyrins and Molecular Squares: Development of a Mechanistic Model?, poster presentation at Catalysis Club of Chicago Spring Symposium, Evanston, IL, May, 2003.
? Curet-Arana, M.C. (speaker), Snurr, R.Q. and Broadbelt, L.J. ?Molecular Squares as Hosts for Catalyzed Epoxidation Reactions?, 18th North American Catalysis Society Meeting, Cancun, Mexico, June, 2003.
? L.J. Broadbelt (speaker), R.Q. Snurr, S.A., McMillan, D.Majumder, and M. C. Curet-Arana, ?Multiscale Modeling in Catalysis?, ACS Colloid and Surface Science Symposium, Georgia Tech, June 15, 2003.
? M. C. Curet-Arana (speaker), L.J. Broadbelt, and R.Q. Snurr, ?Styrene Epoxidation Catalyzed by Self-Assembling Systems?, BP, June 30, 2003.
? Majumder, D. (speaker), Curet-Arana, M.C., and Broadbelt, L.J. ?Multiscale Modeling of ?Molecular Square? Catalysts?, poster presentation at Foundations of Molecular Modeling and Simulation 2000, Keystone, CO, July, 2003.
? L.J. Broadbelt (speaker), ?Unraveling Catalytic Kinetics using Multiscale Modeling?, Annual Scientific Meeting of the Center for Catalysis and Surface Science, Northwestern University, September 16, 2003.
? Curet-Arana, M.C., Gurney, R.W., Nguyen, S.T., Snurr, R.Q. and Broadbelt, L.J. ?Experimental and Quantum Chemical Methods Used to Develop a Mechanistic Model for Epoxidation Reactions Catalyzed by Mn-Porphyrins and Molecular Squares?, poster presentation, International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis, Evanston, IL, July, 2003.
? Curet-Arana, M.C., Gurney, R.W., Nguyen, S.T., Snurr, R.Q. and Broadbelt, L.J. ?Mechanistic Analysis of Styrene Epoxidation Catalyzed by Manganese Porphyrins and Molecular Squares?, poster presentation, Center for Catalysis and Surface Science Annual Meeting, Evanston, IL, September, 2003.
? Curet-Arana, M.C., Gurney, R.W., Nguyen, S.T., Snurr, R.Q. and Broadbelt, L.J., ?Multiscale Model for Epoxidation Reactions Catalyzed by Manganese Porphyrins and Molecular Squares?, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, CA, November, 2003.
? C.E. Huang, H. Du, Y.J. Kim, M.C. Kung, L.J. Broadbelt, R.Q. Snurr, ?Effect of Solvents on the Liquid Phase Oxidation of Olefins with Titanium Silicalite-1,? AIChE Annual Meeting, Indianapolis, IN, November 2002.
? C.E. Huang, M.C. Kung, L.J. Broadbelt, R.Q. Snurr, ?Effect of solvents on the liquid-phase epoxidation of 1-hexene with titanium silicalite-1,? 18th North American Catalysis Society Meeting, Cancun, Mexico, June 2003.
? C.E. Huang, S. Chempath, M.C. Kung, L.J. Broadbelt, R.Q. Snurr, ?Effect of Solvents on the Liquid-Phase Oxidation of Olefins with Titanium Silicalite-1,? (poster) 11th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, Evanston, IL, July 2003.
? Q. Zhao, R.Q. Snurr, ?Self-diffusion Studies of Binary Systems in NaX Zeolites using Pulsed Field Gradient NMR,? Chicago Area NMR Discussion Group, Naperville, IL, November 2003.
? L. X. Cao, M. C. Hersam, and M. J. Bedzyk, ?Macrostep and Large Terrace Formation on Evaporated Hematite Surface,? poster presentation, Center for Catalysis and Surface Science, Annual Scientific Meeting, Evanston, Illinois September 2003.
? S. T. Christensen, C. Y. Kim, M. J. Bedzyk, and M. C. Hersam, ?Atomic force microscopy studies of treated oxide surfaces,?poster, Center for Catalysis and Surface Science Annual Scientific Meeting, Evanston, Illinois, September 2004.

? H.Y. Law, A. Kozlova, H.H. Kung, M.C. Kung, ?Nitrogen production efficiency in lean NOx reduction by acetaldehyde over TiO2,? Poster presentation at NAM meeting, Cancun, June 2003.
? H.Y. Law, A. Kozlova, H.H. Kung, M.C. Kung, ?Nitrogen production efficiency in lean NOx reduction by acetaldehyde over TiO2,? Poster presentation at Gordon Research Conference, June 2004.
? H.Y. Law, A. Kozlova, H.H. Kung, M.C. Kung, ?Diesel NOx Abatement: a different perspective?, 13 International Congress on Catalysis,? July, 2004.
? W.-M. Xue, A. Kozlov, M.C. Kung, H.H. Kung, S. Nguyen, J.T. Miller, X. Zhou, A. Santos, F.E. Kuehn, ?Investigation of Methyltrioxorhenium(VII) in Catalytic Trans-Epoxidation Reaction,? North American Catalysis Society Meeting, June 1-6, 2003.
? Franz M. Geiger (speaker), "Surface Chemistry of the Environment Probed in Real Time with Ultrafast Lasers?, Department of Chemistry, Evanston, IL" May 2003.
? Franz M. Geiger (speaker), "Real time and in-situ Studies of Chromate Binding to Quartz/Water Interfaces Using Second Harmonic Generation", Telluride Science Research Center Workshop on Chemical Reactivity of Aqueous Species at Mineral Surfaces, Telluride, CO, June 2003.
? Franz M. Geiger (speaker), "Environmentally Important Surfaces and Interfaces Studied by Nonlinear Laser Spectroscopy", University of Wisconsin, Milwaukee, WI, September 2003.
? Franz M. Geiger (speaker), "Investigation of Physical and Chemical Processes at Silica/Water Interfaces Relevant to Chromium Contamination in the Environment, " Geosciences Department, Northwestern University, Evanston, IL, October 2003.
? Franz M. Geiger (speaker), "Nonlinear Optical Laser Studies of Environmentally Important Surfaces and Interfaces" , Wayne State University, Detroit, MI, October 2003.
? Franz M. Geiger (speaker), "Nonlinear Optical Laser Studies of Environmentally Important Surfaces and Interfaces", Chicago Catalysis Club, Chicago, IL, January 2004.
? Franz M. Geiger (speaker), "Surface Processes Studied in Real Time Using Nonlinear Optical Laser Spectroscopy: From Geochemistry to Atmospheric Chemistry", University of Wisconsin, Madison, WI, February 2004.
? Franz M. Geiger (speaker), "Environmentally Important Surfaces and Interfaces Studied by Nonlinear Laser Spectroscopy", University of Iowa, Iowa City, IA, February 2004.
? Franz M. Geiger (speaker), "Broadband Sum Frequency Studies of Surface-bound Organic Species Relevant to Atmospheric Oxidation Reactions", ACS Meeting, Anaheim, CA, March 2004.
? Franz M. Geiger (speaker), "Chromate Binding to Organic Adlayers at Silica/Water Interfaces Studied by Second Harmonic Generation", Goldschmidt Conference Copenhagen, Denmark, June 2004.
? Franz M. Geiger ,"New Siloxane Scaffolds for Environmental, Biological and Materials Chemistry Studied by SFG", Poster Feature Presentation, Gordon Conference on Vibrational Spectroscopy , July 2004.
? Franz M. Geiger (speaker), "Nonlinear Optical Laser Studies of Environmentally Important Surfaces and Interfaces: From Geochemistry to Atmospheric Chemistry", Carleton College, Northfield, MN, September, 2004.
? Franz M. Geiger (speaker), "Environmentally Important Interfacial Processes Studied by Second Harmonic and Broadband Sum Frequency Generation: From Geochemistry to Atmospheric Chemistry", University of Minnesota, Minneapolis, MN, September, 2004.
? Smita Edulji (speaker), SonBinh T. Nguyen, "Fe(salen) Complexes -- Prospects for 'Green' Catalysis", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, October 2004.
? Qi Zhao (speaker), Randall Q. Snurr, "Pore Size Characterization and Binary Diffusion Studies in Nanoporous Materials Using NMR", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, October 2004.
? Chen Ramachandran (speaker), "Solvent Effects in Liquid Phase 1 - Hexene Epoxidation with TS-1", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, October 2004.
? Franz M. Geiger (speaker), "Tracking Environmentally Important Interfacial Problems Using Sum Frequency and Second Harmonic Generation: From Geochemistry to Atmospheric Chemistry", University of California, Irvine, CA, November, 2004.
? Wolfgang M.H. Sachtler (speaker), "Nano Particles in Catalysis", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, November 2004.
? Harold H. Kung (speaker), "Nanotechnology and Heterogeneous Catalysis", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, November 2004.
? SonBinh T. Nguyen (speaker), "From Ligated Metal Complexes to Supramolecular Platforms -- Two Complementary Ideas in Homogenous Catalysis", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, November 2004.
? Osami Sakata (speaker; former IEC research member (M.J. Bedzyk Group)), "Quick Characterization of 1D and 2D Nanostructures by X-Ray Diffraction", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, December 2004.
? Peter C. Stair (speaker), "UV Raman Spectroscopy Catalysts: An Overview", Center for Catalysis and Surface Science Seminar Presentation, Northwestern University, Evanston, IL, December 2004.

Sharing Information:

Scientific meetings and seminar presentations provides information on our main research topic, catalysis, as well as related multi-disciplinary issues.

Contributions

Contributions within Discipline:

With the size and scope of the Institute for Environmental Catalysis, there already have been and will be in the future numerous contributions to the science and technology of catalysis and environmental engineering. Several examples are given here.

A new synthesis technique has been employed to obtain phase pure, high-surface area catalysts.These catalysts can be used for reactor studies that will give an insight to the reaction pathway of the oxidative dehydrogenation of light alkanes.

The project has contributed to the knowledge of how catalysts, particularly nanometer gold particles, function. Kung's work on the effect of chlorine has shown that there is more to making an active gold catalyst than just small particle size. Sachtler has found new chemistry on metals in zeolites. With this information and understanding it should be possible to develop new catalysts with specific properties.
The photo-catalytic destruction of environmental contaminants at titanium-dioxide/air and titanium-dioxide/water interfaces typically proceeds via contaminant adsorption by the catalytic surface. Larger adsorption often correlates with greater photo-catalytic efficiency. The new methodology devised in IEC is capable of providing quantitative adsorption information with very good sensitivity.
UV-Raman spectroscopy has been further developed into a technique that can analyze surfaces of highly absorbing metal oxide samples. Furthermore, the potential for UV Raman to detect localized surface structures on specific metal oxide samples has been realized.
The project led to a better understanding of the reaction of hydrocarbon with NOx on an oxide catalyst. It has also resulted in the formulation of novel approaches to remediate NOx in the exhaust of lean burn engines. This could help improve the air quality, especially in the urban areas, since there is still no satisfactory NOx treatment systems for such an application.
A much more detailed elucidation of the reaction pathways of MTO with alkenes has been performed, which suggests that the information available in the literature thus far was incomplete. The results obtained questioned some of the proposed reaction mechanisms related to the interaction of MTO with epoxides.
The origin of the high catalytic activity of supported nanoparticles of Au has been a subject of intense research in the part decade. Our work has helped to identify the reasons behind the apparent large differences in the activity on different supports, and in the case of alumina support, the large variation from samples to samples. The results help eliminate some of the confusions in the literature, and focus the attention to the underlying chemistry of the active sites. Any insight on the nature of the active site would have an immediate impact on a related reaction of water-gas shift, which is important in the fuel cell technology.
Through collaboration and publications, we helped researchers in this field understand gold catalysis. Our experimental techniques and results extended knowledge of this unique catalyst. Furthermore, our research on rutile oxide surface showed its oxygen deficient nature, which would help explain catalytic reaction, surface reconstruction and metal surface interaction related to this surface.
Potential success of the project will have broad societal impact in terms of reduced NOx and related pollution from automobile and other exhaust systems. The quality of breathing air would greatly improve if our project proves successful and deployed in the field.
Through this project, the atomic force microscope in the Hersam laboratory has been optimized for the study of catalytic oxide surfaces. This physical resource will be play an important role in future research at Northwestern University and in research projects with external collaborators that are interested in the morphology of complex oxide surfaces. Information resources have also been developed and disseminated via the internet for the Nanomaterials course recently developed by Hersam.
By deepening our understanding of catalytic oxide surfaces, the research results themselves also have the potential of improving hematite based photocatalysis which plays an important role in the degradation of aminophenol and oxidation of sulfoxonium. These developments in catalysis will likely enhance the public welfare through economic and environmental improvements.
Metal siting in zeolites has been an active area of research for many years. However, only indirect evidence for the location of the metal is available in most cases. In contrast, we are able to probe these sites directly with quantum chemical calculations. Our calculations clearly show that the site of the zeolite framework and the position of the substituted aluminum atoms must be considered simultaneously, and we have challenged the notion that there is a one-to-one correspondence between sites and spectroscopic signatures. The output from these calculations is sufficiently rich that many experimental pieces of evidence can be consolidated to form a coherent and consistent picture of where metals are located in zeolites
Despite the large literature on oxidation reactions with porphyrins, there is still considerable debate about the reaction mechanisms. In addition almost no kinetic data are available û and, naturally, none for the artificial enzyme systems since they have only recently been developed here.
The TS-1 results support a growing appreciation in the literature that physisorption is extremely important to understanding and tailoring zeolite catalysis.
This work provides a valuable service for general society by supplying a foundation for a new wastewater treatment technology that can be used where conventional technologies fall short. This system could be a potential solution for many of the endocrine disrupting compounds that are great concern today. This will have even more far-reaching scope as population grows and water conservation and re-use increase, meaning we must further tighten restrictions on the quality of wastewater we can discharge to our environment.
Valuable insight into structure/function relationships in TiO2 photocatalytic systems; detailed importance of solid-solid interface; identified new active sites located at interface.

Our research has allowed us to develop an analytical approach to quantitatively characterize a complex organic matrix û both structurally and functionally (Cu complexation).

Elucidation of the structure of manganese oxides produced by L. discophora SP-6 will provide insight into their enhanced catalytic and cation adsorption properties. Additionally, the physicochemical and surface science techniques developed to probe the X-ray diffraction amorphous biogenic MnOx can be extended to other environmental oxide systems.

Transition metal oxides have been studied extensively over the last few decades, owing to their electro-optical and catalytic properties. The overall properties of these oxides and the heterostructures that can be built on them depend upon their surface structure, composition and morphology. However, the available information on the surface structures of transition metal oxides is very scarce and often contradictory. Our research provides insight into the surface reconstruction of these oxides under different thermodynamic conditions (temperature, pressure, atmosphere). The outcome of the project may be potentially useful not solely for catalysis but also for thin film growth and other areas of materials science, chemistry, and physics.

Solution of the surface structures of catalytic oxides is one step in the larger process of understanding the mechanisms of heterogeneous catalysis and therefore eventually making chemical processing more efficient and environmentally friendly thus drastically reducing the volume and toxicity of chemical wastes.

Through collaboration with other research groups, we have combined our techniques to strive for a full understanding of the SrTiO3 surface. Additionally through collaboration with BP Amoco, we have observed the catalytic activity of Mg3V2O8, and we are working to correlate that to our TEM observations. This is a unique situation where we can apply these techniques, which until now have been used on model systems, for actual catalysts.

We published several key findings regarding the use of supramolecular systems in site-isolation and single-site catalysis. We also produced several new catalysts for the environmental-friendly productions of fine chemicals and polymers.

This project has contributed to understanding how the factors of surface structure and control the formation of bonds to molecular radicals. The observation of oxidative chemistry produced by oxides of uranium and surface chlorine show the importance of specific oxidizing species in hydrocarbon oxidation.

The results of this work will enhance the ability to design catalysts for selective oxidation of small hydrocarbons.

Contributions to Other Disciplines:

One of the first determinations of atomic structures at the water/solid interface have been carried out.

We are developing a multiscale 'feasible and appropriate' technology for analysis of physico-chemical properties of complex systems, based upon a hybrid classical/quantum mechanical methodology. Resulting algorithms and computer programs permit us to predict properties of newly synthesized and not-yet synthesized materials.

Simulations and theoretical modeling of structures and chemical reactions at complex interfaces and surfaces provide analysis tools with high spatial resolution, in cases where experiment is often impossible, too costly, or too slow. Current work reveals which types of chemically important structural defects in catalytic oxides are most likely to be present. The hybrid classical/quantum methodology is shown to be feasible and appropriate technology in the form of algorithms and computer programs.

Novel and creative experimental design now makes it possible to perform in-situ studies of the surface structures present under realistic reaction or natural environment conditions. We have developed new experimental tools that allow molecular level probing of complex systems and phenomena.

The first is that we are integrating the insights gained from the use of fundamental chemical tools to explain system behavior and the second is that we are engaged in an effort to couple chemical and biological catalysis. The products of chemical catalysis are used to select for an optimum set of biocatalysts that exhibit the properties of stability, resilience and diversity.

Novel concepts of the chemistry and catalysis of oxo ions were discovered during this work.

The results obtained so far indicate that the formation of biofilms may be crucial in the environmental response of microbial communities to heavy metal stress. A reliable assay to examine biofilm formation under heavy metal stress conditions was developed.

Single crystal growth via the traveling solvent floating zone technique has led to the growth of large single crystals. The information learned during the growth of the iron oxides can be used in the growth of other single crystals of interest to the center.

Elucidation of the structure of manganese oxides produced by L. discophora SP-6 provides insight into their enhanced catalytic and cation adsorption properties. Additionally, the physicochemical and surface science techniques developed to probe the x-ray diffraction amorphous biogenic MnOx can be extended to other environmental oxide systems studied within the center.

Single-crystals of magnesium vanadates, magnesium molybdates, and iron oxides as well as polycrystalline MnOx model compounds samples are available to groups for various studies.

Synthesis and characterization (structure) are two critical components of the field of materials science. Thus, our project has already tangibly contributed to these two areas in terms of fabrication equipment, and applications as well as protocol for characterization.

Our project transcends several disciplines. The methodology and fabrication of equipment for PVD encompasses fields of mechanical design, mechanical engineering, chemical and materials engineering. Characterization and interpretation cross the boundaries into chemistry, physics and statistics.

This project has contributed to physical, institutional, and information resources for science and technology by the development of:

- a jet-enhanced nanoparticle deposition apparatus (JENDA) system has been developed for synthesis of metal-support catalyst systems.
- A protocol for characterization, especially for ToF-SIMS has been developed which will prove useful for the broad community.

The atomically flat morphology of CVT hematite (0001) has not been previously observed with AFM. Our follow-up work on SrTiO3 and TiO2 surfaces suggests that the underlying physical mechanism that controls the evolution of this surface morphology may be general for a wide range of low miscut angle oxide surfaces. Future work will strive to develop a model that quantitatively agrees with the observed experimental data.

Since many applications for hematite û including heterogeneous catalysis, magnetic data storage, and spintronics û depend sensitively on surface structure and morphology, this work has broad potential impact for many disciplines of science and engineering. In addition, the long term air stability of this controlled nanoscale morphology suggests that CVT grown hematite (0001) surfaces may serve as effective templates for the growth, patterning, and embossing of nanostructures.

We are contributing to the development of multi-length and multi-time scale modeling capabilities for describing structure and function of complex materials. By combining atomistic simulations with quantum methodologies, we move toward a dynamical evolving modeling process, with inputs from experiment as well as theory. Such methods, sometimes called 'on-the-fly' approaches offer the possibility of continuous improvement of materials models spanning the Angstrom to micron size scales.

Materials technology depends upon the knowledge base of physics and chemistry. Basic understanding needed to design, formulate, and process the next generation of materials depends upon advancement of basic knowledge. Through collaborations with Mechanical and Civil Engineers in an IGERT at NU focused on a 'Virtual Tribology Laboratory: from Angstroms to Drive Trains' we contribute to transportation technologies of the future.

The use of computational methods in conjunction with experiments is growing in all disciplines. The successful demonstration in this project of using quantum mechanics to reinterpret experimental measurements is a testament to the value of computations as an integral part of studying complex problems. We had many mechanical engineering students over the period of this grant enrolled in our class on Applied Molecular Modeling where we teach the techniques that are central to this project, suggesting that other disciplines are recognizing the contribution that quantum chemistry can make to their research questions.

This project has greatly advanced the area of combined chemical-biological treatment systems by, for the first time, investigating how effluent composition affects biological reactor performance and therefore overall system effectiveness. This work also has introduced molecular techniques into the area of combined chemical-biological water treatment and will allow us to make great strides in understanding how substrate composition affects microbial community diversity and how this in turn relates to process performance. This work accelerates the potential for using these combined treatment systems for real biorecalcitrant and inhibitory wastewaters, such as in the textile industry, pulp and paper mills, the petrochemical industry, and the pharmaceutical industry.

This work has furthered the understanding of how substrate diversity and type affect microbial diversity, a significant issue in microbial ecology and water treatment, and how microbial diversity affects process stability, resistance, and resilience.

Both of these projects contribute to engineering sustainable technologies: the photocatalysis involves use of renewable energy; the metal-microbe stress project illustrates natural strategies for reducing metal toxicity

Our surface studies are crucial for the study of catalysis, because the active sites on the surface of a material are of extreme importance. However, this is not the only discipline where atomistic knowledge of a surface is important. This knowledge and these techniques can be used for the study and development of surface coatings or substrates for thin film growth, for example.

Our work explores very fundamental aspects of science. Understanding oxide surfaces can be used to engineer better products, but the knowledge of how these surfaces behave will help in the better understanding of nature itself.

We discovered how to Fourier invert a set of XSW measurements to create a direct space image of impurity and/or surface atoms with respect to the primitive unit cell of a host crystal. This model independent approach opened up the way to study more complicated (multi-site) interfacial structures on the atomic-scale.

The XSW technique developments are used in biophysics, electrochemistry, organic-film self-assembly, semiconductor heteroepitaxy, enviro-geochemistry, and catalysis.

This project has enabled fruitful collaborations with our engineering colleagues. It has contributed to both the homogeneous and heterogeneous catalysis communities by showing that homogeneous catalysts can be immobilized and recycled when they are modified with the proper anchoring group. It has demonstrated to the membrane technology group that mesoporous aluminum membranes are robust and useful materials for catalyst immobilization and applicable to forced-flow-catalytic membrane reactor. We have also shown that chromophores with short-lived excited state are capable of sensitizing TiO2, and that the catechol moiety is a good anchoring group for this process.

Contributions to Human Resource Development:

A total of 43 postdoctoral associates, 53 PhD students, and 27 undergraduate students have worked on projects in the Institute for Environmental Catalysis. These researchers all had significant opportunities to collaborate with researchers in national facilities (Advance photon source, high resolution electron microscopy at Oak Ridge National Lab), and other researchers interested in this topic. Some of the collaborative work included graduate students from South Africa.

We have trained undergraduate and graduate students, postdocs, and visiting scientists in the most modern experimental, theoretical and computational materials synthesis and analysis methods.

Most importantly, the institute helped to develop capable new scientists with both expertise in catalysis and skills in synthetic and analytical chemistry. These researchers are well versed in the preparations of inorganic, organic, and organometallic compounds. They understand catalysis and the relationship between catalyst structure and functions. They are also keenly aware of environmental issues such waste treatment, bio-degradable process, and recycling.
The Institute has also trained more that 50 middle school and high school science teachers to use catalytic experiments as part of their curriculum.

Contributions to Resources for Research and Education:

We design and implement advanced computational clusters for simulations and quantum mechanical materials analyses. We contribute to the world-wide scientific databases in terms of publications, talks, algorithms, and shared codes.
The Materials World Module helps students integrate various science disciplines they study in high school and provides a context to help them make connections to the real world. Here are some examples of how concepts introduced in the Environmental Catalysis module are connected to different disciplines in the high school setting:
Chemistry: catalysis, energy of reaction, redox reactions, by-products of chemical reactions, product yield, hydrolysis and condensation, solutions, acids and bases, neutralization reactions, mixtures polymers
Biology: enzymes, health effects of pollution, life processes, nutrients, effects of acids on the environment, photosynthesis
Physics: electromagnetic radiation, nanotechnology,
Earth science: minerals, soil quality, water treatment
Technology education: automotive exhaust system, industrial catalysis

Contributions Beyond Science and Engineering:

Beyond science and engineering, the general public has been impacted through efforts to include catalysis as an important component of the new physical sciences exhibit that is being developed at the Chicago Museum of Science and Industry. The Chicago Museum of Science and Industry receives ~2 million visitors per year from a diverse range of locations including inner city Chicago, rural Illinois, and domestic and foreign tourists.

Modern industrial society is highly dependent upon the flow of new materials and technologies- ranging from lighter and tougher structural ceramics, to nanoparticle bioactive materials, to more efficient and 'green' catalysts, to less-polluting power systems, etc. Our contributions at the level of basic science help sustain the economic health of the country and its continued leadership in world affairs.

The MWM module helps students understand what catalysis is, how catalysis is used presently, and where it can be applied to benefit the environment. From the Environmental Catalysis module, students learn that raw materials are converted into useful products produced by various industrial processes. Many products are made with catalysts in order for them to be produced economically, quickly, and environmentally sound. Catalysis, however, does not stop there. In any industrial process there are also unwanted side (waste) products, i.e. pollution. Before they are released into the environment, these waste productsùwhich could be in the air, water, or soilùare treated using catalysts and, if possible, recycled for reuse in the industrial process. Pollution treatment is not perfect, though, so there is always some residual release of waste material into the environment, affecting people, animals, plants, land, air, and oceans. Students also learn that nature has its own rich variety of catalytic processes. By studying how these natural processes work and by witnessing the effects of our influence on the environment, we can gain knowledge on how to improve industrial processes and pollution treatment.

Hopefully, not only will the present general populous becomes more informed, but some of the students will pursue a variety of science and engineering career connected with environmental engineering.

The MWM has contributed to the public welfare by raising the public awareness of the importance of studying catalysis and its effects on the environment. As a whole this has resulted in a greater focus on policy issues toward a 'greener' environment achievable via research on a variety of catalytic processes applied in three main areas: industrial processes, pollution treatment, and natural processes.

Categories for which nothing is reported:

The attached pages represents Activity Sheets and teacher's planning guides developed for the IEC's Materials World Module. *(total 103 pages)*

Part I: Activity Sheets

1. Catastrophe or Catalysts;
2. Using a Metal Catalyst to Degrade an Air Pollutant;
3. Homogeneous and Heterogeneous Acid Catalysts;
4. Catalyzing a Reaction Using a Heterogeneous Acid Catalyst;
5. Catalyzing with Platinum Black;
6. Our Dependence on Catalysts;
7. Searching for Catalysts;

Experiment:

- Catalyzing a Reaction Using a Heterogeneous Acid Catalyst;

Introduction/Activity Sheet:

- Luminol: What Makes Blood Glow;

Exercise:

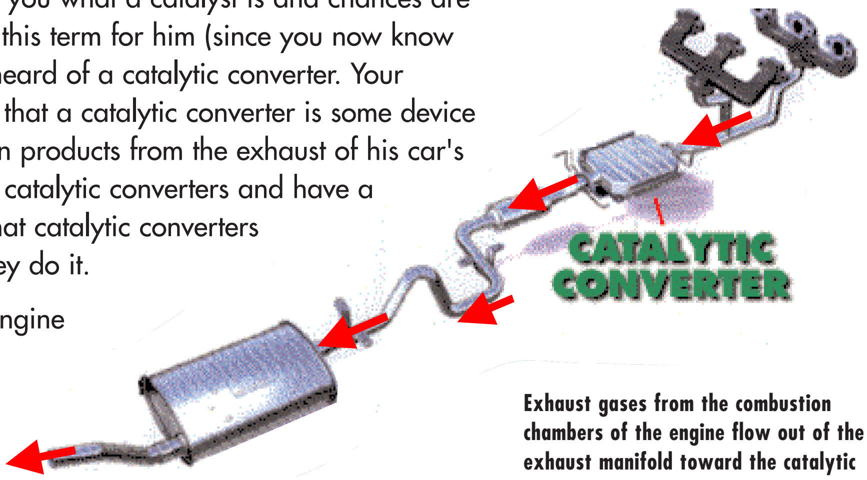
- Catalyzing with Platinum Black;
- (Introduction and Exercise):
  Conceptual Design for Environmental Catalysis

Part II: Second Edition, Teacher's Planning Guides

- Teacher's Planning Guide 4: Using a Metal Catalyst to Degrade an Air Pollutant;
- Teacher's Planning Guide 5: Photocatalysis;
- Teacher's Planning Guide 5: Using Photocatalysis to Degrade a Water Pollutant

Catastrophe or Catalysts

Ask your next-door neighbor if he can tell you what a catalyst is and chances are that he won't be able to. After you define this term for him (since you now know what catalysis is), ask him if he has ever heard of a catalytic converter. Your neighbor will probably be able to tell you that a catalytic converter is some device in his car that removes harmful combustion products from the exhaust of his car's engine. While most people have heard of catalytic converters and have a vague idea of what they do, few know what catalytic converters actually remove from exhaust and how they do it.



Exhaust gases from the combustion chambers of the engine flow out of the exhaust manifold toward the catalytic converter. The reacted gaseous products then flow out of the catalytic converter and proceed through the resonantor, the exhaust pipe, muffler, and eventually out of the tailpipe.

Automobile exhaust flows from the car's engine through pipes that lead to the catalytic converter. Once inside the catalytic converter, the exhaust flows through a structure that is covered with tiny particles of metal catalysts, such as platinum and rhodium. A number of chemical reactions take place on the surface of the catalyst particles. (Because the reactants are gases and the metal catalysts are solids, the catalysts are heterogeneous catalysts.) The catalyzed reactions remove carbon monoxide (CO), VOCs (volatile organic compounds), nitrogen dioxide (NO_2), and nitric oxide (NO) from the exhaust before it flows out of the catalytic converter and is emitted into the air through the car's tailpipe.

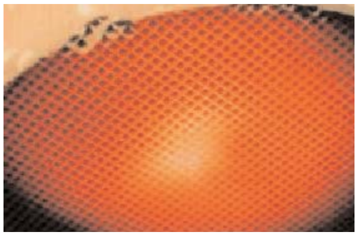
The substances that are removed from the exhaust are pollutants because they are potentially harmful to human health and the environment. CO is an odorless, colorless, poisonous gas that can cause headache, nausea, difficulty breathing, and even death. VOCs are carbon-containing compounds that evaporate easily. In the atmosphere, in the presence of sunlight, VOCs, NO, and NO_2, react in a complex set of reactions to form photochemical smog, which contains ozone (O_3) and other harmful substances. Smog is often times seen as a brownish haze hovering over large cities. Whereas ozone in the upper atmosphere protects life on Earth by absorbing the sun's ultraviolet rays, ground-level ozone is a pollutant. Ozone can cause coughing and difficulty breathing. It is especially harmful to people who have asthma or other respiratory conditions. Ozone is also harmful to vegetation and certain materials, such as rubber. Besides contributing to the formation of ozone, NO_2 also reacts with water (H_2O) vapor in the air to form nitric acid (HNO_3), a component of acid rain. Acid rain is harmful to organisms and can deteriorate structures, such as building and statues, over time.

CONCEPT behind the ACTIVITY

Heterogeneous metal catalysts can be used to clean polluted air by catalyzing the conversion of pollutants into safer substances.

Catastrophe (Continued)

A catalytic converter removes pollutants from engine exhaust by chemically changing, or converting, them into safer substances, such as oxygen, carbon dioxide, nitrogen, and water, as shown by the following reactions.



$$\underset{\text{carbon monoxide}}{2CO} + \underset{\text{oxygen}}{O_2} \xrightarrow{\text{catalyst}} \underset{\text{carbon dioxide}}{2CO_2}$$

$$\underset{\text{volatile organic compounds}}{VOCs} + \underset{\text{oxygen}}{O_2} \xrightarrow{\text{catalyst}} \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{nitrogen dioxide}}{2NO_2} \xrightarrow{\text{reactant}} \underset{\text{nitrogen}}{N_2} + \underset{\text{carbon dioxide}}{CO_2}$$

$$\underset{\text{nitric oxide}}{2NO} \xrightarrow{\text{reactant}} \underset{\text{nitrogen}}{N_2} + \underset{\text{carbon dioxide}}{CO_2}$$

A properly functioning catalytic converter removes over 95% of the pollutants from a car's exhaust before it is released into the air. Why is a catalytic converter so effective? The answer lies in the shape of its internal structure and the size of its catalyst particles. The internal structure of a catalytic converter consists of a honeycomb-shaped ceramic material that has thousands of channels. The channels are coated with a porous material that is impregnated with catalyst particles, as shown in the illustration. The particles are extremely small in size, about 1 to 20 nanometers. (A nanometer is one-billionth (10^{-9}) of a meter.) Taken together, the channels of the honeycomb structure, the porosity of the coating, and the minute size of the catalyst particles result in a tremendously large surface area that ensures maximum exposure of the exhaust gas to the catalyst. In addition, because the catalyst nanoparticles have a large surface area, less catalyst is needed. That's a good thing, because the catalysts are very expensive.

Cars were first equipped with catalytic converters in 1974. Before that time, cars ran on gasoline that contained lead and, as a result, emitted large quantities of lead with their exhaust. Lead is poisonous, especially to children. Lead poisoning can cause abdominal pain, irritability, confusion, and even brain damage. Lead was eventually banned from gasoline, but not for health reasons. While researchers were working on developing catalytic converters for cars, they discovered that the lead in gasoline interfered with the performance of the catalysts. With time, the catalysts quit working because the lead was binding to them and deactivating them. In other words, lead was "poisoning" the catalysts.

Catastrophe (Continued)

Because scientists couldn't find a catalyst that wasn't poisoned by lead, installing catalytic converters on cars meant that gasoline had to be reformulated so that it no longer contained lead. Today, all cars run on unleaded gasoline.

There are many other examples of the use of a catalyst to remove pollutants from air. For instance, many air cleaning units in homes and buildings have catalysts incorporated into their filters, in order to destroy VOCs and airborne pathogens, such as certain bacteria and viruses. You will learn more about the catalytic treatment of indoor air in Activity 5.

The use of catalysts in reactions involving gases, called gas-phase catalysis, is not limited to the treatment of air, however. Gas-phase catalysis is also used to make various products. For example, the production of polyethylene (a plastic used to make milk jugs and grocery bags), polystyrene (a plastic used to make foam cups and packaging), and ethylene oxide (a chemical used to make antifreeze) all involve passing gas-phase reactants over a catalyst.

You know that without catalysts, many chemical reactions would not take place. But how do researchers determine what is the best catalyst for a particular process? It almost always requires a great deal of testing. (Although sometimes the best catalyst is found by accident.) Researchers have to consider many factors when developing a catalyst and designing a catalytic process. For example, they have to consider the type of structure that will support the catalyst (such as the honeycomb structure in catalytic converters), the best concentration of reactants to use, and the temperature and pressure under which the reaction will occur. Researchers also have to think about the rate at which the catalyst is poisoned and how the catalyst can be regenerated when it becomes poisoned.

In all this testing, researchers often discover that there is no uniquely suited catalyst for a particular reaction—one catalyst is best under one set of conditions and another is best under a different set of conditions. (In Activity 5, you will explore different conditions that may affect the performance of a catalyst.) Typically, in industry, the catalyst and set of conditions that produce the highest yield of products at the lowest cost are chosen. More and more frequently, however, environmental factors, such as harmful waste products and energy use, are seriously considered. Such factors may ultimately determine catalyst and process selection.

Using a Metal Catalyst to Degrade an Air Pollutant

Purpose
- To model the catalytic treatment of an air pollutant
- To compare the performance of a copper and an iron catalyst

If you've ever used a household cleaner containing ammonia, you may have noticed the label on the bottle warning not to inhale the vapor released from the liquid cleaner. The vapor is ammonia gas that had been dissolved in the liquid. Ammonia is irritating to the skin, eyes, and respiratory tract, and is potentially toxic.

Besides household cleaners, other sources of ammonia include gasoline-powered vehicles, decomposing livestock wastes, fertilizers, and sewage-treatment plants. In many cases, the ammonia is released into the air. The airborne ammonia may eventually become deposited by rain onto land or into bodies of water, such as lakes and river. At certain levels, the ammonia is toxic to fish and other aquatic organisms.

In this activity, you will use ammonia to model the catalytic treatment of an air pollutant. You will compare, as a class, the performance of an iron catalyst and a copper catalyst in breaking down, or degrading, ammonia.

Half of the groups in the class will use copper filings for the catalyst, while the other half uses steel wool, which consists mostly of iron.) Your class will test these two catalysts under a certain set of conditions. You will use a simple apparatus that will allow you to pass an air stream containing ammonia gas over either metal catalyst while the catalyst is being heated with a flame. The chemical equation below shows that ammonia (NH_3) gas can be degraded into nitrogen (N_2) gas and water (H_2O) vapor by reacting it with oxygen (O_2) gas. As in Activity 1 in which the oxidation of methanol vapor occurred on the surface of the platinum black, the oxidation of ammonia in this activity occurs on the surface of the iron or copper. In contrast to the first activity, however, the oxidation reaction in this activity also requires heat for the reaction to go forward rapidly.

Think about these questions as you do the activity:

? How do the two metal catalysts differ?

? Why is ammonia solution in the flask pink?

? What does it mean when the liquid in the beaker turns pink?

? How can you tell that the catalyst has become poisoned?

$$\underset{\text{amonia}}{4NH_3} + \underset{\text{oxygen}}{3O_2} \xrightarrow[\text{metal catalyst}]{\text{heat}} \underset{\text{nitrogen}}{2N_2} + \underset{\text{water}}{6H_2O}$$

During the activity, you will determine how long it takes the metal catalyst you are testing to start catalyzing the oxidation of ammonia and how long it takes for the metal catalyst to become inactivated, or poisoned. Based on your group's data and those obtained by other groups, you will conclude which metal catalyst works better under the conditions of the activity.

Concept behind the Activity

Heterogeneous metal catalysts can be used to clean polluted air by catalyzing the conversion of pollutants into safer substances.

Hypothesis

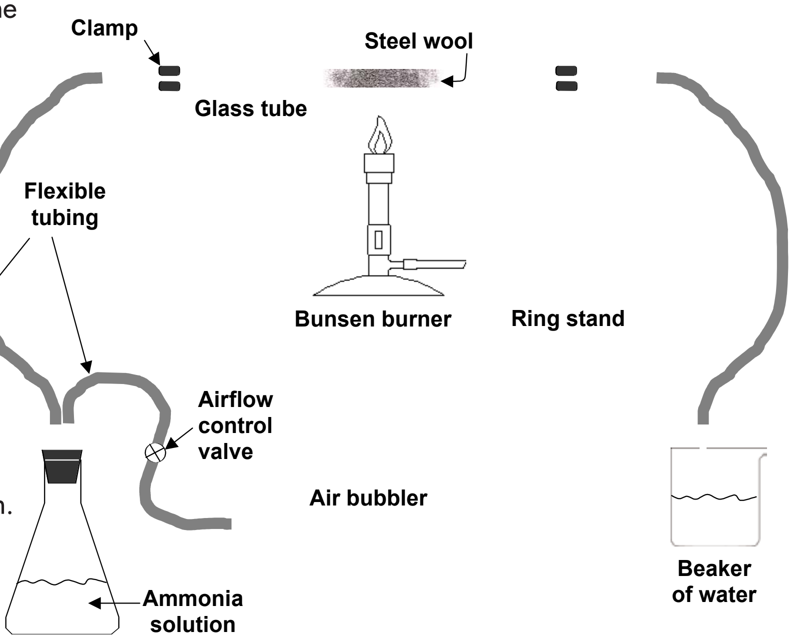
A metal surface, such as the platinum black in Activity 1 and the copper and iron catalysts in this activity, reacts with oxygen to form metal oxides that promote the transfer of electrons from the reactants to produce reaction products. Eventually the metal regenerates itself back to metal to begin the reaction cycle again. Knowing that irons tends to rust (forming a certain iron oxide compound) more easily than copper, therefore, their higher affinity for oxygen, come up with a hypothesis that predicts the outcome of the the different metal catalyst's ability to degrade ammonia by oxidation.

▶ Predicted Outcome

Which metal, copper or iron, do you think will begin catalyzing the oxidation of ammonia sooner? Which metal catalyst do you think will become poisoned faster? Record your predictions and your reasons for making them. Do this on your data table provided.

Procedure, Data, and Observations

1. Compare the appearance of the two metal catalysts ¾ copper filings and steel wool ¾ inside the glass tubes. Record your observations in your data table.
2. Label six beakers Control, #1, #2, #3, #4, and #5, respectively. Fill each beaker with 100 mL of water and add 5 drops of phenolphthalein to the water. Phenolphthalein is an indicator that turns pink in the presence of a base, such as ammonia. CAUTION: The phenolphthalein solution is flammable. Keep it away from open flames.
3. If your teacher has not done so for you, set up the apparatus as shown. Follow your teacher's directions. The ammonia solution in the flask consists of ammonia gas dissolved in water. The ammonia solution is pink because phenolphthalein has been added to it. **CAUTION:** Ammonia gas is a skin, eye, and respiratory irritant. Do not breathe in vapors from the ammonia solution.
4. Place the flexible plastic tubing that extends from the glass tube containing the catalyst into the Control beaker. The tip of the medicine dropper that is attached to the plastic tubing should be in the liquid in the beaker.
5. Turn on the fish-tank air bubbler. The hose clamp that is attached to the plastic tubing leading from the air bubbler can be adjusted to change the degree to which it squeezes the tubing, thereby controlling the amount of air that is passing through the tubing into the ammonia solution in the flask. The air should bubble into the solution at a slow rate, about five bubbles per second. The bubbling air will force the ammonia gas out of the solution. The gas will move from the flask, through the glass catalyst tube, and into the liquid in the beaker.



6. Leave the tubing inside the Control beaker for 5 minutes, allowing gas to bubble into the liquid. If the liquid in the beaker doesn't turn pink during the 5 minutes, continue bubbling gas into the liquid until it does turn pink.
7. Quickly remove the tubing from the Control beaker and place it in beaker #1. While bubbling gas into the liquid in beaker #1, evenly heat the catalyst in the glass tube by swiftly moving the flame of the Bunsen burner back and forth across the tube. Do this for 5 minutes. CAUTION: Do not touch the heated glass. Hot glass does not appear hot. If the liquid in the beaker changes to a pink color during the 5 minutes, record in your data table the amount of time it took the liquid to turn pink. Also record the intensity of the pink color after 5 minutes. Then proceed to step 7. If the liquid in beaker #1 doesn't change to a pink color during the 5 minutes, continue to heat the catalyst tube and allow gas to bubble into the liquid until it does turn pink. Record the amount of time that passed and the intensity of the color. Then proceed to step 8.
8. Switch the tubing to a new beaker, in consecutive order, every 5 minutes as long as the liquid in each beaker turns pink by the end of the 5 minutes. Do not stop heating the catalyst as you switch beakers. Remember to move the flame swiftly across the catalyst tube. For each beaker, record in your data table the amount of time it took the liquid to change to a pink color and the intensity of the color after 5 minutes. If the liquid remains clear after 5 minutes, keep bubbling gas into the liquid until it turns pink. Record the amount of time and the intensity of the color. Then proceed to step 8.
9. Switch the tubing to a final beaker, and allow gas to bubble into the liquid for 5 minutes. Record whether the liquid became pink and if so, how long it took to do so. Also record the intensity of the color.
10. Turn off the Bunsen burner. Quickly switch the tubing from the final beaker to the Control beaker. Allow gas to bubble into the liquid in the Control beaker for 5 more minutes, so that any ammonia vapor remaining in the apparatus bubbles into the liquid as the catalyst cools. Then, unplug the fish-tank air bubbler carefully.
11. Compare the appearance of the used catalyst in the glass tube with that of a sample of unused catalyst (either copper filings or steel wool, depending on the catalyst you used in the activity). Record your observations. CAUTION: Do not touch the glass tube, as it will still be hot.
12. Share your data with other groups.
13. Dispose of the liquids in the beakers and flask down a sink drain and flush with plenty of water. Your teacher will tell you whether you should disassemble the apparatus.

Interpretations of Data & Conclusions—*Be thorough and use complete sentences.*

1. Based on your observations of the copper filings and steel wool, which catalyst do you think had a greater total surface area? Explain.

2. What caused the liquid in the beakers to change to a pink color?

Interpretations of Data & Conclusions Continued

3. What evidence did you observe that indicated ammonia was being oxidized?

4. What evidence did you observe that indicated the catalyst was no longer active, in other words, that it had become poisoned? Explain.

5. Explain the difference you observed at the end of the activity between the used catalyst and the sample of unused catalyst.

6. Which catalyst, the copper or iron, began to catalyze the oxidation of ammonia sooner? Explain.

7. Which catalyst was poisoned more quickly?

8. Why was it important for air to be bubbled slowly into the ammonia solution? differences.?

9. How do your observations compare with your predictions? Give possible reasons for any differences.

Interpretations of Data & Conclusions Continued

10. Was the catalyst you used in the activity a heterogeneous catalyst or a homogeneous one? Explain.

11. Under the conditions of this activity, which metal catalyst—copper or iron—was more effective in catalyzing the oxidation of ammonia? Explain.

12. How might the conditions of the activity be changed such that different results are obtained?

13. How does the total surface area of a catalyst affect the rate of the reaction that it catalyzes?

14. If you could reduce the copper and iron catalysts used in the activity to the size of nanoparticles, what effect do you think that would have on the rate at which they catalyze the oxidation of ammonia? Explain.

15. What do you think are the advantages and disadvantages of using metal catalysts to degrade pollutants?

16. In your group, come up with at least two questions about the use of metal catalysts in degrading air pollutants.

EXPANDING on the CONCEPTS

In this activity, you compared the effectiveness of two metal catalysts--copper and iron--in the oxidation of ammonia under certain conditions. The following article explains why one metal was a better catalyst than the other. Do the explanations agree with your observations?

Under the conditions of the activity, it is likely that you found the copper filings to be a more active catalyst than the steel wool, or iron, in the oxidation of ammonia. In other words, the copper catalyzed the oxidation of ammonia at a faster rate than did the iron. There are two sets of factors, physical and chemical, that can explain these observations. In heterogeneous catalysis, the total surface area of the catalyst is a key factor in the catalytic process. The greater the total surface area of the catalyst, the faster is the rate of the catalyzed reaction, because the reaction occurs on the surface of the catalyst. In the activity, the total surface area of the copper filings in the glass tube was much larger than that of the steel wool. That is because the copper filings were packed into the tube at a much higher density than the steel wool fibers. Another reason is that the filings were smaller in size than the fibers. The diagram shows the relationship between particle size and surface area by comparing the surface area-to-volume ratio of a small sphere to that of a large sphere. A material's volume (V) defines how much space the material takes up. The surface area (S) of a material relates how much of the material's atoms are exposed and therefore can participate in a chemical reaction. As you can see in the diagram, a small sphere's surface area-to-volume (S/V) ratio is larger than that of a large sphere. Thus, because a catalyzed reaction occurs on the surface of the catalyst, the reaction occurs at a faster rate when the catalyst particles are smaller.

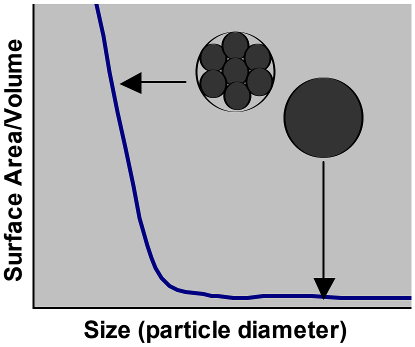
However, even if you were to perform the activity using similar catalyst surface area, you would probably still find that the performance of the copper was superior to that of the iron. The reason for this is related to the chemical interactions between the metal catalysts and oxygen.

First, recall that in chemical reactions, oxidation involves the loss of electrons, and reduction involves the gain of electrons. The two processes are coupled—the oxidation of one compound (electron loss) is caused by the reduction of another (electron gain). The chemical equation given at the beginning of the activity that describes the oxidation of ammonia (NH_3) by oxygen (O_2) to nitrogen (N_2) and water (H_2O). The overall reaction can be thought of as a sum of two steps:

$$2NH_3 \rightarrow N_2 + 6H-\ast$$

$$\frac{3}{2}O_2 + 6H-\ast \rightarrow 3H_2O$$

Here H-✱ represents a hydrogen atom bound to the catalyst surface atom.



Comparison of surface area-to-volume ratios of small and large particles. Total surface area is much higher for smaller particles occupying comparable volume as that of a larger particle.

The first reaction describes the oxidation of nitrogen in ammonia to nitrogen gas, and the second reaction is the reduction of oxygen. Now when the two reaction steps are added, the overall reaction is:

$$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$$

Molecular oxygen (O_2) is extremely stable, however. Either a large input of energy or a catalyst is required to dissociate the oxygen-oxygen bond in the molecule, thereby allowing it to oxidize other chemicals. A metal surface, such as the platinum black in Activity 1 and the copper and iron catalysts in this activity, reacts with oxygen to form intermediate oxygen compounds (called metal oxides) that promote the transfer of electrons. You might say that the metal "activates" the oxygen.

The equations below show the steps in the copper-catalyzed oxidation of ammonia.

$$3Cu^{(0)} + \frac{3}{2}O_2 \xrightarrow{\text{heat}} 3CuO$$

$$3CuO + 2NH_3 \xrightarrow{\text{heat}} 3Cu^0 + 3H_2O + N_2$$

In the first reaction, at the elevated temperatures used in the activity, the copper atoms (Cu°) are oxidized by oxygen to form copper oxide (CuO). (In the activity, oxygen was present in the glass tube containing the copper catalyst.) In the second reaction, the ammonia is oxidized by the activated oxygen of the copper oxide, rather than by molecular oxygen. Notice that copper is involved in the reaction, but it is returned to its original form, Cu°, and so can continue to activate oxygen. Thus, the copper functions as a catalyst. The overall reaction (the sum of the two reactions) is the same as the one shown above:

$$2NH_3 + \frac{3}{2}O_2 \xrightarrow[\text{catalyst}]{\text{heat}} N_2 + 3H_2O$$

However, in the catalyzed reaction, the pathway taken to get from the reactants (ammonia and oxygen) to the products (nitrogen and water) is an alternative mechanism. It consists of a series of steps that includes a reaction intermediate (copper oxide) and that has a lower overall activation energy than the uncatalyzed reaction.

In the case of the steel wool, a slightly different mechanism occurs. In the course of manufacturing steel wool and subsequent exposure to air, the iron on the surface of the fibers becomes oxidized and forms a variety of iron oxides. One example of the many possible oxidation reactions forms magnetite (Fe_3O_4), as shown below.

$$3Fe^{(0)} + 2O_2 \rightarrow Fe_3O_4$$

Thus, when steel wool is used as the catalyst, oxygen is already activated and can readily oxidize ammonia. Assuming that the activated form of oxygen is present as magnetite (Fe_3O_4), the oxidation of ammonia occurs as follows:

$$3Fe_3O_4 + 2NH_3 \xrightarrow{\text{heat}} 9FeO + 3H_2O + N_2$$

$$9FeO + \frac{3}{2}O_2 \xrightarrow{\text{heat}} 3Fe_3O_4$$

Notice that in this proposed reaction scheme, the oxidation of ammonia results in the production of another form of iron oxide, ferrous oxide (FeO). This iron oxide combines with oxygen to reform Fe_3O_4, which can continue to oxidize ammonia. Thus, iron oxide acts as a catalyst. If we add the two reactions above, we arrive at the same overall reaction for the oxidation of ammonia:

$$2NH_3 + \frac{3}{2}O_2 \xrightarrow[\text{catalyst}]{\text{heat}} N_2 + 3H_2O$$

Both the copper and the iron catalysts serve to break the N-H bond in ammonia and O-O bond in oxygen, and facilitate forming the N-N bond in nitrogen and forming water, but they do so at different rates. It is easier for copper oxide to oxidize ammonia than it is for iron oxide. One possible reason is because copper has a weaker affinity for oxygen than does iron. It takes less energy to break the copper-oxygen bond than the iron-oxygen bond. Thus, the copper catalyst reacts more rapidly to oxidize the ammonia.

You might wonder why it was necessary to heat the catalysts in the activity. Neither catalyst alone can sufficiently lower the high activation energy required for the oxidation of ammonia to proceed. Therefore, heat energy needs to be applied to the catalysts so that the energy barrier of the reaction can be overcome. The heat also helps to overcome the high energy barrier associated with the formation of the metal oxides, or oxygen activation.

As the oxidation of ammonia proceeds, both the copper and iron catalysts become ineffective because they become deactivated, or poisoned. With time, the copper and iron react with oxygen to form various oxides that are less reactive with ammonia. That is, these oxides are less able to oxidize ammonia. The gradual formation of less reactive oxides on the surfaces of the catalysts slowly deactivates the surfaces for ammonia oxidation. Iron becomes deactivated sooner than copper because iron tends to form a wider variety of oxides than does copper. In addition, chemicals other than ammonia and oxygen may be present in the gas that flows over the catalysts. (Recall, for example, in the activity that the ammonia in the flask was dissolved in water. Thus, water vapor also passed over the catalysts.) These chemicals may contribute to the deactivation of the catalysts as well. To know exactly why ammonia oxidation slows and then stops on the copper- and iron-catalyst surfaces (albeit at different rates), one would have to analyze the poisoned surfaces to determine the kinds of chemicals that are present.

The detailed reaction steps that occur on both metal surfaces are very complicated. It is impossible to know exactly what steps the oxidation of ammonia takes without doing a lot of testing. There can be more than one reaction pathway also. In the activity, the oxidation of ammonia was assumed to occur as follows:

$$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$$

However, you did not monitor the reaction by testing for all the products, because that would have been too difficult. Rather, you used pH to monitor the degradation of the ammonia (NH_3). Since ammonia solution is basic (has a high pH), its degradation resulted in a decrease in the pH of the liquid in the beakers, which you observed as a fading of the pink color of the indicator phenolphthalein.

Thus, it is not certain what final products were produced by the catalyzed oxidation of ammonia in the activity. It is also possible, for example, that in the case of the copper-catalyzed reaction, the following products were formed:

$$5CuO + 2NH_3 \rightarrow 5Cu + 3H_2O + 2NO$$

Recall from the Introduction that nitric oxide (NO) is a pollutant that is involved in the formation of ozone. Thus, in comparing the effectiveness of the copper and iron catalysts, it is not sufficient that the copper catalyst oxidizes ammonia faster than does the iron catalyst, if it does not convert the ammonia to a harmless product, such as nitrogen (N_2). When comparing catalysts, it is important to evaluate how specific and selective the catalysts are relative to the desired reaction. A highly specific catalyst reacts only with the reactants of the desired reaction and produces only the desired products. But for any mixture of reactants, there are many possible reactions that produce different products. Therefore, it is essential to have highly selective catalysts. Although in the activity, you could not detect the products that formed, in industry, great effort is made to detect and measure all the reaction products for a particular chemical reaction.

When researchers evaluate the selectivity of a catalyst, they must consider the conditions under which the reaction occurs, because the catalyst might perform differently under different conditions. For the reaction you monitored in the activity, there might be a different set of conditions under which iron performs better than copper. For instance, at a higher temperature, iron oxide's iron-oxygen bond would be more cleaved faster, and so the catalytic oxidation of ammonia by iron might proceed more rapidly than by copper. There are a number of other conditions that can be varied and tested (e.g., gas flow, ammonia concentration, and partial pressure of oxygen) in order to find a set of conditions that favors iron over copper. In industry, researchers consider all the conditions that might influence a catalytic reaction. They systematically vary the conditions relative to one another to determine the optimum set of conditions for the particular reaction and catalyst. The final choice of catalyst depends on the costs associated with maintaining the optimum conditions and the amount of product relative to unwanted by-products that is produced.

Homogeneous and Heterogeneous Acid Catalysts

INTRODUCTION

Inorganic acids, such as sulfuric, nitric, and hydrofluoric acids, are used as catalysts in many industrial chemical processes. For example, nitric acid is used to make nylon, and hydrofluoric acid is used in one of the steps that convert crude oil to gasoline. Sulfuric acid is believed to be the single highest volume chemical used in industry. In 1997, about 157 million metric tons of sulfuric acid, valued at about $8 billion, were used worldwide. Sulfuric acid has a large number of uses, including oil refining, manufacturing of fertilizers and car batteries, and processing of ores and metals.

Framework of a zeolite catalyst used in the production of gasoline.

Acid catalysts may be used as liquids or solids. When the acid catalyst is the same phase (solid, liquid, or gas) as the reactants, it is said to be a homogeneous catalyst. When the acid catalyst is in a different phase from the reactants, it is a heterogeneous catalyst. Because most chemical reactions occur when the reactants are in the liquid phase, homogeneous acid catalysts are usually liquids and heterogeneous acid catalysts are usually solids.

Typically, liquid acid catalysts are aqueous solutions. For example, concentrated aqueous sulfuric acid is about 98% sulfuric acid and 2% water; concentrated aqueous nitric acid is 70% nitric acid and 30% water.

Zeolites are one type of inorganic solid acid catalyst. Zeolites have many uses, including catalyzing the breakdown of crude oil to produce gasoline. They are crystalline minerals that have an intricate network of pores. The pores provide a large surface area and thus a large number of sites where the catalyzed reaction can occur. The catalyzed reaction occurs inside a zeolite, as well as on its outer surface.

Overall, heterogeneous acid catalysts are safer and less detrimental to the environment than homogeneous acid catalysts. For example, liquid acid catalysts are usually used at very high concentrations that pose significant health and safety hazards to workers. A great deal of care has to be taken in storing and handling the acid solutions, making sure that fumes are not released and that workers do not come in direct contact with the acids. In contrast, solid acid catalysts are easier to store and handle, and they do not release fumes.

Because catalysts are not consumed in a reaction, they can be used repeatedly. In general, catalyst reuse is more simply accomplished with heterogeneous catalysts than with homogeneous catalysts because the solid catalysts are more easily separated from the reaction mixture (such as by filtering the mixture) or because

CONCEPT behind the ACTIVITY

There are a number of safety and environmental benefits to using heterogeneous acid catalysts rather than homogeneous acid catalysts.

Acid Catalysts (Continued)

the solid catalysts are in an immobilized state. With homogeneous catalysts, however, the liquid catalyst, the reactants, and the products are all in the same phase. Thus, the separation of the catalyst from the reaction mixture is often costly and energy intensive, requiring extra chemicals, materials, and/or process steps.

Eventually, all catalysts have to be cleaned or disposed of due to their contamination, damage, or inactivation. Heterogeneous acid catalysts can often be cleaned by heating them or washing them with acid to recover their lost activity. If cleaning is not possible, the spent solid catalysts can be disposed of in landfills. Some heterogeneous acid catalysts contain precious metals, such as platinum. In some cases, these metals can be recycled prior to the disposal of the catalysts.

In general, the cleaning or disposal of a homogeneous acid catalyst is much more problematic. It is difficult to "clean" a solution after extensive use has rendered it inactive. In some cases, it is possible to reclaim the catalyst by distilling it from the deactiviating substances in the solution. However, once they are spent, concentrated liquid acids cannot simply be dumped down drains or disposed of in waterways. These acids are extremely toxic to life and are highly corrosive. The disposal of homogeneous acid catalysts requires that the waste acids first be neutralized with an alkali solution, generating a large volume of brine (salty water), prior to their discharge into municipal sewers or bodies of water.

There are, however, some disadvantages to using heterogeneous acid catalysts in reactions. First, in some cases, it may be difficult to get the reactants to the surface of the solid catalyst. Second, by-products of the reaction might inactivate, or poison, the catalyst with time if they become permanently attached to the catalyst's surface. Finally, if the solid catalyst has to be supported on another type of material, that material may alter the activity of the catalyst.

Industries weigh the advantages and disadvantages of different kinds of catalysts before deciding on the best catalyst to use to make a particular product. For many years, industries were primarily concerned with making as much product as cheaply as possible. They selected catalysts based on product yield, not on their effect on the environment. Then, in the 1970s, environmental laws were passed that required industries to reduce the amount of pollutants they produced. Industries that did not comply were fined. Thus, damage to the environment became a business cost. Today, to reduce such costs, many industries are choosing to use heterogeneous acid catalysts.

Catalyzing a Reaction Using a Heterogeneous Acid Catalyst

Imagine biting into a ripe, juicy orange. You can taste its flavor on your tongue. You can smell its distinctive odor. The flavor and aroma of an orange, as well as those of other fruits, are produced by chemicals called esters. Industries use esters, for example, as flavor enhancers in processed foods, fragrances in perfumes, and solvents in paints and varnishes.

In this activity, you will use a heterogeneous (solid) acid catalyst to catalyze the hydrolysis of an ester called methyl acetate, as shown by the equation on the right. Notice that during the hydrolysis reaction, both the methyl acetate molecule and the water molecule split and recombine, forming the products acetic acid and methanol. The hydrolysis of methyl acetate proceeds very slowly in neutral solution, but it can be accelerated by adding an acid catalyst. The acidity of the catalyst helps to speed up the hydrolysis reaction. The addition of heat further accelerates the reaction.

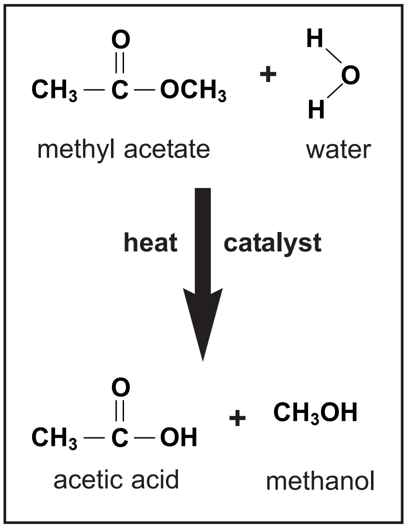
Since all the reactants and products in the reaction are colorless, there will be no color change when the reaction occurs. So how can the reaction be monitored? Notice that one of the products is an acid. A simple way to detect the presence of an acid is to drip some reaction mixture onto sodium bicarbonate, which will bubble, due to the formation of CO_2, if an acid is present.

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{sodium bicarbonate}}{NaHCO_3} \rightarrow \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

After using the solid acid to catalyze the hydrolysis of methyl acetate, you will observe how easily the catalyst can be separated from the reaction mixture and reused.

Purpose

- To use acid catalyst resin beads to catalyze the hydrolysis of methyl acetate to acetic acid and methanol.
- To confirm that the acid catalyst is necessary for the hydrolysis reaction to occur and then to clean and reuse the catalyst in the hydrolysis reaction.



Hypothesis

Read through the procedure. In which beaker do you think acetic acid will form? How long will it take for the acid to form? How will reusing the solid acid catalyst affect the results of the activity?

Predicted Outcome

Make predictions about which beaker the formation of acid will occur in. Include how long the acid will take to form. Also, predict what will happen when you reuse the solid acid catalyst beads. Do this on Data Table 1 provided.

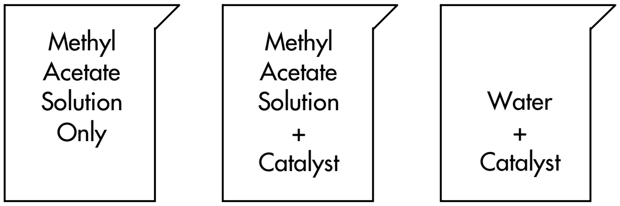
Concept behind the Activity

In heterogeneous catalysis, the reactants and catalyst are in different phases, allowing easier separation and reuse of catalyst.

Think about these questions as you do the activity:

? How do the contents of the three small beakers differ?
? What does the baking-soda test show?
? What is the effect of the solid acid catalyst?
? What happens when the solid acid catalyst is reused?
? How do calatyst amount, solution temperature, and degree of solution mixing affect the rate of reaction?

Procedure, Data, and Observations



1. As shown in the illustration, label the three small beakers *Methyl Acetate Solution Only, Methyl Acetate Solution + Catalyst,* and *Water + Catalyst,* respectively.
2. Add 2 g of the acid catalyst resin to the beaker labeled *Methyl Acetate Solution + Catalyst* and to the beaker labeled *Water + Catalyst.* Closely examine the catalyst beads and record your observations. ***CAUTION:*** *Be careful not to spill any of the beads, as they are difficult to clean up and slippery when walked on.*
3. Pour a small mound of baking soda onto each of the three watch glasses.
4. Your teacher will provide for the class: heated tap water, heated distilled water, and heated methyl acetate solution (methyl acetate dissolved in water). **Work quickly when working with these liquids to minimize their cooling.** Pour about 100 mL of heated tap water into each of the three large beakers.
5. Add 10 mL of heated methyl acetate solution to the beaker labeled *Methyl Acetate Solution Only* and to the beaker labeled *Methyl Acetate Solution + Catalyst.*
6. Pour 10 mL of heated distilled water into the beaker labeled *Water + Catalyst.*
7. Place each small beaker into one of the large beakers containing water. Record the time. Stir the contents of the small beakers continuously. After three minutes, use a medicine dropper to transfer a few drops of liquid from one of the small beakers onto the baking soda on one of the watch glasses. Record your observations. Then do the same to test the liquid from the other beakers. Use a clean dropper for each test.
8. Repeat the baking-soda test as described in step 7 after 6, 9, 12, and 15 minutes. Use the appropriate dropper for each transfer of liquid. Record your observations.
9. Add a small amount of baking soda to the beaker labeled *Water + Catalyst.* Record your observations.
10. Remove the small beakers from the beakers of water. Let the catalyst beads settle. Then slowly decant the liquid, trying not to lose any of the beads, and dispose of the liquid down a sink drain. Flush the methyl acetate solution down the drain with plenty of water.
11. Wash the beads two times with distilled water, decanting the water each time. Then, add enough distilled water to the beakers to cover the beads. Leave the beads in the water overnight.
12. The next day, decant the water from the beakers containing the catalyst beads. Repeat the experiment, reusing the beads.
13. When you are finished with the activity, decant the liquid in the beakers and dispose of the liquid down a sink drain. Flush the methyl acetate solution with plenty of water. Dispose of the beads in the trash.

Interpretations of Data & Conclusions—*Be thorough and use complete sentences.*

1. How do your results compare with your predictions? Give possible reasons for any differences.

2. Compare the reactions of the liquids from the three small beakers with the baking soda. Explain any differences you observed.

3. Did the solid acid catalyst make the liquid in the beaker acidic? How do you know?

4. How did increasing the reaction time from 3 to 15 minutes affect your results? Explain.

5. What was the effect of reusing the acid catalyst?

6. What were the controls in the activity? Explain why they were used.

7. Based on your data, what can you conclude about where in the reaction mixture the hydrolysis of methyl acetate took place? Explain.

8. If you were to repeat this activity using a homogeneous acid catalyst, what kind of catalyst would that be? What part of the activity would you not be able to repeat?

Name____ **Date**__________________

Period________________

Data Table 1. Predictions, Observations, and Data for Part A

Predictions about the formation of acetic acid
Predictions about reusing the solid acid catalyst
Observations of the solid acid catalyst

Day 1 – New Beads					
Contents of beakers	Observations				
	3 minutes	6 minutes	9 minutes	12 minutes	15 minutes
Observations when adding baking soda to the beaker containing water and catalyst					

Day 2 – Reused Beads					
Contents of beakers	Observations				
	3 minutes	6 minutes	9 minutes	12 minutes	15 minutes
Observations when adding baking soda to the beaker containing water and catalyst					

EXPANDING on the CONCEPTS

In this activity, you observed a reaction catalyzed by a heterogeneous (solid) acid catalyst. Does the explanation below of how the catalyst works agree with your observations?

Many reactions are catalyzed by acids or bases, or both. An acid, such as nitric acid (HNO_3), is a compound that releases hydrogen ions (H^+) when placed in water. An acid catalyzes a reaction by converting a reactant to a cation (positively charged ion), making it more favorable or attractive for attack by another reactant that is attracted to positive charge. Usually, this conversion involves the transfer of H^+ from the catalyst to the reactant. Thus, for any catalyzed reaction, where A is a reactant:

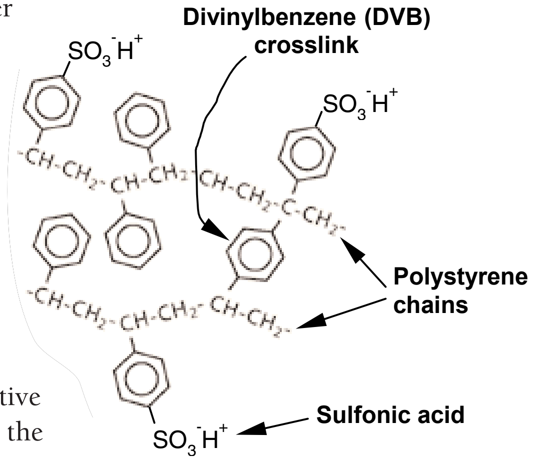
Step 1 $A \xrightleftharpoons{\text{catalyst}} AH^+$

Step 2 $AH^+ \longrightarrow \text{Product}$

The reaction intermediate, AH^+, is the activated complex, which provides a lower energy pathway along which the reaction proceeds more rapidly to completion.

When a liquid homogeneous catalyst releases H^+ in water, the ions disperse throughout the liquid without staying in one location. In the example above the H^+ spread out in the water once they have separated from the NO_3^-. This dispersion occurs because there is a partial negative charge on the oxygen atom in the water molecules (H_2O) that attracts the H^+. Likewise a partial positive charge on the hydrogen atoms in water attracts the NO_3^-. A heterogeneous (solid) acid catalyst also releases H^+ when placed in water—in this case, from its surface. Each H^+ released from a solid acid leaves behind a negative charge on the solid's surface. Because opposite charges attract, the H^+ released stay close to the negatively charged solid. The partial negative charge on the oxygen atoms in the water does not "pull" the H^+ away from the solid because it is not nearly as strong as the negative charge on the solid's surface. In fact, all the H^+ released by a solid acid bead remain in a thin layer of water wrapped around the bead's surface. The catalyzed reaction occurs near the surface of the solid acid, at the sites (called active sites) where the H^+ are present.

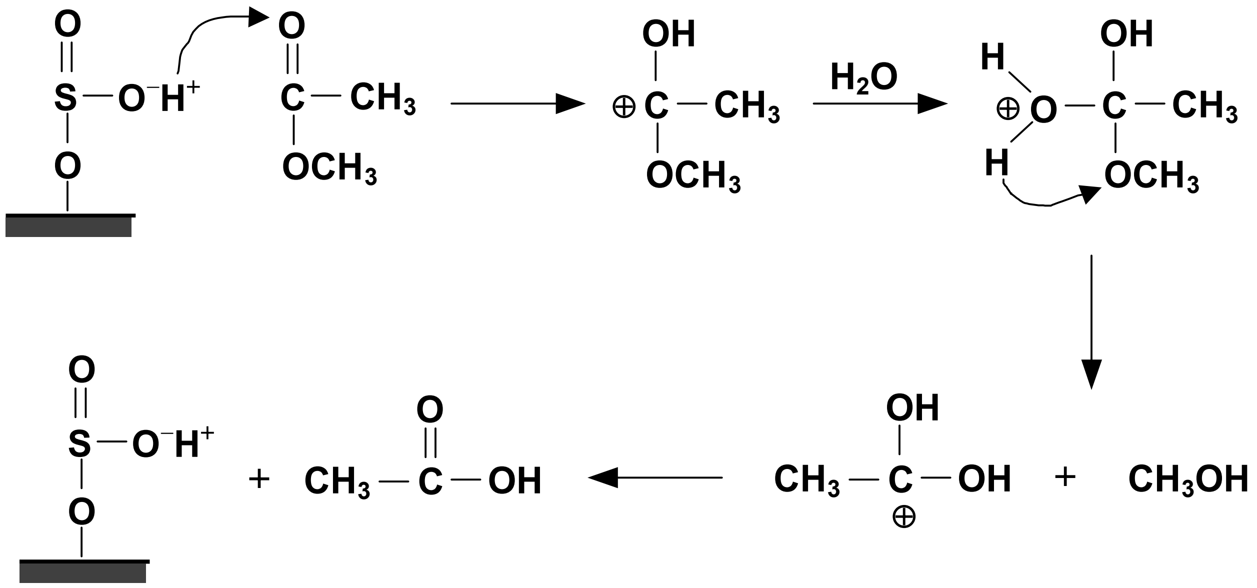
The acid resin you used in the activity is an organic solid acid catalyst. The beads are made of a polymer containing styrene and divinylbenzene (DVB). A polymer is a giant chain molecule consisting of repeating units. Notice in the illustration that the styrene molecules are joined in long chains. The DVB molecules link the chains to each other.



The molecular structure of acid resins made from crosslinked polystyrene-divinylbenzene copolymer with sulfonic acid groups attached to the polymer.

Because of the way the acid resin was made, the beads you used in the activity also had pores (channels and voids, such as those seen in sponges) within the spheres. The beads are made by dissolving styrene and DVB molecules in a solvent in a mixing vat. The polymer forms as porous spheres, or beads. The beads are then treated with concentrated sulfuric acid, which reacts with the surface on the exterior of the beads and the surface surrounding the pores inside the beads. This reaction permanently attaches sulfonic acid groups ($-SO_3H$) to the surfaces. These strong acid groups make the beads act as an acid. Notice that the H^+ that are released stay close to the SO_3^- attached to the beads. The pores greatly increase the total surface area of the beads. The inner pores, like the outer spherical surface of the solid acid, have H^+ as well, and therefore increase the total number of active sites for the given volume of solid acid. The catalyzed reaction occurs both inside the beads and on their exterior surface, at the sites where the H^+ are located.

The illustration below shows what happens at one of the active sites of a bead during the hydrolysis of methyl acetate. An activated complex is formed when the H+ from the sulfonic acid group is transferred to a molecule of methyl acetate. A water molecule attacks the activated complex, causing both the molecule of methyl acetate and the molecule of water to split. This leads to the formation



Postive hydrogen ion from the sulfonic acid group attached to the catalyst bead begins to react with a molecule of methyl acetate in its vicinity. The activated complex that is formed then reacts with a water molecule. Both the methyl acetate molecule and the water molecule split and recombine, forming the products acetic acid and methanol. The H^+ that was part of the the activated complex returns to the SO_3^- on the bead.

of acetic acid and methanol, the products of the reaction. Notice that the H^+ that was part of the activated complex returns to the SO_3^- on the bead. Because the H^+ was not used up, the same site can be used once again to catalyze the hydrolysis of a methyl acetate molecule.

As efficient as the solid acid catalyst was in increasing the amount of products formed over time—that is, increasing the reaction rate—compared to the uncatalyzed reaction, what can be done to raise the reaction rate even further? Increasing the amount of catalyst, the solution temperature, and the degree of solution mixing can all increase the rate of reaction. As the amount of catalyst increases so does the number of active sites where the hydrolysis reaction occurs. Thus a greater number of reactions take place and more products are produced at any one time. In other words, the reaction rate goes up. Raising the temperature of the solution gives the molecules more thermal (heat) energy, which can lead to higher reaction rates, as well. The increase in thermal energy causes more molecules to collide with one another. The more collisions there are, the more likely reactions take place and products are formed. In general, increasing temperature can often increase the reaction rate. Mixing the solution further increases reaction rate by circulating the reactants toward the active sites around and within the solid acid catalyst beads. This allows newly-formed products to leave the active sites so that more reactants can move in for reaction. Similarly, stirring circulates the beads to parts of the solution with unreacted reactants. All of this movement increases the production of products over time and, thus, the reaction rate. Thus, taking these step will make better use of already efficient catalysts, minizing time and waste.

A solid acid catalyst can be reused many times before it eventually becomes neutralized (inactivated) and needs to be replaced. Because the acid in a solid acid catalyst stays with the solid, separating the acid from a liquid or gaseous reaction mixture is accomplished easily by filtration or decantation. For the same reason, solid acid catalysts are much safer to handle than liquid acid catalysts and are safer for the environment.

Catalyzing with Platinum Black

TEACHER NOTES

Materials and Setup

MATERIALS (per group)

- *safety glasses*
- 3 different types of paper with platinum black (see Advanced Preparation below)
- 1 mL methanol
- 10-mL graduated cylinder
- 100- to 150-mL beaker
- 100-mm-diameter watch glass
- 1-L beaker three-quarters filled with cold water
- long-handled metal tongs
- stopwatch, or watch with second-counting capability

ADVANCE PREPARATION

Platinum black, which can be purchased from a science-supply company, is relatively expensive. You will need a very small amount, about 1 mg, for each group.

Provide three different types of paper, such as those listed below, for each group to test. You might want each group in the class to test the same three types, or you might vary the three types from group to group. Choose papers that vary in composition, thickness, and porosity. Be sure to test each type of paper before allowing students to work with it, as some of the papers will give off more smoke than others.

Types of paper: regular white photocopy paper, high-grade (thicker) white photocopy paper, paper towel, cardstock, chromatography paper, tissue paper, unbleached or bleached coffee filter.

For each group, cut each type of paper into two 2-cm squares. Fold one side of each square to form an L-shape, such that one side is longer than the other. On one of the L-shaped pieces, use the eraser end of a pencil to tap a tiny amount of platinum black onto the inner surface of the long side of the L. The amount of catalyst influences the reaction rate, so aim to tap a consistent amount of platinum black onto the pieces of paper. If too little platinum is used, the reaction will either proceed slowly or not all. A light gray spot about 1 cm in diameter should be sufficient. To be certain, follow the steps of the activity to test a platinum-treated sample of each type of paper before students do the activity themselves.

ESTIMATED TIME

- 50 minutes

To save time, give each group only one type of paper to test, but vary the type from group to group; then groups can share their data.

Optional Demonstration

Flash paper, obtainable from a magic store, has a very low auto-ignition (flash) point. When treated with platinum black and placed near methanol as described in the activity, it will spark immediately and ignite the methanol. It is recommended that you practice the flash-paper demonstration beforehand. A 1-cm square piece of flash paper is sufficient for the demonstration. See note on page 2.

Purpose

To introduce students to catalysis by demonstrating that the heat generated by the catalytic oxidation of methanol by platinum black can cause paper to burn.

Summary of the Activity

To observe the effect of a catalyst, students hold three types of paper both treated and untreated with the catalyst platinum black over a beaker of methanol. They infer that a reaction has occurred by observing whether the paper burns. Based on their knowledge of the reactions that took place, students form a hypothesis as to why some of the papers burned faster.

Activity Objectives

Students will:

- compare the reactivity of different types of paper in the presence of methanol and oxygen with and without the catalyst platinum black
- compare the time it takes for the different types of paper to start to burn
- learn the sequence of reactions that led to the burning of the papers

Caution and Safety

- Students should extinguish any smoldering pieces of paper before they create too much smoke and dispose of them in the beaker of water.
- Students should keep methanol away from open flames, as it is a flammable liquid.

Background Information

Chemical reactions in which electrons are transferred from one chemical species (that is, an element, a compound, or an ion) to another are called oxidation-reduction (redox) reactions, or electron-transfer reactions. This transfer of electrons necessarily involves a change in the charge between the atoms and therefore a change in the oxidation states of the individual atoms within each species. Consider a reaction between two species, A and B. If an atom in A gains electrons in the course of the reaction, then its oxidation state is lowered, and A is said to undergo reduction. If an atom in the reactant B loses electrons in the reaction, then its oxidation state is raised, and B is said to undergo oxidation. In this case, B is called the reducing agent because it causes a reduction in A (as it, itself, undergoes oxidation). Likewise, A is the oxidizing agent because it causes an oxidation in B (as it, itself, undergoes reduction).

In this activity, the oxidation of methanol is represented as:

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O + \text{heat}$$

For methanol (CH_3OH), the oxidation states of the atoms are C^{-2}, H^{+1}, O^{-2}; for oxygen (O_2), O^0; for carbon dioxide (CO_2), C^{+4}, O^{-2}; and for water (H_2O), H^{+1}, O^{-2}. Note that carbon goes from an oxidation state of -2 to $+4$; thus, methanol loses electrons, undergoing oxidation and acting as the reducing agent. Oxygen goes from an oxidation state of 0 to -2; thus, it gains electrons, undergoing reduction and acting as the oxidizing agent.

Note on Flash Paper

Flash paper is nitrocellulose. It is made by soaking paper in nitric acid or a mixture of nitric and sulfuric acids. Nitro groups are incorporated into the paper, serving as an internal oxidizer. Thus, flash paper has a very low auto-ignition point. The heat produced by the platinum-catalyzed methanol-oxidation reaction is sufficient to ignite the paper, which burns as a flash. ***Caution:** Because the flash paper burns with an open flame, the methanol liquid catches fire easily and will continue to burn until it is extinguished.* It is recommended that you practice the flash-paper demonstration before showing it to the class. Remember that only a 1-cm square piece of flash paper is necessary for the demonstration. You might want advanced students to test the flash paper themselves. If they do, be sure to provide close supervision.

Flammability of Gases

There are three essential ingredients for a fire to occur: a fuel (that is, a combustible substance), an oxidizer (such as oxygen in air), and an ignition source (for example, a flame, spark, or hot spot). The fuel is sometimes the vapors over flammable liquids, such as gasoline, charcoal lighter fluid, ether, cooking oil, or alcohol. Note that it is the vapors, not the liquids themselves, that burn, as students observed in the case of methanol in the activity. To extinguish a fire, one of the three above ingredients must be eliminated. Many times, that ingredient is the oxidizer, air. That is why a grease fire in a cooking pan can be extinguished by covering the pan~~the~~ oxygen supply is cut off.

Tips from the Trenches

I collected all burned paper samples in a large beaker of water to avoid a mess in the sinks or a trash-can fire. At the end of the day, I discarded all the wet paper samples into a trash-can.

Susan Bober
Chemistry teacher
Schaumburg High School
Schaumburg, Illinois

Historical Background

In 1815, the English chemist Sir Humphry Davy invented the miner’s safety lamp. The presence of the explosive gas methane in mines requires that the lamps which miners use be designed so as not to ignite the methane. The Davy safety lamp consists of an open flame surrounded by a platinum gauze. The platinum catalyzes the oxidation of methane such that it burns (without producing a flame) before it reaches the lamp's flame, thereby preventing an explosion.

Note About Platinum Black

Students might wonder why platinum black is black, whereas pure platinum is silvery-white. Remind them that the color of an object depends on the wavelengths and intensity of light it reflects. A white object reflects all wavelengths of light; a black object absorbs all wavelengths. Tell students that the surface of platinum-black particles is very rough, with many peaks and valleys, and because the particles are very small, they have a high surface area. As a result, light waves that bounce off the surface are scattered in all directions. Eventually, these scattered light waves become trapped in the “valleys”on the particle surface and are absorbed by the particles, causing the particles to appear black.

Procedure, Data, and Observations

- Instead of giving each group the same three different types of paper to work with, you might want to give different types of papers to different groups and then have them share their data at the end of the activity. Have them record their data on the chalkboard to compile class data.
- Remind students to keep the methanol away from open flames. Be sure that the watch glass is larger in diameter than the beaker. Keeping the beaker covered with the watch glass will allow methanol vapor to accumulate over the liquid, which will accelerate the reaction.
- Instead of the 1-L beaker, any comparably-sized fire-safe container that can hold water can be used to extinguish burning paper.
- The piece of paper is folded to maximize the exposure of the paper to the surface of the methanol. If it were not folded, only the edge of the paper would be close to the liquid surface. Long-handled metal tongs, instead of forceps, should be used to hold the paper, in case the methanol and/or paper ignites.
- Students should observe the paper carefully as they time the reaction. For this reason, it is preferable that students use a stopwatch.
- The burning papers will smolder, or burn slowly without flame. Instruct students to extinguish the burning pieces of paper in water immediately, before they create too much smoke.
- The rate of burning of the papers is not fast enough to support an open flame, so it is unlikely that the methanol will ignite. However, as a precaution, tell students that if the methanol does ignite, a pale blue flame will form that is difficult to see. They should place the watch glass on top of the beaker if they hear a “whoosh” sound or see a flame. If this does not extinguish the flame, they should pour the beaker of water over it.
- Students may see small specks of light falling from the treated papers. These are caused by particles of platinum black falling through the methanol vapor/air mixture. The light is the burning of methanol at the platinum.

Interpretations of Data & Conclusions

- Most students probably predicted that the papers treated with platinum black will start to burn faster than those not treated. However, some students might not have predicted that some types of papers will burn faster than others.
- The papers that were not treated with platinum black served as controls. They showed that the burning of paper was due to the presence of platinum black.
- The burning of the papers indicated that heat was generated, which in turn indicates that the reaction between methanol vapor and oxygen gas took place.
- Some students may say that the papers untreated with platinum black would eventually burn; others may say that the papers would never burn. (The papers, in fact, will never burn in the absence of platinum black.) In either case, students should give the reason that no catalyst was present to speed up the reaction between methanol and oxygen.

Summary of Results

The papers treated with platinum black will burn within about one minute, whereas the untreated papers will not. The papers will smolder (burn slowly without flame) and produce smoke. Some types of paper will start to burn faster than others, depending on the auto-ignition points of their additives. Also, porous paper, such as paper toweling and tissue paper, will burn faster than nonporous paper, such as photocopy paper.

Troubleshooting

If students do not observe a reaction of a catalyst-treated paper within one minute, it might mean that there is insufficient oxygen around the paper. Tell students to gently blow into the beaker to introduce more oxygen.

Enriching Science Experience

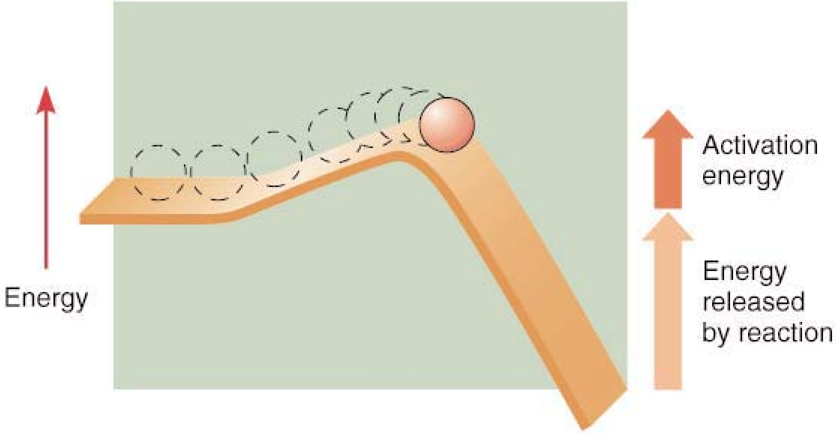
Have students repeat the activity using ethanol instead of methanol. ***Safety Note:*** *Like methanol, ethanol is flammable and should be kept away from open flames.* Write the chemical formulas of methanol (CH_3OH) and ethanol (CH_3CH_2OH) on the board and have students predict on the basis of the formulas whether platinum black will catalyze the oxidation of ethanol. Upon doing the activity, students will observe no reaction. The primary reason is that the rate of catalytic oxidation of ethanol over platinum is much slower than that of methanol. The much slower rate of heat release is not sufficient to raise the temperature of the paper to the paper’s auto-ignition point. The lower vapor pressure of ethanol compared to methanol also contributes to the slower rate.

The non-reactivity of ethanol in the presence of platinum black is an example of catalyst specificity. A catalyst reacts with only specific reactants and catalyzes a specific reaction. In this case, the platinum black reacts not with any alcohol, but with methanol specifically.

- Students may hypothesize why some types of paper started to burn faster than others by thinking about how the papers looked and felt different and how these differences might have contributed to their burning times. One possible reason was that some papers were more porous than others. The larger spaces between the fibers of the more porous papers allowed oxygen to reach the platinum black within the fibers more quickly, thereby causing those papers to start burning more quickly.
- Based on their data, students should conclude that platinum black acted as a catalyst by speeding up the reaction between methanol and oxygen. platinum black catalyzed the reaction of methanol vapor with oxygen gas in the air. The methanol was oxidized, which means it lost electrons. Methanol oxidation occurred at the surface of the platinum particles via a shortcut pathway that has a much lower activation energy than the reaction between methanol and oxygen in the absence of platinum black.
- Encourage students to further explore questions such as: how platinum black was made, practical uses for platinum black, or how platinum black affected the reaction between methanol and oxygen.

Using Analogies

You might use an analogy to help students understand the action of a catalyst. Tell them to think of a chemical reaction as a ball rolling over a bump (a barrier). The rate at which the ball rolls over the bump depends on the height of the bump. The higher the bump, the lower the rate. A catalyst increases the rate of a chemical by lowering the height of the “bump.”



Connection to Literature

Tell students that the novel *Fahrenheit 451* by Ray Bradbury is a futuristic story about a society that prohibits book reading. Have interested students read *Fahrenheit 451* and report on the significance of the title to the activity. (In the book, firefighters burn books. 451°F is the ignition temperature of book paper.)

Connection to Chemistry

Use the equation showing the oxidation of methanol to discuss oxidation-reduction reactions. Have students work out the oxidation states of each atom and identify the oxidizing and reducing agents. (See Background Information above.)

Our Dependence on Catalysts

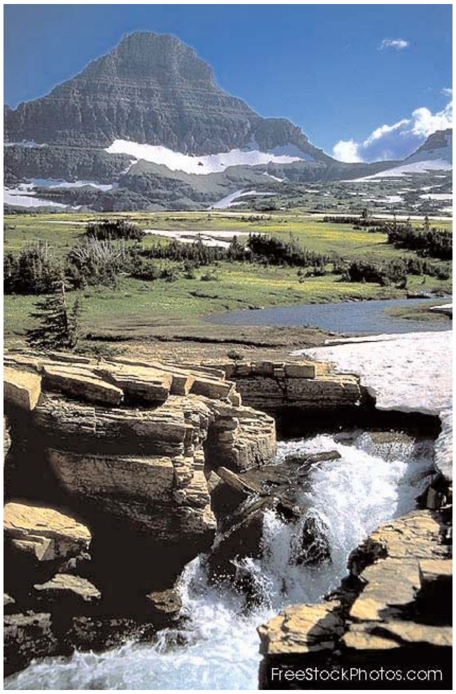
INTRODUCTION

Think about all the things that you used since you got up this morning—the fabrics of your sheets, towels, and clothes; the food you ate for breakfast; the plastic bottle that contained the milk or juice you drank; the fuel used to heat your home and school and to energize the car or bus that drove you to school; the nylon of your backpack. All are produced by catalyzed reactions. The list of materials and products that are produced by catalysis is endless.

There are thousands of different types of catalysts. A catalyst can be a chemical with a very complex structure, or simply an acid or base. Mineral or metal surfaces also can serve as catalysts. These can be very inexpensive, such as iron oxides (rust), or very expensive, such as platinum. All organisms depend on catalysts, called enzymes, in their cells to carry out essential life processes. However, not all catalysts are found in nature. Many catalysts that are used in industry are synthesized by scientists and engineers in laboratories.

As you know, catalysts increase the rate of a chemical reaction by providing a shortcut pathway that the reactants take in their transformation to products. This "shortcut" not only accelerates the reaction rate, it also directs the reaction so that there are fewer side reactions and unwanted by-products (wastes). Often, these wastes are harmful to the environment and therefore are pollutants. The high rates and selectivity of catalyzed reactions mean that less energy and fewer raw materials (reactants) are consumed and fewer pollutants are produced than in uncatalyzed reactions. Thus, catalysts help to preserve and protect the environment. Their use is an example of Green Chemistry, which includes the design, manufacture, and use of chemicals and chemical processes that prevent or reduce damage to the environment.

Besides protecting the environment, catalysts are also important to industry and the economy. Catalysts are used in over 90% of the manufacturing processes in the U.S. chemical industry, which produces over 7,000 different products worth an estimated $375 billion per year. In the year 2003, the sales of catalysts is projected to be divided roughly equally among the areas of chemical production, plastics production, oil refining, and waste treatment.



The use of Green Chemistry helps to preserve our precious environment, such as this scenic view of Montana.

The manufacturing of catalysts themselves is a $10 billion industry worldwide. The development of new catalysts holds the key to increasing the rates of production, improving product yields, reducing production costs, and eliminating the production of harmful wastes during manufacturing.

CONCEPT behind the ACTIVITY

Catalysts allow us to use less energy and fewer raw materials and to produce less harmful waste in the manufacturing of products. Thus, catalysts are essential to protecting and preserving the environment.

Searching for Catalysts

Catalysts allow industries to transform raw materials into a vast array of commercial products—foods, fuels, medicines, plastics, textiles, and chemicals. Catalysts are important in processes used to reduce pollutants (wastes) produced by cars, homes, and industries. These pollutants include harmful gases released into the air and toxic chemicals released into waterways and the soil. Catalysts are also involved in natural processes, including geological, physical, and biological processes, which shape our planet and allow life on Earth to exist. For example, plants use catalysts to make sugar during the process of photosynthesis. Now that you know what catalysts are and how they are helpful to us, you will search for information about catalysts on the Internet.

Purpose

- To conduct an Internet search to identify catalysts used in industrial processes, pollution treatment, and natural processes.
- To share your findings with the class for analysis.
- To compare and contrast the catalysts and draw conclusions about them.

▶ **Think about these questions as you do the activity:**

? Is the catalyst used in an industrial process, in the treatment of wastes, or in a natural process?
? What process does the catalyst accelerate?
? Can the process occur without the catalyst?
? Does the catalyst benefit or harm the environment?

Procedure, Data, and Observations

1. You will use the Internet to search for information about catalysts that are used to make a commercial product; to clean the air, water, or soil; and in natural processes (geological, physical, or biological). Think of keywords that might help you find the information. Record them in Data Table 1.
2. Use one or more of the keywords you chose to find information about a catalyst that is used by industry to make commercial products. If those keywords don't lead you to the kind of information you are looking for, try using other keywords. Print out the information you find.
3. In your data table, record the keywords you used to find information about the catalyst, the URL of the website where you found the information, the name of the catalyst, and the category to which the catalyst belongs (making a commercial product, cleaning the environment, natural process).
4. Read the information you printed out. In your data table, write a description of the chemical process that is catalyzed. You can write a chemical equation for the process or describe it in your own words. Be sure to identify the reactants and products.

Concept behind the Activity

Catalysts are used in a wide variety of areas, including industrial processes, pollution treatment, and natural processes.

5. Record any necessary conditions (e.g., temperature, light, pressure, and pH) for the process and any waste products produced.
6. Repeat steps 2–5 for a catalyst that is used to clean the air, water, or soil and one that is used in natural processes.
7. Share the information you found with your classmates, and record it in Data Table 2.

Interpretations of Data & Conclusions—*Be thorough and use complete sentences.*

1. In general, how would the processes described in your data table be different if they were not catalyzed? Consider the reactants, products, and reaction conditions needed.

2. Compare and contrast the catalysts listed in the class data table. Can different substances catalyze the same process? Are some substances capable of catalyzing a variety of processes? Give examples to support your answers.

3. What do most catalysts that are used to make commercial products have in common?

4. How do those catalysts differ from catalysts used in natural processes?

5. Did you find any surprises during your search for catalysts? Explain.

6. What are your thoughts about our dependence on catalysts?

7. Traditionally, synthetic (human-made) catalysts have been designed to maximize the amount of product produced. If you wanted to protect the environment, what else would you want a catalyst to do?

8. Does catalysis always benefit the environment? Give examples. (Hints: Think about how some catalysts are obtained and their possible effects on the environment when disposed of. Also consider the possible effects of the products on the environment.)

9. What new questions do you have about the three categories of catalysts? Write two or more questions and give a reason why you want to learn the answer to each.

Name______________________________________ Date__________________

Period________________

Data Table 1. Group Data Table

Possible keywords to use:

Keywords used	URL of website	Name of catalyst	Catalyst category	Description of process	Necessary conditions	Waste products

Name______________________________ **Date**________________

Period________________

Data Table 2. Class Data Table

	Name of catalyst	Catalyst category	Description of process	Necessary conditions	Waste products
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					

EXPANDING on the CONCEPTS During your Internet search, you learned about catalysts that are used to make commercial products; to clean the air, water, or soil; and in natural processes. Read the article below to learn more about these catalysts.

A catalyst may be organic, which means it is carbon-based, or it may be inorganic. Both kinds of catalysts are involved in natural processes. The catalysts in your body, or enzymes, are organic. Most enzymes are proteins. All organisms depend on the catalytic activity of enzymes. Without them, they would not be able to live, grow, and reproduce. For example, enzymes in your cells help break down proteins, starches, fats, and other large, complex molecules into small, simple molecules. Your cells use the simple molecules for energy or to make other kinds of molecules. Other enzymes in your cells do the opposite—they help make complex molecules from simple ones. The complex molecules are used to make cell structures or to regulate the cells' activities. Your cells make thousands of different enzymes, each catalyzing a different reaction. Without enzymes, biological reactions would take place too slowly, and life as we know it could not exist.

Catalysts that are used in industry are mainly inorganic. Many inorganic catalysts are rare or expensive metals, such as rhodium and platinum. Inorganic acids and bases, such as sulfuric acid and sodium hydroxide, respectively, also are used to catalyze industrial processes. Most catalyzed industrial processes involve the refining of petroleum or the production of chemical compounds, including pharmaceuticals. Some examples of chemicals produced by catalyzed reactions are listed below.

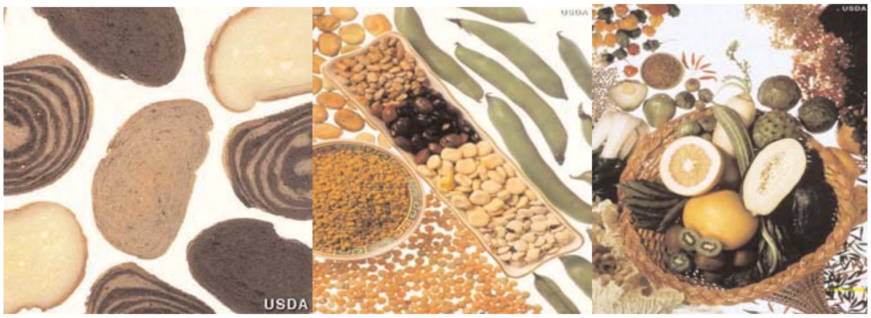
- Ammonia
- Sulfuric acid
- Synthetic rubber
- Polyethylene (milk bottles and other containers)
- Isopropyl alcohol (rubbing alcohol)
- Ibuprofen (anti-inflammatory drug)

Over the past few decades, scientists have learned more about pollutants produced by industrial processes and have developed technologies to minimize these pollutants. There are two approaches to combating pollutants: (1) avoid their generation altogether and (2) remove pollutants after they are formed, a process called remediation. To avoid the generation of pollutants, industries have made a significant effort modifying their methods of manufacturing. For example, they have developed new catalysts that help produce fewer harmful by-products during reactions. However, industries more commonly use remediation.

With remediation, it is much more efficient to remove the pollutants at the point where they are generated instead of after the pollutant is released into the environment. For example, a major source of pollution is the combustion of fossil fuels—petroleum, coal, and natural gas—by vehicles, power plants, and furnaces. The combustion of fossil fuels releases carbon monoxide, nitrogen oxides, and other harmful gases into the air. In cars, these pollutants are part of the engine's exhaust. To remove the pollutants, cars are equipped with a device called a catalytic converter, which uses the catalysts platinum, palladium, and rhodium to change the harmful gases in the exhaust to safer gases, such as oxygen, nitrogen, water, and carbon dioxide. A properly functioning catalytic converter removes well over 95% of the pollutants from engine exhaust before it is released into the air. Other kinds of pollutants that are removed by catalytic reactions are listed below.

Removed from Wastewater
- Ammonia
- Heavy metals (e.g., lead, copper, cadmium)

Removed from Air
- Carbon monoxide
- Nitrogen oxides
- Sulfur oxides
- Ozone
- Volatile organic compounds (e.g., odors, solvent vapors, chemicals in cigarette smoke)



Biological Catalysts, called enzymes, are used by the body to break down the large, complex molecules in food, such as those found in breads, legumes, and fruits.

Searching for Catalysts

TEACHER NOTES

Materials and Setup

MATERIALS (per group)

- Internet access
- data tables (or paper for students to create their own)

ESTIMATED TIME

- 35 minutes to conduct the Internet search
- 15 minutes to share findings with classmates

  To save time, you can assign the search as homework. The next day, follow up with a 15-minute class discussion of students' findings.

Introducing the Topic

Lead into a discussion of catalysts that are used in natural processes by showing students a sample of meat tenderizer. Explain that the tenderizer is actually a catalyst found in papaya. The catalyst, called papain, breaks down proteins in the cells of a papaya. Similarly, when used as a meat tenderizer, the catalyst breaks down the proteins in meat, making the meat more tender. Papain is also used to make cleaning solutions for soft contact lenses, treat indigestion, accelerate the healing of skin wounds, and treat insect stings and bites.

Note About Green Chemistry

Shortly after the Pollution Prevention Act of 1990 was passed, the Environmental Protection Agency (EPA) established the Green Chemistry Program. The goal of the program is to promote the research and development of chemical products and processes that prevent pollution. The EPA's Green Chemistry Program works with universities, industries, other government agencies, and nongovernment organizations. In 1995, President Clinton announced the Presidential Green Chemistry Challenge, which promotes the development of educational programs about Green Chemistry.

Students can learn about the Green Chemistry Program of the EPA at http://www.epa.gov/greenchemistry.

Purpose

To help students recognize the wide variety of uses of catalysts.

Summary of the Activity

Students conduct an Internet search to identify catalysts that are used in industrial processes, natural processes, and pollution treatment. After sharing their findings with classmates, students compare and contrast the catalysts and draw conclusions about them.

Activity Objectives

Students will:

- use the Internet to search for information about catalysts that are used in industrial processes, pollution treatment, and natural processes
- identify the keywords they used to find the information
- describe the catalyzed processes that they found information about, including identifying the catalysts, reactants, desired products, waste products, and reaction conditions
- share their findings with classmates

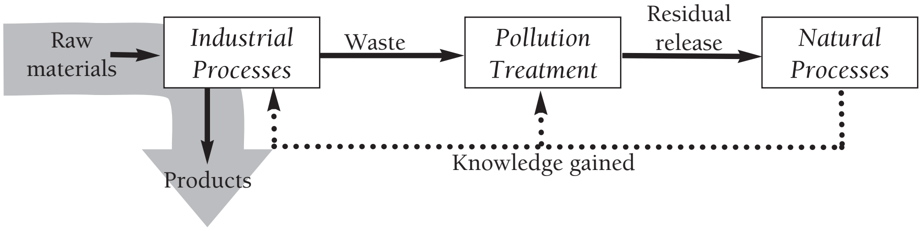
Background Information

A catalyst accelerates a chemical reaction because, in providing an alternate reaction pathway, it lowers the activation energy of the reaction. The overall equation for the reaction, however, is the same in the absence or presence of the catalyst. Catalysts do not alter reaction equilibrium. Rather, they speed up the rate at which equilibrium is attained. This means that a catalyst accelerates the forward and reverse reactions by the same factor. A good synthetic catalyst increases the reaction rate about a million (10^6) times. (This factor is ideal when making a useful chemical product but unfortunate when the chemical is catalyzing an unwanted reaction, such as the destruction of the stratospheric ozone layer by chlorohydrocarbons.) A biological catalyst, or enzyme, on the other hand, can cause a reaction to proceed at a rate that is anywhere from 10^8 to 10^{20} times faster than the uncatalyzed reaction. There are few synthetic catalysts that have activities comparable to those of enzymes.

CONCEPTS behind the ACTIVITY

When it comes to studying catalysis and its effects on the environment, the variety of catalytic processes can be categorized into three main areas: industrial processes, pollution treatment, and natural processes. Consider the diagram below.

Raw materials are converted into useful products produced by various industrial processes (gray arrow). Many products are made with catalysts in order for them to be produced economically, quickly, and environmentally sound. Catalysis, however, does not stop there, as shown in the loop on the right side of the diagram (solid and dashed arrows). In any industrial process there are also unwanted side (waste) products, i.e. pollution. Before they are released into the environment, these waste products—which could be in the air, water, or soil—are treated using catalysts and, if possible, recycled for reuse in the industrial process. Pollution treatment is not perfect, though, so there is always some residual release of waste material into the environment, affecting people, animals, plants, land, air, and oceans. Nature has its own rich variety of catalytic processes. By studying how these natural processes work and by witnessing the effects of our influence on the environment, we can gain knowledge on how to improve industrial processes and pollution treatment (dashed backward arrows).



Selectivity vs. Specificity

For any mixture of reactants, there are many possible chemical reactions. Often, however, only one of these reactions is desirable. Therefore, an important function of a catalyst is to facilitate only the desired reaction. How well a catalyst can accomplish this is its selectivity. Catalysts can be very specific, too, facilitating the reactions of certain chemicals to products and showing no reactions with other reactants. This specificity depends on the structural details of the catalyst's active sites, which occupy only a very small portion of the surface or volume of the catalyst.

Using Analogies

You might use an analogy to help students understand the concept of catalyst selectivity, i.e., the ability of a catalyst to direct a reaction so that there are fewer side reactions and unwanted by-products. On the chalkboard, draw a bucket of water with pipes leading from the bucket to a number of different containers. Tell students that the bucket of water represents a mixture of reactants, the pipes represent possible reactions, and the buckets represent possible products. Explain that the use of an appropriate catalyst is like widening only the pipe that leads to the desired container, such that as much water is collected there as possible.

Procedure, Data, and Observations

- Keywords that students might use include *catalyst, industrial catalyst, natural catalyst, enzymes, environmental catalyst, soil pollution, air pollution, water pollution, digestion, carbon monoxide, nitrogen dioxide, ozone, plastics, textiles, fuel, food, cells,* and *photosynthesis.*
- If students write chemical equations for the reactions, they should make sure that the equations are balanced.
- The search can be organized in a variety of ways. If students are working in groups of three, each member can be responsible for one of the three categories of catalysts. To ensure variety, assign each group a specific example of catalysis within each category. For instance, within the category of making commercial products, one group could search for catalysts used to make textiles; another, fuels or polymers, and so on. Alternatively, you might wish to challenge groups to find as many catalysts as possible, turning the activity into a competition. To make the activity less structured, you can make it open-ended, allowing groups to search for any materials or processes that are made possible by catalysis.

Interpretations of Data & Conclusions

- Students might say that without the catalysts, more reactants would be consumed, the processes would require more energy or wouldnot take place at all, less desired product would be produced, and/or more unwanted by-products would be produced.
- Different substances may catalyze the same process. Students might have found, for example, that various catalysts are used to refine crude oil. Rhodium or iridium is used to catalyze the production of acetic acid from methanol and carbon monoxide. Catalytic converters in cars use various catalysts, such as platinum, palladium, and rhodium, to catalyze the conversion of harmful exhaust gases to safer gases.
- Some substances can catalyze more than one kind of reaction. Zeolites, which are porous crystalline minerals, and metals, such as platinum, rhodium, and palladium, are examples of such substances. As noted above, rhodium is used to catalyze the production of acetic acid, as well as the conversion of harmful gases in car exhaust. Zeolites are also used as catalysts in the synthesis of various pharmaceuticals and cosmetics and in the refining of crude oil. Ziegler-Natta catalysts, which are complexes of metal halides with organometallic compounds (typically triethylaluminum-titanium trichloride), are used in the synthesis of various straight-chain polymers, including polyethylene, polypropylene, and polyisoprene (natural rubber).
- Most industrial catalysts are inorganic compounds, such as metals and inorganic acids and bases, and are used in reactions that occur at elevated temperatures and pressures and extreme pH.
- Catalysts used in natural processes usually are proteins, which are organic compounds. They usually catalyze reactions that occur at moderate temperatures, pressures, and pH.
- In addition to producing the greatest possible yield, a catalyst should also minimize the amount of energy required for the reaction to occur, reduce the amount of reactants needed, and reduce the amount of unwanted by-products (wastes) produced that are harmful to the environment.
- Catalysis does not always benefit the environment. For example, some catalysts, such as heavy metals and concentrated acids, are toxic and therefore are harmful when released or disposed of in the environment. Also, heavy-metal catalysts have to be mined, which may impact the environment. Another consideration is the environmental impact of the products of catalyzed reactions. For example, our use of petroleum and petroleum-based products, such as plastics, depends on catalysis. Unfortunately, the burning of oil releases pollutants into the air, as well as greenhouse gases that may lead to global warming. Plastics that are disposed of in landfills take an indefinite amount of time to degrade.

Portfolio Project

Have students place into their portfolios the printouts of the Internet articles they find during the activity. As they progress through the module, students may wish to continue searching the Internet for information that specifically relates to the topic of each activity and add this information to their portfolios.

Enriching Experience

Have students look up the number of Nobel prizes awarded to scientists for discoveries of new catalysts. Information can be found at http://www.nobel.se/. Discuss how these discoveries changed people's lives.

Synthetic Rubber

Isoprene ($CH_2=C(CH_3)CH=CH_2$) is one of nature's favorite building blocks. Natural rubber, for example, is *cis*-polyisoprene. When polyisoprene is made synthetically without using a catalyst, a mixture of *cis*- and *trans*-polyisoprene is produced, due to competing side reactions. As a result, the synthetic polymer lacks the elastic properties of natural rubber. In the 1950s, scientists developed a method of making synthetic rubber using a catalyst. The catalyst, which is a mixture of triethyl aluminum and titanium tetrachloride, is called a Ziegler-Natta catalyst, named for the scientists (Karl Ziegler and Guilio Natta) who developed it. The presence of the Ziegler-Natta catalyst during the polymerization reaction causes stereoselective polymerization so that about 98% of the molecules produced are cis-polyisoprene. Ziegler and Natta both received the Nobel Prize in 1963 for their accomplishments in catalyzed polymerization. You can learn more about their work at http://www.nobel.se/chemistry/laureates/1963/press.html.

Connection to Chemistry

Because it produces less waste than an uncatalyzed reaction, a catalyzed reaction shows higher product yield. Have students research the concept of product yield in chemistry. Ask them to define the terms *theoretical yield, actual yield,* and *percent yield* and to write a sample problem that requires the calculation of percent yield. Encourage students to exchange problems and solve them.

Connection to Biology

Biological molecules, which can be both broken down or built up by enzymes, perform a variety of functions in living cells. Have students find out the roles of starches, proteins, and fats in nutrition.

Connection to Chemistry

Review with students the building blocks of proteins (amino acids), starches (sugars), and fats (glycerol and fatty acids). Explain that different enzymes speed up the synthesis and breakdown of each of these nutrients, but that the nutrients are synthesized and broken down in basically the same way—by condensation and hydrolysis, respectively. On the chalkboard, show that condensation and hydrolysis are opposite reactions, both of which involve water. In condensation, water molecules are released as the small molecules are joined to form the large molecules. In hydrolysis, water molecules are added to the large molecules, breaking them down into the small molecules.

Catalyzing a Reaction Using a Heterogeneous Acid Catalyst

TEACHER NOTES

Materials and Setup

MATERIALS (per group)

The amounts of some of the following materials, especially the chemicals, will depend on you do the OPTIONAL reaction rate part of the activity (see page xx for more detail).

- *safety glasses*
- 3 100-mL beakers
- wax pencil
- scoopula
- weight boat
- balance
- 3 watch glasses
- 3 400-mL beakers
- 10-mL glass graduated cylinder
- 3 medicine droppers
- stopwatch, or watch with second-counting capability
- 3 stirring rods
- baking soda (sodium bicarbonate)
- Dowex M-31 acid catalyst resin
- 300 mL heated tap water on day 1 and on day 2
- 20 mL heated methyl acetate solution on day 1 and on day 2
- 10 mL heated distilled water on day 1 and on day 2
- distilled water for washing beads

ADVANCE PREPARATION

Dowex M-31 acid catalyst resin can be purchased from Sigma-Aldrich (1-800-325-3010). Each group will need 4 g of the resin.

Prepare hot (60°C) tap water for the class. Each group will need about 300 mL on day 1 and day 2 of the activity.

Prepare hot (60°C) distilled water for the class. Each group will need 10 mL on day 1 and day 2 of the activity.

In a fume hood, prepare a 10% methyl acetate solution for the class. ***Caution:*** *Pure methyl acetate is very flammable and is a skin, nose, and lung irritant. Keep it away from open flames, and wear safety glasses and gloves while preparing the solution. Use a glass pipette or graduated cylinder to transfer the methyl acetate, as it dissolves plastic.* Stir the dilute solution while heating it to 60°C. Continue to stir occasionally to keep the methyl acetate in solution. Each group will need 20 mL on day 1 and day 2 of the activity.

ESTIMATED TIME

- Day 1: 50 minutes (using the resin beads)
- Day 2: 40 minutes (using the resin beads)
- **Optional Day 3: 50 minutes (testing one variable)**

  To save time, pre-measure the catalyst and pre-label the beakers.

Caution and Safety

- Students should wear safety glasses while doing the activity.
- Students should handle the acid catalyst resin carefully to avoid spills.

Purpose

To have students use a heterogeneous acid catalyst to catalyze a hydrolysis reaction, to observe that the catalyst can be reused easily because it is a solid, and **(OPTIONAL)** to analyze the factors that influence the rate of the reaction.

Summary of the Activity

Students use acid catalyst resin beads to catalyze the hydrolysis of methyl acetate to acetic acid and methanol. In Part A, they determine whether the reaction occurred by using baking soda to test for the presence of acetic acid. After confirming that the acid catalyst is necessary for the hydrolysis reaction to occur, students clean and reuse the catalyst. **OPTIONAL.** In addition, students determine the effect that catalyst amount, solution temperature, and degree of solution mixing have on the rate of the hydrolysis reaction.

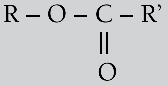
Activity Objectives

Students will:

- use a heterogeneous (solid) acid catalyst to hydrolyze methyl acetate into acetic acid and methanol
- determine whether the hydrolysis reaction occurred by testing for the presence of acetic acid
- observe that without the catalyst the reaction does not occur
- infer that the catalyzed reaction occurs at the surface of the solid acid catalyst
- observe that the solid acid catalyst can be reused easily
- analyze some factors that influence the rate of the reaction.

Background Information

Methyl acetate is an ester, which is an organic compound with the formula:



$$R-O-\underset{\displaystyle \overset{\|}{O}}{C}-R'$$

Esters are used for their odors to make perfumes, as flavor enhancers in processed foods, and as solvents in paints, lacquers, and varnishes. They are also used to make plastics and explosives. The hydrolysis of methyl acetate to acetic acid and methanol is a reversible reaction and is catalyzed in both directions by an acid. The reverse reaction, which produces the ester and water, is known as Fischer esterification, named for the German chemist Emil Hermann Fischer who discovered the reaction in 1895. Choosing which direction of the reversible reaction predominates is accomplished by adjusting the conditions of the reaction, especially the water content. To cleave an ester, a great excess of water is used. Conversely, to form an ester, dry conditions are used, e.g., a mixture of liquid methanol, acetic acid, and sulfuric acid (or acid resin beads) with no water. There are other ways to make esters, including alkylation of carboxylic acids (reactions with alkyl azides or alkyl halides).

$$\underset{\text{methyl acetate}}{CH_3COOCH_3} + \underset{\text{water}}{H_2O} \overset{H^+}{\rightleftharpoons} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{methanol}}{CH_3OH}$$

Specific vs. General Acid Catalysis

There are two types of acid catalysis, specific and general. In the case of specific acid catalysis, the reaction rate depends on the concentration of a specific acid species, the AH^+ species. Whereas in the case of general acid catalysis, the rate of reaction is increased by the total concentration of acid present in solution, not simply the AH^+ species. In general, the stronger the acid, the better the catalyst. The catalyst used in this activity belong to the specific type.

Note About Dowex Acid Resin Beads

The acid resin used in the activity is an organic solid acid catalyst. The beads are made of polymers containing styrene and divinylbenzene (DVB). Styrene molecules are joined in long chains, and the DVB molecules link the chains to each other, forming a cross-linked network.

The size of Dowex acid resin beads is controlled by the rate of mixing and the viscosity of the solvent used in the polymerization process. Because of the beads' porous structure, 99% of the reaction sites are on the walls of the pores, in the interior of the beads. The %DVB of the beads affects their mechanical hardness. More DVB leads to more cross-linking of the polymer, which leads to harder beads. However, more DVB also hinders the swelling of the beads in water. This, in turn, hinders the reactants' access to the pores inside the beads, thereby slowing the reaction kinetics. Eight percent DVB is widely used as a good balance, producing beads that are hard enough to survive normal use while having good kinetic characteristics.

Since the hydrogen ions in Dowex acid resin beads are essentially held in place by electrostatic attraction, they can be displaced by other cations, especially those that are polyvalent. Such beads, for example, are used for the separation of heavy metals from liquids. To restore their acid catalytic activity, the beads are regenerated with strong acid.

Acid Catalysis

Acid catalysis is used extensively throughout the petroleum refining and petrochemical industry. A common example is alkylation, which is the addition of an alkyl group to another hydrocarbon. Although there has been some research to replace homogeneous acid catalysts with heterogeneous acids catalysts, much of the industrial-scale alkylation is still conducted with concentrated sulfuric acid or liquid sulfuric and hydrofluoric acid mixtures.

Heterogeneous acid catalysts, such as zeolites and other silica-alumina materials, are the catalysts of choice in cracking (breaking down hydrocarbons), converting methanol to alkenes, and isomerizing hydrocarbons.

Sulfuric Acid Production

Sulfuric acid has been produced for at least 500 years. In the middle of the eighteenth century, sulfuric acid was made by the lead-chamber process. In this process, sulfur was burned to form sulfur dioxide, which was then reacted with nitric oxides in a lead-lined chamber, producing relatively weak aqueous sulfuric acid.

Today, *pure* sulfuric acid is usually made by the contact method, in which sulfur dioxide gas is passed over a heated tube that contains the catalyst platinum black or vanadium pentoxide mixed with alkali metal sulfates. This reaction produces sulfur trioxide, which is then dissolved in concentrated (98%) aqueous sulfuric acid. The sulfur trioxide reacts with the water, forming pure liquid sulfuric acid. The pure acid can be diluted with water to the desired concentration.

Organic Acid Resins

Unlike zeolites, which are inorganic, organic acid resins, such as the beads students worked with in the activity, cannot be used at elevated temperatures. This property limits these resins to reactions in liquid, which are typically used on a smaller scale to produce smaller volumes of products. Organic acid resins are used commercially in a variety of applications, such as the dehydration of alcohols to olefins and ethers, the alkylation of phenols to alkyl phenols, and ester hydrolysis.

Procedure, Data, and Observations

Catalyzing a Hydrolysis Reaction with a Solid Acid Catalyst

1. Be sure that students clearly label their beakers. Tell them that the methyl acetate solution consists of methyl acetate dissolved in water.

3. Have students spread out the mound of baking soda on each watch glass so that they can retest their liquid samples in different locations on it.

4. Place the hot tap water, hot distilled water, and hot methyl acetate solution in a central location, and have groups bring their small beakers to that location. Remind students to work quickly.

Students can use the calibration on the large beakers to pour about 100 mL of hot tap water into each beaker.

5. Students should use a *glass* graduated cylinder to measure the methyl acetate solution because methyl acetate may dissolve plastic.

7. To keep the procedure uniform, students should be consistent about the degree to which they stir the contents of all the small beakers to keep the methyl acetate dissolved in the water.

Make sure students transfer only liquid (no catalyst beads) to a small area of the baking soda.

8. Tell students to repeat the baking-soda test on different parts of the watch glass. Make sure they use the same dropper each time they transfer liquid from a particular beaker to avoid cross-contamination.

9. Students add baking soda to the beaker containing water and catalyst to observe that the surface of the beads is acidic.

10. Tell students to decant the liquid from the beakers carefully. To help ensure that students do not pour any of the beads down the sink drain, have them decant the liquid into a waste beaker and then pour the liquid down the drain.

Interpretations of Data & Conclusions

2. The liquid from the beaker containing water and catalyst did not react with the baking soda because no acetic acid was present. The hydrolysis reaction did not occur, due to the absence of methyl acetate. The liquid from the beaker containing methyl acetate solution only did not react with the baking soda because no acetic acid was present. The hydrolysis of methyl acetate did not occur, due to the absence of the solid acid catalyst. The liquid from the beaker containing methyl acetate solution and catalyst reacted with the baking soda because acetic acid was present, due to the catalyzed hydrolysis of the methyl acetate.

3. The solid acid catalyst did not make the liquid in the beaker acidic, since the liquid from the beaker containing water and catalyst did not form bubbles when transferred to the baking soda.

4. Increasing the time increased the extent of the reaction, as evidenced by increased bubbling.

5. Reusing the catalyst produced similar results.

6. The controls were the beaker containing only methyl acetate solution and the beaker containing water and catalyst. The beaker containing only methyl acetate solution was used to show whether only methyl acetate and water are necessary for hydrolysis to occur. The beaker containing water and catalyst was used to show whether the solid acid

Summary of Results

In Part A, acetic acid is produced in the beaker containing methyl acetate solution and catalyst, as evidenced by the bubbling that occurs when liquid from the beaker is added to baking soda. Bubbling begins about 9 minutes after the reaction mixture is prepared and increases after that.

Acetic acid is not produced in the beaker containing methyl acetate solution only nor in the beaker containing acid catalyst and water, as no bubbling occurs when liquid samples from the two beakers are added to baking soda.

Adding baking soda to the beaker containing water and catalyst causes bubbles to form in the water near the surface of the beads but not in the rest of the water.

Reusing the acid catalyst produces similar results if none of the beads are lost during the decanting process.

Troubleshooting

Students should decant the liquid from their beakers slowly to avoid losing beads. You may wish to have them decant over filter paper to capture any beads that flow out of the beaker with the liquid.

IMPORTANT NOTE on Comparing Results Among Groups

In order for groups to compare their results among each other, it may be helpful to create a common "degree of bubbling" scale. In the activity, students are asked to record the degree of bubbling that they observe as they add the supernatant dropwise to the baking soda. It may be helpful if the entire class had a common scale with which to judge the bubbling. For instance, you could create a 5-point scale, where 0 means "no bubbling" and 5 means "vigorous bubbling." This scale will be especially helpful in Part B of the activity where students are asked to test certain factors that can affect the rate of reaction.

catalyst itself causes the liquid in the beaker to become acidic or whether the acidity of the liquid is produced only by the hydrolysis of methyl acetate.

7. In determining where in the reaction mixture the hydrolysis took place, students should consider their observations when they transferred liquid from the beaker containing water and catalyst to the baking soda and when they added baking soda directly to the liquid in the same beaker. During the former, no bubbles formed, indicating that there was no acid in the liquid. During the latter, bubbles formed next to the surface of the catalyst beads, indicating that the surface was acidic. From these observations, students should conclude that, since the acidity of the catalyst speeds up the hydrolysis reaction, the reaction must occur at the surface of the beads.
8. Any liquid acid solution, such as aqueous hydrochloric, nitric, or sulfuric acids, might be used if the activity was repeated using a homogeneous acid catalyst. However, it would be impossible to remove the liquid acid catalyst from the rest of the liquid in the beaker.

Connection to Earth Science

Have interested students research the use of zeolites to improve the quality of soil for better plant growth. They might contact landscapers for this information and for samples of zeolites that landscapers use. Ask students to share their findings with the class.

Note About Zeolites

Natural zeolites were discovered in 1756 by the Swedish mineralogist Axel Fredrick Cronstedt while collecting crystals from a copper mine. He named his discovery *zeolite* from the Greek words *zein,* meaning to "boil," and *lithos,* meaning "rock," because he had observed that the zeolites released steam when heated. Today, natural zeolites are mined in many parts of the world. However, most zeolites that are used commercially are synthetic. The first synthetic zeolite was produced in 1948 by the New Zealand-born British chemist Richard Barrer.

Zeolites are inorganic solid acids with the chemical formula $(Al_xSi_{1-x}O_2)H_x$. The H in the formula exists as a hydrogen ion (H^+). According to the formula, the larger the value of x, the higher is the concentration of hydrogen ions in the solid. Some zeolites have an acid strength equivalent to 80% concentrated sulfuric acid. Hydrogen ions are inside a zeolite as well as on its surface. Thus, a zeolite provides a large number of sites where the catalyzed reaction can take place.

Zeolites' hydrogen ions can be replaced with other cations, such as sodium ions (Na^+). Such zeolites are used as water softening agents in detergents. They act as ion exchangers, exchanging their sodium ions for calcium (Ca^{+2}) and magnesium ions (Mg^{+2}) in water, which cause hardness. By removing the water-hardening cations, the cleaning ability of the detergent is improved.

Enriching Science Experience

Tell students that many catalytic reactions require high concentrations of the catalyst. Explain that since the reaction sites of solid catalysts are on the surface, the concentration of these catalysts is increased by increasing the amount of surface area per mass of catalyst. Next, give each student a ball of modeling clay. Challenge students to demonstrate how they can increase the surface area of their clay sample (they could divide it into smaller pieces, poke holes (pores) into it, or form spikes on the surface of it).

In this activity, students do not directly compare heterogeneous acid catalysis with homogeneous acid catalysis. If you would like them to do so, perform the Optional Demonstration on page 5. It uses a homogeneous acid catalyst (aqueous hydrochloric acid) to catalyze the hydrolysis of methyl acetate. After observing the demonstration, students should conclude that it is easier to reuse a heterogeneous acid catalyst than a homogeneous one.

Connection to Chemistry

Ask students to calculate the volume of concentrated hydrochloric acid (12*M* HCl) that contains the same number of moles of protons as 1 gram of the solid acid catalyst they used in the activity. The solid acid catalyst, Dowex M-31, releases 4.7 mmol H^+ per gram.

Answer: (1 g catalyst) × (4.7 mmol/g catalyst) × (1 mL HCl/12 mmol) = 0.39 mL HCl

Ask students to show that the equations in the student edition are balanced. Have them explain how the molecules of methyl acetate and water split and then combine with each other to form acetic acid and methanol. Similarly, have them balance and explain the equation of the reaction with sodium bicarbonate that shows the detectection of acetic acid.

OPTIONAL Activity: Determining the Effect of Different Factors on Reaction Rate

Student activity and logsheets are provided in the following pages (pp.6-8).

Procedure, Data, and Observations

- Be sure that a group varies only one factor at a time. For instance, if Group 1 is testing how the catalyst amount affects reaction rate, they might have three beakers: one with 1 g, another with 2 g, and a third with 4 g. Each reaction vessel, though, whould have the same degree of solution mixing and be at the same temperature.
- Here is one way to structure the activity. Assuming there is a Group 1 with the above set up, Group 2 could have the same set up as the first and have the same degree of mixing, but be at a different temperature . Thus, Group 1, independently, will be able to see the effect of catalyst amount on reaction rate at their temperature. Similarly, Group 2, independently, will be able to see the effect of catalyst amount on reaction rate at their temperature. Then Groups 1 and 2 could compare their results and draw conclusions on the effect of temperature on reaction rate. In the same vain, there could be a Group 3 who could test the three different catalyst masses and use the same temperature as Group 1, but have a different degree of mixing. Thus, Groups 1 and 3 could compare their results and draw conclusions about the effect of mixing on reaction rate. And so on.
- You may wish to have more than one group doing the exact set of variables in order to compare different procedures and the accuracy of their results and to ensure that there is good data for the class.
- To ensure consistent results, you may wish to use fresh resin beads for all groups.

Interpretations of Data & Conclusions

- Students may mention the following ways to improve their procedure in Part B: measuring chemicals or controlling temperature or stirring rate more carefully, running the experiment more than once to get more accurate data, and comingup with a better way to quantify the extent of hydrolysis reaction.
- When asked what they learned about heterogeneous catalysis from doing this activity, students might say they learned that heterogeneous acid catalysts are typically solids, they are easy to work with, and they can be recovered easily from a reaction mixture for reuse, making them safer for the environment.

Summary of Results

In this optional part of the activity to determine the effect of different factors on reaction rate, increasing the amount of catalyst, the solution temperature, and the degree of solution mixing all increase the rate of reaction.

Factors to Test

Below is a list of suggested factors to test and their possbile values. Be sure that students clearly note under which conditions they will we conducting Part B of their experiment.

Suggested variables to test:	**Possible values for that variable:**
Catalyst amount	1 g, 2 g, 4 g
Solution temperature	60°, 70°, 80°
Degree of solution mixing	no mixing, occasional mixing, constant mixing

Note that the class as a whole will need to define what is "occasional mixing" (i.e., how many turns of the stirring rod and how often) to ensure consistent data that can be compared from group to group.

Connection to Mathematics

Challenge students to compare the surface area-to-volume ratio of an object without internal pores to that of a similar object with internal pores. You might start with a solid cylinder and compare the surface area and volume calculations to that of a cylinder with a channel running lengthwise through it (like a donut).

OPTIONAL Demonstration

Demonstrate the use of a homogeneous acid catalyst [aqueous hydrochloric acid (HCl)] to catalyze the hydrolysis of methyl acetate, by following the procedure below. The aqueous solution of cerium ammonium nitrate solution (CAN) $[(NH_4)_2Ce(NO_3)_6]$ is used to detect methanol, which is one of the products of the reaction. CAN undergoes a color change in the presence of short-chain alcohols.

Synthesis of CAN:

Caution: *The acidified cerium ammonium nitrate solution is toxic and corrosive and must be handled with care. Prepare the solution in a fume hood.*

1. Add 0.65 mL of concentrated nitric acid to 20 mL of distilled water in a small beaker.
2. To a 25-mL volumetric flask, add the acidified water and 5.48 g of cerium ammonium nitrate.
3. Swirl until all of the solid is dissolved.
4. Top off the solution to 25 mL with distilled water
5. Stopper the flask, and invert several times to mix.

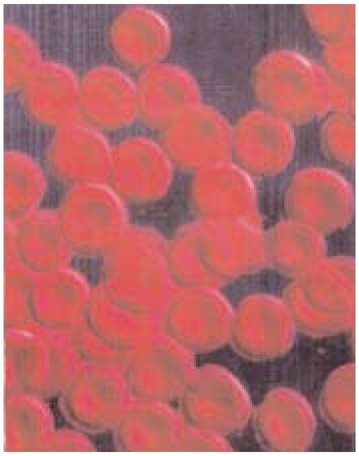
Catalytic hydrolysis of methyl acetate with aqueous HCl:

1. Heat about 20 mL of distilled water to 60°C. ***Caution:*** *Keep open flames away from the methyl acetate to be used in step 2, as it is very flammable.*
2. In a fume hood, add 8 mL of heated distilled water, 1 mL of methyl acetate, and 1 mL of concentrated HCl to a small beaker. ***Caution:*** *Wear safety glasses, gloves, and an apron while handling the methyl acetate and acid. Use a glass pipette or graduated cylinder to transfer the methyl acetate, as it dissolves plastic.*
3. Add 9 mL of heated distilled water and 1 mL of methyl acetate to a second small beaker.
4. Add 9 mL of heated distilled water and 1 mL of concentrated HCl to a third small beaker.
5. After 10 minutes, transfer 5 drops of solution from one of the beakers to 1 mL of CAN solution. Swirl to mix. If the color of the mixture changes from yellow to red, the hydrolysis reaction has occurred.
6. Repeat step 5, using the solutions in the other two beakers.

Students should observe that only the liquid in the beaker containing water, methyl acetate, and catalyst changed color. After students view the demonstration, ask them how they would go about removing the liquid acid catalyst from the reaction mixture so that the catalyst can be reused. Lead them to recognize that it is more difficult to reuse a homogeneous catalyst than a heterogeneous catalyst.

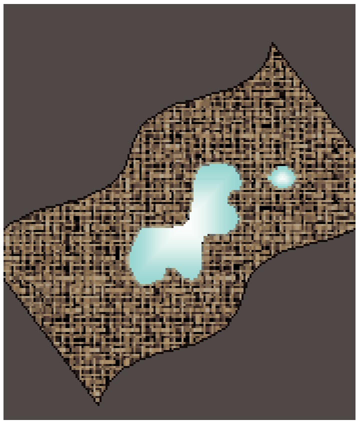
Luminol: What Makes Blood Glow

INTRODUCTION


A sample of red blood cells

How do investigators solve a mystery? How do they look for a crime scene when, for example, a person goes missing "without a trace"? What if the criminal has been careful to clean up all signs of the crime? Even if nothing appears suspicious to the human eye, often a criminal will leave behind invisible clues. Investigators have special tools for detecting this hidden evidence. They even have tools for finding invisible traces of blood. Forensic scientists (experts in reconstructing a crime from the remaining physical clues) have developed a way of making traces of blood glow in the dark—even blood that is years old! To detect the leftover blood in a crime scene, they use luminol, a chemical that emits a greenish-blue glow when it comes into contact with blood.

Forensic scientists mix luminol, a powdery substance that also goes by the name 3-aminophthalhydrazide, with a liquid containing hydrogen peroxide. They then spray this liquid over the crime scene. In the presence of hemoglobin, an iron-rich protein in the blood, the luminol and the hydrogen peroxide react with one another to produce a compound called 3-aminophthalate and little packets of visible energy called photons.


Blood stain with luminol

How does hemoglobin make luminol and hydrogen peroxide glow? The iron in the hemoglobin acts as a catalyst, a substance that brings about a chemical reaction by providing a new and faster pathway that the reactants take in their transformation to products. Notice that the luminol and hydrogen peroxide, mixed together in the liquid spray, do not react with each other. It is only when they came in contact with blood (i.e., iron from hemoglobin) that a reaction occurs. In the presence of iron, the luminol undergoes a chemical change, becoming 3-aminophthalate. After this reaction, the 3-aminophthalate is in an excited state, meaning that its electrons occupy a higher energy level than they normally would. But then the electrons naturally return to their original level, emitting the extra energy in the form of visible light (photons).

But luminol can react with other substances besides blood. Some metals besides iron, for instance, produce an immediate glow that quickly fades, while iron glows longer. A trained forensic investigator can perceive these differences and then perform more decisive tests to determine whether the blood is human. The only problem is that the reaction between the luminol and the blood can destroy other evidence in the crime scene. So the police don't rush into a crime scene and spray every surface with luminol.

CONCEPT behind the ACTIVITY

A catalyst is sometimes required to make a reaction proceed, and the results of the reaction can be dramatic, as well as useful.

Catalyzing with Platinum Black

Normally, if you wanted to burn a piece of paper, you would use a flame to ignite the paper, right? But have you ever tried to burn paper without using a flame? This is possible with a substance called a catalyst, as you will see in this activity. A catalyst is something that makes a chemical reaction go faster without being used up, or consumed, in the reaction. Thus, a catalyst can be used over and over again.

In this activity, you will test the effect of a catalyst to initiate buring of three types of paper, both treated and untreated with the catalyst platinum black, by holding them over a beaker of methanol.

Purpose

- To test the flamability of treated and untreated with the catalyst platinum black, over methanol.
- To make a connection between the catalyzed reaction with methanol and the burning of the papers.

▶ **Think about these questions as you do the activity:**

? How do the three types of paper differ?
? Why are the papers held over the methanol?
? What reaction or reactions are taking place?
? Why do the papers burn?
? What is the role of platinum black in the reaction(s)?

A smoldering sample

Hypothesis

Read through the procedure. What difference do you expect to observe as you test different types of paper? Come up with a hypothesis that predicts the outcome of the experiment for each type of paper.

▶ **Predicted Outcome**

Make predictions about how the different papers—both treated and untreated with platinum black—will react. State the reasoning behind your predictions. Do this on Data Table 1 provided.

Procedure, Data, and Observations

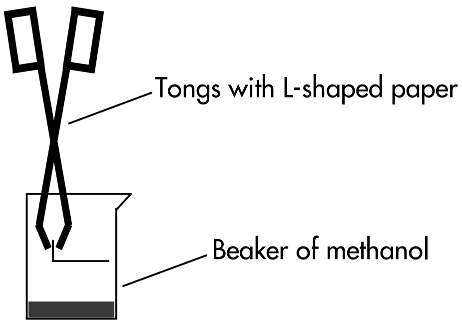
Safety Note: *Wear safety glasses.*

1. Your teacher will give you three types of paper, two pieces of each type. One of the two pieces will have platinum black on it; the other piece will not. Be careful not to rub off any of the platinum black from the treated pieces of paper. Use the untreated pieces of paper to compare the three types of paper, noting their appearance, thickness, and texture. Record your observations of how the papers differ.

Concept behind the Activity

A catalyst increases the rate of a chemical reaction without being consumed in the reaction. Catalyzed reactions are sometimes coupled.

2. Add 1 mL of methanol to the small beaker, and cover the beaker with the watch glass. The watch glass will allow methanol vapor to accumulate above the surface of the liquid methanol. ***Caution:*** *Methanol is a toxic, flammable liquid and can ignite quickly. Keep it away from open flames. If any methanol spills, wipe it up immediately with paper towels.*
3. Place the large beaker of water nearby for safety. Use it to extinguish any pieces of paper that burn.
4. Remove the watch glass from the small beaker. ***Caution:*** *Keep the watch glass nearby for safety. If the methanol catches fire at any point during the activity, cover the beaker with the watch glass to extinguish the fire.* Notice that the pieces of paper that your teacher gave you are folded into an L-shape, with one side longer than the other. As shown in the illustration, use the tongs to hold the corner of one of the pieces of paper not treated with platinum black such that its longer side is parallel to the surface of the methanol, about 2 cm above the methanol. Use a stopwatch to determine the amount of time it takes for a reaction to occur. Observe the paper for up to one minute. ***Caution:*** *If the paper starts to burn, immediately discard it by placing it into the beaker of water.* Record the amount of time and your observations of the paper in your data table. Re-cover the beaker with the watch glass.



5. Repeat step 4 using the same type of paper but treated with platinum black. As you hold the piece of paper over the methanol, the side with platinum black should face upward.
6. Repeat steps 4 and 5 with the other types of paper.
7. After testing all the paper pieces, dispose of them in the trash. Then discard the methanol and the water in the beakers down the drain. Flush the methanol with plenty of water.

Interpretations of Data & Conclusions—*Be thorough and use complete sentences.*

1. Compare your predictions with the results of this activity. Were you surprised by any of the results? Explain.

2. How did your observations of the papers not treated with platinum black differ from those of the papers treated with platinum black?

3. Why was it important to test papers that were both treated and not treated with platinum black?

4. In the activity, the platinum black catalyzed the reaction of methanol vapor and oxygen gas at room temperature, which generated heat. What evidence did you observe that heat was generated?

5. If you continued to observe the papers that were not treated with platinum black, do you think they would eventually burn? Explain.

6. Which of the papers you tested started to burn most quickly? Why did some types of paper start to burn faster than others? (Hint: Look back at your recorded observations of the different papers.)

7. A catalyst is a substance that speeds up a chemical reaction. How might platinum black have acted as a catalyst during the activity?

8. Come up with at least two questions for further research about platinum black and its uses.

Name____ **Date**__________________

Period_________________

Data Table 1. Predictions and Observations

Predictions about the different types of paper in the presence and absence of platinum black, and your reasons for the predictions

Types of Paper	Observations of Paper	Observations of Non-Treated Paper Held Over Methanol	Observations of Platinum-Treated Paper Held Over Methanol

EXPANDING on the CONCEPTS How did platinum black affect the reaction between methanol and oxygen in the activity? What were the products of the reaction between methanol and oxygen? Read the following article to find out.

Platinum black is a catalyst, which means it is a substance that makes a chemical reaction go faster without being consumed in the reaction. Many reactions proceed very slowly, or never start at all. However, with the help of catalysts, some reactions proceed a million times faster than they would without the catalysts! Pure platinum is a heavy, lustrous, silvery-white metal. It is soft and has a high melting point. The catalyst platinum black is pure metallic platinum that has been finely divided into a powder with a rough surface, which gives it its black color. Platinum black is used in the production of certain chemicals.

Catalysts speed up a chemical reaction by lowering the reaction's activation energy. The activation energy is an energy barrier that the reaction has to overcome in order for it to proceed to completion. A catalyst lowers the activation energy by providing an alternative pathway that is a shortcut to the same end point. Although the catalyst participates in the reaction, because it is not consumed, it can be used over and over again. However, all catalysts have a finite lifetime. Some catalysts last only a few days of use, while others last years.

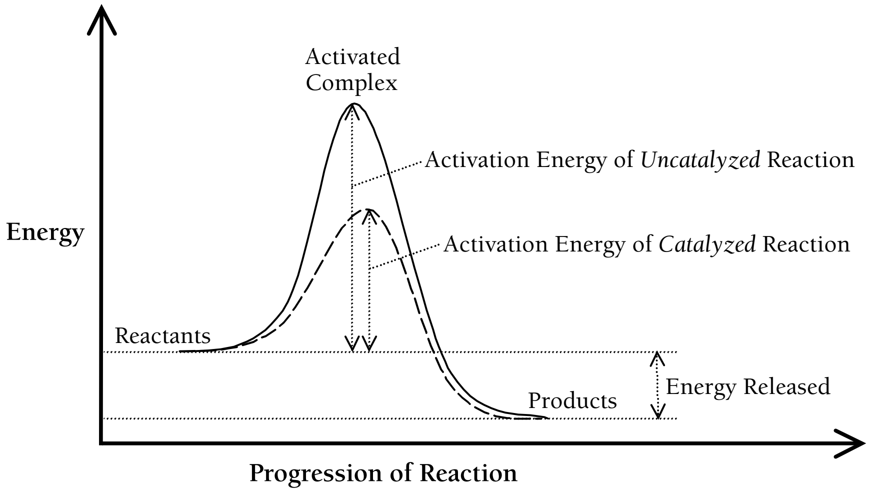
The graph on the right (solid line) shows the energy changes that occur during an exothermic reaction. Notice that the energy content of the reactants is higher than that of the products. As the reaction progresses, the reactants absorb energy from their surroundings, as shown by the uphill part of the curve. This increased energy makes the reactant molecules collide more frequently and with greater force. Eventually, the reactants form a transitional structure called an activated complex. The energy required for the activated complex to form is the activation energy. When the reactants are in this transitional state, they have enough energy for their bonds to break. As the bonds break, new bonds are formed, resulting in the formation of the products of the reaction. The latter releases energy to the surroundings, as shown by the downhill part of the curve.

The dashed line shows the energy effects of a catalyst on the same reaction. Notice that the energy contents of the reactants and products and the amount of energy released are the same in the catalyzed reaction as in the uncatalyzed reaction. However, the activation energy, and thus the energy content of the activated complex, is much lower in the catalyzed reaction. This decrease allows the products to form faster.

In the activity, platinum black catalyzed the reaction of methanol vapor with oxygen gas in the air. The methanol was oxidized, which means new carbon-oxygen and hydrogen-oxygen bonds are formed. Methanol oxidation occurred at the surface of the platinum particles via a shortcut pathway that has a much lower activation energy than the reaction between methanol and oxygen in the absence of platinum black. During the catalyzed reaction, both methanol and oxygen reacted with platinum first, which then made it easier for them to react with each other, in terms of the amount of energy required. As the oxidation of methanol is completed, the platinum returned to its original form. The equation below show the overall catalyzed reaction between methanol vapor and oxygen gas.

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O + \text{heat}$$

Although platinum (Pt) is involved in the reaction, it is not consumed,



and consequently, it does not appear as a reactant or product in the equation. Note that it is the same as a noncatalyzed reaction.

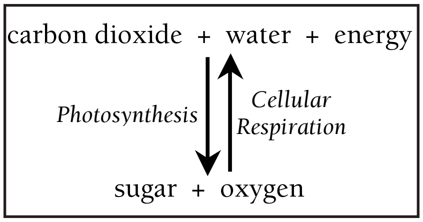
As you can see, the oxidation of methanol generates heat. It is this heat that started the combustion of the paper in the activity. The steps involved in the combustion of paper, which is typically comprised of plant fiber called cellulose, a type of long-chain (polymer) carbohydrate, are very complex. However, combustion requires oxygen and eventually produces carbon dioxide, water, and heat, just like the oxidation of methanol.

Why was heat needed to start the combustion of the paper in the activity? Typically, combustion, once started, is a highly favorable reaction and rapidly goes to completion as long as there is enough oxygen present. However, combustion isn't always easy to get started. That is because there is a large initial energy barrier, or activation energy, that must be overcome. Even though a combustion reaction releases energy and is thus thermodynamically favorable, some energy must be input to get over the barrier. During the activity, the heat generated from the methanol-oxidation reaction raised the temperature of the paper above its auto-ignition point, thereby overcoming the energy barrier.

Auto-ignition point is the temperature at which a material ignites when exposed to heat. The temperature depends on the molecular structure of the material. The auto-ignition point of pure paper is about 230 °C. In the activity, you probably noticed that some types of paper started to burn faster than others. One possible reason was that they were treated with different chemical additives, thereby varying their auto-ignition points. Another possible reason was that some papers were more porous than others. The larger spaces between the fibers of the more porous papers allowed oxygen to reach the platinum black within the fibers more quickly, thereby causing those papers to start burning more quickly.

In the activity, there were two strategies in overcoming the energy barrier to a reaction. In the first reaction, between methanol and oxygen, the activation energy was lowered with a catalyst; thus, the reaction was able to proceed faster compared to the reaction without the catalyst. In the second reaction, between paper and oxygen, the activation energy was overcome by the heat generated in the first reaction. Thus, the two reactions were *coupled* through heat energy. In some other reactions, the products of one reaction is a reactant for the next reaction. In that case, the reaction is coupled through molecules.

Nature, which is highly efficient, couples reactions all the time, never letting the product of a reaction go to waste. For example, the processes of photosynthesis and cellular respiration are coupled reactions. As you can see in the chemical equation below, the products of photosynthesis—sugar and oxygen—are the reactants of cellular respiration. Likewise, the products of cellular respiration—carbon dioxide, water, and energy—are the reactants of photosynthesis.



Photosynthesis and cellular respiration are not simple reactions. In fact, they are complex processes consisting of series of reactions, many of which are catalyzed.

Conceptual Design for Environmental Catalysis

Innovation, Inc., is a fledgling company comprised of retired researchers and developers of a variety of products. Their collective experience covers many different areas of science and technology, including chemistry, medicine, engineering, physics, among others. They wish to expand their business into environmental protection. However, because of their diverse backgrounds, they cannot seem to decide on what environmental problem to tackle first. Thus, they have devised an open competition where teams present their ideas and try to persuade them to accept their project.

Because of your knowledge about catalysis and its potential to help the environment, they would like you and your team to enter the competition. You must come up with a catalytic solution to an environmental problem and explain how you would go about designing it. Innovation, Inc., values creativity, so you'll have to present your design in an interesting way if you hope to win.

the Design CHALLENGE Your goal is to come up with an original solution to an environmental problem you've researched and to outline conceptually how you would design, construct, test, evaluate and redesign your prototype. The following steps will guide you through the design process.

Think about these questions as you work on your prototype:

- ? What are some features of an environmentally-friendly catalytic system?
- ? Which techniques and materials will be useful to you in creating it?
- ? How can you test the effectiveness of your design?
- ? How could you convince someone else of the benefits of your design over another team's design?

Keeping a Design Log

Your group should keep a design log as you participate in the design challenge. Your teacher may give you a set of worksheets to use as a log. These worksheets follow the process described below. You can also keep your own design log. Be sure to document all of the steps you follow as you conceptually design, construct, test, evaluate, and redesign your prototype. Record all of your ideas, even the ones that you don't use. They may prove helpful when you redesign your prototype. You will also use your design log to help you write a final report.

Brainstorm Designs

Think about some of the environmental issues you've learned about from this module or elsewhere. Can some of them be helped by use of a catalyst? How? Brainstorm some possible designs that could be benefitial to the environment. Refer back to your results from the activities for ideas about which materials and techniques to use and how to construct your prototype.

Propose Prototypes

Propose designs for a set of three prototypes in which a single element is varied. By testing a set of prototypes that differ in a single variable, your group will be better able to understand why one prototype would perform better than another. Include a labeled diagram of each prototype.

> **It's what you learn after you know it all that counts.**
>
> John Wooden,
> American basketball coach

Decide on Criteria for Evaluating Your Prototypes

Think about the purpose or function or your proposed catalytic system. What qualities or characteristics must the prototype have in order to be effective? Make a list of criteria that you can use to evaluate your prototypes and decide how you would test your prototypes to determine which prototype best meets the criteria. Consider how many tests you would need to perform and in what order. You will also need to decide how to combine your assessments of each criterion into an overall evaluation of a prototype's performance. For example, you might want to give a certain number of points for each criterion a prototype meets.

Predict How Your Prototypes will Perform

Once you determine how to evaluate your prototype, make a prediction about how each prototype would perform in your tests. Rank the prototypes in order from the one you think would perform the best to the one you think would perform the worst. Give reasons for your predictions.

Use a Repeatable Procedure to Construct Your Prototypes

Write down the materials you would need and the steps you would follow to construct your prototypes. Your construction procedure should be repeatable—that is, another team should be able to read your design log and follow your procedure to construct the same set of prototypes. Make detailed drawings of how you would construct your prototypes.

Use a Repeatable Procedure to Test Your Prototypes and Record Your Data

Write down the tests you would perform on the prototypes. List the materials you would use and the steps you would follow for each test. Make one or more data tables in which you would record the results of your tests.

Interpret the Results

Draw conclusions about the overall performance of your three prototypes. Which prototype performed the best? The worst? Give reasons for your evaluations.

Reflect on Your Results and Predictions

Compare your expected results with your predictions. Offer explanations for your results. Analyze possible sources of experimental error in your construction and testing procedures.

Present Your Prototypes

Show the drawings of your prototypes to your classmates and describe how you proposed to make them. Present your procedures and expected test results and explain how you would interpret them. Discuss whether any of the prototypes met the criteria set forth. Explain why you think each prototype would perform as you expect it would. Ask your classmates to evaluate your designs, your construction and testing procedures, and your interpretation of the results. Write down their comments and suggestions. Then evaluate other groups' presentations.

Redesign Your Prototype

Propose an improved design for your catalytic system based on what you learned from the presentations and any additional research you do. Explain the reasons for the changes you make. Repeat the cycle of conceptual design, construction, testing, and evaluation for another set of prototypes.

Prepare a Final Report

Write a report for Innovation, Inc., that describes your proposed design, construction, and testing procedures, as well as your redesigned prototypes. Include background research that shows the importance of your prototype. Present the best prototype option you came up with. Convince Innovation, Inc., that they should address your environmental issue with your catalytic solution.

Draw Conclusions About the Design Process

Explain what you learned about materials and techniques used in environmental catalysis and about the design process from this project. Evaluate how well your group met the design challenge. If you enjoyed this project, you might consider pursuing a career in materials science or engineering.

> **Why is it we never have time to optimize the design the first time, but always have time to revise the design when something fails?**
>
> Anonymous engineer

Conceptual Design for Environmental Catalysis

TEACHER NOTES

Materials and Setup

MATERIALS (per group)

Internet access to research background information on their environmental issue and solution.

ESTIMATED TIME

- Three or four class periods
- During the first class period, students meet, research an environmental problem of their choosing, develop solutions, and design their prototypes. They must consider not only what they would build to solve the problem, but also the natural environment of the location they plan to use it in. This work may carry over into homework.
- During the second period, students can decide on criteria for evaluating their prototypes and how to conceptually construct and test them. They also predict how their prototypes would perform. They prepare their creative presentation, either a skit, poster, paper, or PowerPoint presentation.
- During the third period, students present their project to the class and evaluate their classmates' presentations.
- During the fourth (optional) period, students redesign their conceptual prototypes. Taking into consideration the feedback they received from you and the class during the third period, they can do additional research and hand in a final report that includes a redesigned version of their prototype.

SUGGESTED GROUPING

Groups of three or four

Leading In to the Project

Use the introductory scenario to start a discussion about the properties of catalysts and their potential to protect the environment. Encourage students to suggest which properties in particular would be important to consider when designing a catalytic system that is meant to protect the environment. Ask them how their design considerations might differ if they were using a catalyst in a controlled setting, such as in a lab.

Ask students to keep the "Think About" questions in the gray box in mind as they do the Design Project.

Researching Examples of Catalysis

Students have done a search on catalysis in Activity 2. Have them refer back to their notes to help them focus their Design Project.

Another approach would be to have students think about some of the problems they encounter in their everyday lives and speculate how a catalyst may be able to solve the problem. For example, noxious odors can be eliminated with the use of a catalyst.

Purpose

To have students utilize knowledge gained in previous activities in designing a conceptual prototype.

Summary of the Activity

Students conceptually design a set of prototype environmentally-friendly catalytic systems. In order to meet specific design and performance criteria, they thoroughly think through the criteria for success and the construction and experimentation of the different prototypes. Students use what they've learned to improve their prototypes by redesigning them.

Activity Objectives

Students will:

- apply concepts they learned about environmental catalysis from doing the previous activities in the module
- work with a team to set and meet goals
- conceptually design, construct, test, evaluate, and redesign prototypes
- record their conceptual design, construction, testing, and evaluation processes
- summarize their procedures and results in a final report

Alternative Design Project

Another way of structuring the Design Project is to give students a known and tested environmentally-friendly catalyst, such as one that was found during the search in Activity 2, and have each group come up with a unique and creative application for it.

The Design Challenge

Explain to students that the goal of the Design Project is to conceptually design a solution to a real environmental problem utilizing at least one catalyst. The properties of this catalytic system should meet the specific criteria the class decides on. Discuss the importance of establishing design and performance criteria before beginning the Design Project. Ask students why they think the criteria are important.

Keeping a Design Log

Design-Log Sheets are designed to guide students through the design process and provide space for students to record designs, procedures, and other information. Photocopy the Design-Log Sheets and hand them out at the beginning of the project or make them available as students do each step. If students need more room to record information, you could have them write on notebook paper and attach those sheets to the appropriate Design-Log Sheets.

If you wish, instead of using the Design-Log Sheets, students can keep their design log in a notebook. Stress that it is important for students to keep running notes as they perform each step of the design process.

Students can keep their design log individually or have a common log for the group. If a group log is used, make sure that each student in the group has the responsibility for keeping the log during some part of the project. You might suggest that individual members of each group keep a separate log throughout the project. Then they can work together to compile a group log to hand in at the end of the project. This log should reflect the ideas and participation of all group members.

Brainstorm Designs

Students can fill out Design-Log Sheet 1 as they discuss possible designs. Point out that focusing on the product's goals as well as its constraints will help them weigh the pros and cons of each design. Encourage them to think beyond the product, specifically about the environment in which the product will reside. Weather conditions, movement of people or animals, or traffic conditions may turn out to be important influences.

You might wish to give students a time frame in which to complete the Design Project. Tell them that researchers often have to meet development schedules. Challenge students to complete their work within the designated time.

Propose Prototypes

You may need to give additional examples of how a single element might be varied in a set of prototypes. For example, students might vary the amount of catalyst, the pH of the solution, or the temperature of the system. Also the location of the prototype needs to be considered. Students should carefully think about the environmental conditions already present at the location. Encourage students to evaluate their set of three prototypes to make sure they differ in only one way.

Design-Log Sheet 2 outlines the elements students should include in the prototype proposals. You may wish to evaluate each group's proposal before they proceed with their conceptual construction and testing.

What's Hard for Students

Design projects may be good contexts for student inquiry, but they aren't perfect. One important difference between design and inquiry is that the goals of each are different. Design goals are usually centered on performance, while inquiry is about understanding.

While these goals can coexist, it's very easy for students to get wrapped up in making their design as good as it can be. One result is that students will try several different design changes at once. While these changes may improve the performance of the design, students can't tell which of these changes were really responsible fore the improvement. Helping students to create good experiments to test their design decisions is an important part of supporting student inquiry.

Engaging students in inquiry through the design process itself requires focused support within the design project. This support includes an explicit explanatory goal, where it is made clear to students that developing an explanation for design performance is part of the project.

Teachers can create opportunities for students to engage in inquiry by structuring the design project to support student inquiry. By making the explanatory goals of inquiry an explicit part of the task, students are prompted to explore and document their explanations and evidence as well as the basic performance of their design.

Criteria for Evaluation

Discuss with students the types of testing and observations that may be necessary to evaluate a prototype's performance. For example, can the catalyst be easily separated from the reactants and products? How? Can the catalyst be easily replaced if spent or poisoned? Design-Log Sheet 3 guides students through this step. Students may want to assign one point for each criterion a prototype meets or they may want to assign more points for criteria they think are most important.

Predictions

Ask students to predict how well each of their prototypes will perform. Have them relate their predictions to the types and quantities of materials used. For help in making their predictions, students should think about their results from previous activities.

Have students rank their prototypes, from the one they expect will perform the best to the one they expect will perform the worst. Advise them that the success of one prototype over another should depend on a combination of many factors. Students can record their predictions on Design-Log Sheet 4.

Construct Prototypes

You may wish to approve students' proposed designs before they continue on to the next part of the design process. Each set of prototypes should focus on a single variable.

Design-Log Sheet 5 is available for students to record the step-by-step procedure they would follow in making the prototypes, the materials they would need, and any potential problems they may encounter during the construction of the prototypes.

Discuss why it is important for researchers to keep detailed records. Point out that other researchers may wish to duplicate the prototypes to run different tests, or a manufacturer may wish to produce the catalytic system. Tell students that their records will be particularly useful later in the project when they redesign their prototypes.

Test Prototypes

Direct students' attention to the prototype design and performance criteria you listed on the board. Explain that their proposed testing strategy must address each of the criteria. Emphasize that they must choose with care the order in which they do the tests because some of the tests they may come up with may involve damaging the prototypes. Also, they must consider what, if any, environmental precautions must be taken when testing their prototypes. Ask students to identify what specific information they hope to gain from these tests and why it is important.

Discuss with students why it is important to record the procedure for testing their prototypes and why, in science, it is important that tests be repeatable and the results reliable. Ask them to consider what might happen if others duplicated the tests and got different results. Students can record their testing procedure and expected results on Design-Log Sheet 6.

Cooperative Roles

To help students focus their energy, you might suggest that each group assign cooperative roles to the different members over the course of the project. For example, one student might be the record-keeper; another student might be the facilitator (keeping the discussion moving, getting supplies, and doing quality control during construction and testing); and two students might be the implementers (making drawings, constructing the prototypes, and doing the tests), working together or independently at their tasks.

Students can switch roles at various points in the project; for example, after the first round of prototyping. Encourage all members to take a turn at each role.

Assessment Tip

When grading students' Design Projects, focus on the design process as well as the products. Consider factoring in items such as students' ability to explain why their designs performed as they did or how their redesigned products showed improvement.

Interpret Results

Students can record their interpretations of the data on Design-Log Sheet 7. Go over the criteria students should use to evaluate their prototypes. Point out that they must evaluate each prototype on the basis of each of these criteria. They might devise a rating system to help them decide which prototype is the best overall. For example, students might give one point to a prototype for each of the criteria that it has met. Alternatively, they might decide to give more than one point for certain criteria they think are more important than the others. To evaluate the overall performance of the prototypes, students could compare each prototype's number of points.

Reflect on Results and Predictions

Students should revisit the predictions they recorded on Design-Log Sheet 4. How close were their predictions to their expected results? If their results did not match their predictions, they should offer possible explanations for the difference.

Point out to students that it is important to analyze the testing process as well as the results of the test. Prompt a discussion about testing methods, in which students can discuss problems they encountered or make suggestions on how to reduce experimental error. Students can record their ideas on Design-Log Sheet 7.

Present Prototypes

Students can use Design-Log Sheet 8 to help them prepare their class presentation. Allow students to make and present visual displays, such as diagrams, pictures, and graphs.

Each group member should be involved in the presentation. One group member could describe the group's design process, another could discuss prototype construction, and so on. Ask students to keep their presentation concise, about three to five minutes. Remind them to speak slowly and clearly and to look at their audience.

Redesign Prototypes

As students approach the task of redesigning their prototypes, they should draw on what they've learned through their own experimentation as well as what they've learned from their classmates. For example, students might examine the best prototype of each group to see whether they had anything in common. Alternatively, they might eliminate materials that caused some of their classmates' prototypes to fail. Ask students to consider any further or on-going testing that would need to be conducted in order to ensure that their prototype is functioning properly over time. What kind of maintanance is involved in using their prototype?

Design-Log Sheet 9 is available for students to use during their redesign. Pass out another set of Design-Log Sheets for students to use as they repeat the cycle of conceptual designing, constructing, testing, and evaluating.

Critique Prototypes

After each presentation, allow time for the class to ask questions and offer suggestions. Foster a spirit of respect among students by discussing how to give and receive constructive criticism. On Design-Log Sheet 8, students can find questions to help them critique the work of other groups. Presenting groups can also use the sheet to record the comments of other students regarding their presentation. Alternatively, students can write a critique of each group's presentation on a separate sheet of paper and give it to the group.

Besides having students critique the content of the presentations, you might have them also critique the presentations' style and format. Students could note whether the presentations were well-organized, whether the presenters spoke clearly and looked at the audience, and whether the visuals were effective.

Lead students to recognize that both giving and receiving constructive criticism are valuable learning tools. Underscore that comments and suggestions are to be given helpfully and respectfully. Stress that classmates' observations may prove quite useful when students tackle the redesign of their roofing tiles.

Prepare Final Report

Guide students to understand that communication is an important part of scientific training and training for the workplace. Students' reports should include the following sections: an introduction, which states the reason for doing the project and the design goals and constraints; a section detailing the materials used and the construction and testing procedures; a section explaining the expected initial test results, and the rationale for a redesign; a conclusion offering an overall evaluation of the prototype's performance and suggesting any improvements the team would still like to make.

Suggest that students refer to their completed Design-Log Sheets as they prepare their final report. If you assign the report as homework, allow groups some class time to discuss a strategy and to assign tasks. Each group member should have a role in writing the report. Students could divide up tasks by topic, with one member discussing design, another construction, and so on. Encourage students to include visual aids, such as tables, diagrams, and graphs.

You might also allow some class time for group members to edit the report together. As part of the writing process, have students edit and proofread their report; they should check for content, clarity, grammar, and spelling.

Remind students that this report should be persuasive, but that any claims they make must be backed up with evidence.

At this time you may wish to have a panel of students from a different class or you yourself assume the role of the people at Innovation, Inc. You might present a plaque or some other award to the winning group.

Draw Conclusions

Ask students to consider what they learned by doing this Design Project. As they respond, you might want to make two lists on the board: Learned About Environmental Catalysis and Learned About the Design Process.

Discuss how the activities in this module related to and led up to the design challenge. Encourage students to describe what they liked best and least about the project.

4
Planning Guide
Using a Metal Catalyst to Degrade an Air Pollutant

Links

TO THE PREVIOUS ACTIVITY In the previous activity, students learned that heterogeneous acid catalysts are safer and easier to reuse than homogeneous acid catalysts. Thus, the use of heterogeneous acid catalysts is less detrimental to the environment. In this activity, students work with another kind of heterogeneous catalyst — a metal catalyst. Using ammonia gas as a model of an air pollutant, they learn that metals can be used to catalyze the degradation of air pollutants and that these catalysts become inactivated, or poisoned, with continued use.

TO THE NEXT ACTIVITY In this activity, students use heat in addition to a catalyst to speed up the degradation of a pollutant by oxidation. In Activity 5, students will learn about the process of photocatalysis, in which light is used in conjunction with a catalyst to increase the rate of a chemical reaction. They will use UV light and titanium dioxide to catalyze the degradation of an organic dye, methylene blue. They will also test the effect of three variables — catalyst concentration, light intensity, and pH — on the photocatalytic degradation rate of methylene blue.

TO THE DESIGN PROJECTS [To come]

Purpose

To compare the performance and rate of inactivation of two different metals — copper and iron — as catalysts in the degradation of ammonia by oxidation

Summary of the Activity

Students use an apparatus in which an air stream containing ammonia gas is passed through a heated glass tube containing a metal catalyst, either copper or iron (as a component of steel wool). The metal's performance in catalyzing the degradation of the ammonia by oxidation is assessed by testing the air leaving the tube for the presence of ammonia, using phenolphthalein as an indicator. By sharing their data, students compare how long it takes each metal to begin catalyzing the oxidation reaction and how long it takes each metal catalyst to become inactivated, or poisoned. Based on their findings, students conclude which of the two metals is the better catalyst for the oxidation of ammonia under the conditions of the activity.

Safety

Discuss safety issues students should be aware of, including:

- wearing proper safety equipment
- avoiding contact with ammonia, as it is a skin, eye, and respiratory irritant
- keeping the phenolphthalein solution away from open flames, as it is flammable
- not eating or tasting any materials
- washing their hands after completing the activity

- handling glassware carefully
- disposing of broken glassware properly
- wiping up spills with paper towels or a mop as soon as possible
- safety issues of particular concern in your classroom

Advance Preparation

1% phenolphthalein solution can be purchased from science-supply stores. It is preferable to dispense the solution in dropper bottles.

Making the ammonia solution

To make 1.5 L of the ammonia solution, mix (preferably in a fume hood) 150 mL of clear ammonia, which can be purchased from a grocery store, with 1350 mL of tap water. Add enough phenolphthalein solution to the prepared ammonia solution to obtain the desired pink color. (One medicine-dropper full should be sufficient.) ***Caution:*** *Ammonia is a skin, eye, and respiratory irritant. Do not breathe in the ammonia vapors. The phenolphthalein solution is flammable. Keep it away from open flames.*

Making the catalyst tubes

For each catalyst tube, you will need 3/8-inch OD Pyrex tubing with 2-mm wall thickness, about 30 cm in length.

To make a copper-catalyst tube, follow the diagram below. Use a long, narrow rod to push the glass wool into the Pyrex tubing. Pour the copper filings, which can be purchased from science-supply stores, into the tubing.

[Insert diagram of copper-catalyst tube]

To make a steel-wool catalyst tube, you do not have to plug the Pyrex tubing with glass wool. Simply push enough steel wool into the tubing to form an 8-cm length. **[ED. NOTE: The following note about heating the steel wool may be deleted. Alex said it isn't necessary.]** The steel wool purchased at hardware stores has oil on it from the manufacturing process. When heated, the oil produces smoke and a strong odor. It is best to preheat the steel wool in a Bunsen burner in a fume hood before assembling the catalyst tubes.

Assembling the apparatus

See the labeled illustration of the apparatus and the materials list on page XX.

Curriculum Connections

Relating Activity 4 to Different Subjects

Connecting to Your Curriculum on page TXX suggests ways in which you can fit the Environmental Catalysis module into your general curriculum. The chart below provides areas for connecting the concepts introduced in this activity with different disciplines. The page numbers in the chart refer to teaching tips in the margins that you can use to make connections to the listed subjects.

Biology
Health effects of pollutants
Nitrogen cycle p. X

Earth Science
Air pollution

Chemistry
Acid-base indicators p. XX
Oxidation-reduction reactions

Physics
Nanotechnology

Mathematics
Surface area-to-volume ratios p. XX

Technical Education
Automotive catalytic converters

[MORE TO COME]

Background Information

Heterogeneous catalysts are solid materials over which a liquid or gas reaction mixture flows. The first stage in the catalytic cycle of reaction is the adsorption of the reactants from the fluid stream passing over the catalyst surface. *Adsorption* is the accumulation of a substance on a surface, as opposed to *absorption,* which is the penetration of a substance into a surface, such as water soaking into a sponge. Adsorption can entail either chemisorption or physisorption. In chemisorption, the reactants form chemical bonds with the catalyst surface. For example, in this activity, oxygen bonds with the copper and iron catalysts. Physisorption is produced by a physical attraction, such as electrostatic attraction, between the reactants and the catalyst surface. In Activity 3, the slightly positively charge reactants are attracted to the negatively charged catalyst surface. **[Ed. Note: Is the previous statement correct?]** Adsorption increases the proximity, and thus the concentration, of the reactants. Usually, the higher the concentration, the higher is the rate of reaction. The second stage of the catalytic cycle is the set of steps in which reactants are transformed into products. The final stage is the desorption, or release, of the products from the catalyst surface.

There may be numerous steps involved in each of these reaction stages, and any one of the stages — adsorption, reaction, desorption — may be rate determining or rate limiting. Usually, particular sites, called active sites, exist on the catalyst where adsorption and reaction take place. In this activity, the active sites are where the metal oxides form. The number of active sites on a catalyst is determined by their surface site density and the catalyst's surface area.

If the reaction products do not rapidly desorb from an active site, the site is not available to interact once again with reactants in the next catalytic cycle. If a substance becomes irreversibly adsorbed to an active site, the catalyst becomes inactivated, or poisoned. Sometimes catalyst activity can be recovered by cleaning the surface using highly acidic or basic conditions, passing a pure fluid (e.g., water, oxygen, solvent) over the surface, or exposing the surface to high temperature.

Using the Internet

Students can find out about catalyst poisoning by choosing a search engine and inputting the key terms ***catalyst poisoning*** and ***catalyst inactivation.***

Cross-Curricular Teaching

This activity can be assigned to coincide with an ecology unit in biology class. Work with the biology teacher to increase students' awareness of environmental problems facing us today, including air pollution.

4
Introduction

To Inspire Questioning and Learning

Before students read the Introduction, ask them if they know what a catalytic converter is and what it does. If students are unfamiliar with the device, have them speculate about its function from the meanings of the words *catalytic* (having to do with catalysts) and *converter* (having to do with change). Record on the chalkboard any questions students might have about catalytic converters. After they read the Introduction, have students answer the questions, based on what they read.

Focusing on Study Skills

Discuss with students the use of illustrations as a study aid. Tell them that illustrations are often used to clarify or expand on information discussed in the text. Encourage students to use the illustrations in the Introduction to help them understand how a catalytic converter helps to reduce air pollution.

Incomplete Combustion

The incomplete combustion of fossil fuels produces carbon monoxide (CO) and volatile organic compounds (VOCs). Incomplete combustion occurs when not enough oxygen is available or the temperature is too low, among other reasons. These conditions are more likely to occur in motor vehicles than in power plants, where it is much easier to maintain optimized combustion efficiency. For example, motor vehicles account for 60% of total CO emissions nationwide. In cities, that amount increases to as much as 95%. However, between 1993 and 2002, total CO emissions decreased by 21 percent, despite a 23 percent increase in vehicle miles traveled, due to more stringent vehicle emission controls.

Note About Carbon Monoxide

Carbon monoxide is an indoor pollutant, as well as an outdoor pollutant. For example, gas appliances produce carbon monoxide, and high levels of carbon monoxide are found in cigarette smoke. Carbon monoxide is an asphyxiant; it interferes with the blood's ability to carry oxygen to cells. That is because hemoglobin in red blood cells, which binds with carbon monoxide to form carboxyhemoglobin, has a higher affinity for carbon monoxide than for oxygen.

Note About Volatile Organic Compounds

While there are some natural sources of VOCs (certain conifers and deciduous trees), most VOC emissions are related to the incomplete burning of fossil fuels. Another source of VOCs is the evaporation of solvents, fuels, and other chemicals used in industry and in products found in homes, such as paints, adhesives, cleaning products, carpets, and pressed-wood furniture. Examples of VOCs include benzene, toluene, formaldehyde, and ethylene glycol.

Studies by the U.S. Environmental Protection Agency (EPA) found indoor levels of about a dozen different VOCs that were two to five times higher than outdoor levels. Health effects of VOC exposure include eye, nose, and throat irritation; headaches; nausea; dizziness; damage to the liver, kidney, and central nervous system; and cancer. Steps that can be taken to reduce indoor exposure to VOCs include using VOC-emitting products in well-ventilated areas, buying small quantities of chemicals to minimize gases leaking from stored containers, disposing of unused chemicals, and purchasing products that contain low levels of VOCs or no VOCs.

Note About Nitrogen Oxides

There are seven known oxides of nitrogen (NO_x): NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5. Two of these —nitric oxide (NO) and nitrogen dioxide (NO_2)— are significant air pollutants produced by the burning of fossil fuels at high temperatures. Most of these NOx emissions (90%) are in the form of NO, which is less of a health concern than NO_2, a respiratory irritant that can lower resistance to respiratory infections. However, in the atmosphere, NO can combine with oxygen to form NO_2. Besides contributing to the formation of photochemical smog and acid rain, NO_2 acts to fertilize nitrogen-limited water systems, such as the Chesapeake Bay. The addition of nitrogen to water stimulates eutrophication (excessive algal production), which can lead to severe depletion of dissolved oxygen.

Note About Lead Poisoning

Lead is a potent neurotoxin that replaces the metals, such as iron and zinc, in certain proteins, including enzymes. The gradual reduction in the use of leaded gasoline by on-road motor vehicles resulted in a drastic decrease in the concentration of lead in the air. For example, in 2002, the average level of lead in the air was 94 percent lower than it was in 1983. Students can learn more about the health effects of lead and the circumstances that resulted in its elimination from gasoline by reading the background article **[TITLE TO COME].**

Note About Ozone

The background article *Photochemical Smog* provides detailed information about the complex reactions involved in the production of photochemical smog. Photochemical smog consists of a number of hazardous oxidants, the most abundant of which is ozone. Ozone is a respiratory irritant. Long-term exposure to ozone can cause permanent lung damage. Ozone is thought to be responsible for most of the damage to agriculture caused by air pollution. The eye irritation that is associated with photochemical smog is caused by some of its other components, such as formaldehyde and peroxyactelyle nitrate (PAN).

The U.S. Environmental Protection Agency (EPA) has established an Air Quality Index (AQI) to report levels of ozone and other air pollutants to protect public health. The index is a scale consisting of ranges of values that correspond to varying levels of health concern. You can go to the EPA's AIRNOW Web site at www.epa.gov/airnow to find the current AQI for ozone in your area, as well as other information about ozone.

4
Activity

[bottom notes]

Leading In to the Activity

Have students relate their experiences using household cleaners that contain ammonia. Point out that because of the ammonia vapors that are released, these cleaners should be used in well-ventilated places. Also, people who are allergic to ammonia should wear gloves while working with it.

Explain to students that organisms release ammonia into the environment as part of their life processes, such as excretion and decomposition. Certain human activities, such as the operation of gas-powered vehicles and the treatment of sewage, also release ammonia into the environment. Lead students to understand that ammonia is regarded as a pollutant when it is at a level in the environment that is harmful to living things.

Tell students that the activity models the degradation of an air pollutant by a catalytic converter. Explain that they will pass an air stream containing a pollutant, ammonia gas, over the surface of a metal catalyst, either copper or iron. You may wish to have students read over the procedure and study the illustration of the apparatus at this time. Ask them to identify the parts of the assembly that are analogous to the parts of a car that are involved in the emission and treatment of air pollutants. (flask emitting ammonia gas–engine; air stream–exhaust; catalyst in glass tube–catalytic converter; tube leading from glass tube–exhaust pipe)

Have students read the questions in the gray box to help them focus on the main points of the activity. The Design Connection question links the activity to the Design Projects. You might have students address the questions before doing the activity and then revisit the questions after completing the activity to see what they learned from the activity.

Predictions

Remind students that steel wool is primarily composed of iron. To help students make their predictions, you might give them samples of the copper filings and steel wool to compare. Students might base their predictions on the appearance of the two materials or on their knowledge of the chemical properties of copper and iron.

Recording Data

Activity-Log Sheet X is available for photocopying, if you wish to provide a sheet on which students can record their predictions, observations, and data.

Materials (per group)
The following is a partial list. Refer to page XX of the Student Edition for other materials needed.

To set up the apparatus:

- 500-mL Erlenmeyer flask
- # two-hole rubber stopper
- 22-cm-long inlet glass tube, OD 7/32 inch, ID 5/32 inch
- 12-cm-long outlet glass tube, OD 7/32 inch, ID 5/32 inch
- 100 mL ammonia solution
- 45-cm-long narrow plastic tubing, OD 7/32 inch, ID 5/32 inch
- 45-cm-long wide plastic tubing, OD 7/16 inch, ID 5/16 inch
- adapter **[Alex: Please give measurements for adapter.]**

To test the catalyst:
- six 400-mL beakers
- 100-mL graduated cylinder
- dropper bottle of 1% phenolphthalein solution

See Advance Preparation on page XX for information regarding the preparations of the ammonia solution and catalyst tubes and the assembly of the apparatus.

Procedure, Data, and Observations

Safety Note: *The activity should be done in a well-ventilated room.*

1. You may wish to point out to students that the steel wool consists of fibers, whereas the copper filings are particles. Students should observe that the copper particles are more numerous and smaller in size than the steel wool fibers.

2. Have students label six beakers, although they may not have to use all six.

3. If students are setting up the apparatus, you may wish to give them photocopies of the assembly directions on page XX. Half of the groups should use copper filings as the catalyst, while the other half uses steel wool (iron).

Make sure students understand that the pink color of the liquid in the flask indicates the presence of ammonia.

5. The rate at which ammonia gas flows through the catalyst tube is directly proportional to the rate at which air bubbles into the ammonia solution. The slower the air bubbles, the slower the ammonia flows through the catalyst tube, and the more time the ammonia spends in the reaction zone with the catalyst. Therefore, have students adjust the hose clamp such that it results in a slow air bubbling rate, about five bubbles per second.

A valve can be used in place of the hose clamp. The valve should be connected between the fish-tank air bubbler and the flexible plastic tubing leading to the glass catalyst tube.

6. The liquid in the *Control* beaker is used to trap any ammonia gas that passes out of the solution in the flask as students adjust the bubbling rate, thereby preventing the ammonia from entering the classroom.

The *Control* beaker is also used to establish that an adequate amount of ammonia is passing through the catalyst tube before students begin heating the catalyst in step 6. Make sure students understand that a change in the color of the liquid in the beaker to pink indicates that ammonia, which is a base, is bubbling into the liquid. The pinker the color, the more ammonia is present.

7 and 8. Swiftly moving the flame of the Bunsen burner will help prevent the glass from overheating. Tell students that if the glass tube begins to turn red or sag, they should stop heating it until it returns to its original appearance. Students should also reduce the flame before they resume heating the glass tube.

Students will eventually observe that the liquid in the beaker stays clear for more than 5 minutes. When this happens, they should wait until the liquid turns pink before proceeding to step 9.

You might have students use plus signs (+) to record the relative intensity of the pink color.

Have students keep all used beakers until the end of the activity so they can compare the color of the liquid in the beakers at that time. The pink color should become progressively paler.

Lead students to recognize that an increase in the amount of time it takes for the liquid in the beaker to turn pink and a decrease in the intensity of the pink color indicate that less ammonia is bubbling into the liquid. That is because the ammonia is being oxidized as it passes through the heated catalyst tube.

9. The liquid in the final beaker should turn pink quickly, indicating that the catalyst has become poisoned and the oxidation of ammonia has ceased.

11. Both kinds of used catalysts (copper and iron) will appear darkened.

12. You may wish to have groups record their data on the chalkboard and copy the class data into their notebooks.

13. The catalyst tubes can be cleaned by using a narrow rod to push out all of their contents, which can be disposed of in the trash.

Interpretations of the Data

1. The surface area of the copper filings was greater than that of the steel wool, because there were more copper filings than steel wool fibers and the copper filings were smaller in size.

2. The bubbling of ammonia gas into the liquid caused it to change to a pink color, due to the presence of phenolphthalein in the liquid.

3. The liquid in the beaker took a longer time to change to a pink color, if it all.

4. After the liquid in one of the beakers took a long time to turn pink, the liquid in the next beaker turned pink quickly. This indicated that the bubbling of ammonia into the liquid resumed, because it was no longer being oxidized.

5. The used catalyst appeared darkened because it was poisoned. Some students may realize that the darkening is due to the oxidation of the metal. Students will read about the process of metal-catalyst poisoning in the Expanding on the Concepts article on page XX.

6. Based on the class data, students should conclude that the copper began to catalyze the oxidation reaction sooner than the iron, because it took less time for the color change in the beaker to diminish when copper was used.

7. Based on the class data, students should conclude that the iron catalyst was poisoned more quickly than the copper catalyst.

Reflections

8. Bubbling the air slowly ensured that the ammonia gas passed slowly through the catalyst tube, which, in turn, allowed more time for the ammonia to be in contact with the catalyst.

9. Accept all reasonable answers. **[ED. NOTE: Can you suggest a comment to include in the TE?]**

Putting It All Together

1. Both the copper and iron were heterogeneous catalysts, because they were in a different phase from the reactants. The catalysts were solids; the reactants were gases.

2. Under the conditions of the activity, copper was more effective because it began to catalyze the oxidation of ammonia sooner, and it became poisoned more slowly.

3. Answers include changing the concentration of ammonia, the ammonia's flow rate through the glass tube, the degree to which the tube is heated, and the total surface area of the catalyst inside the tube.

4. Students should recall from Activity 3 that a reaction that is catalyzed by a heterogeneous catalyst occurs on the surface of the catalyst. Based on their observations that the copper filings had a greater total surface area than the steel wool and that the copper began to catalyze the oxidation of ammonia sooner, students should be able to infer that increasing the surface area of a catalyst increases the rate of the catalyzed reaction.

5. Reducing the size of the copper and iron catalysts to nanoparticles would increase the total surface area of the catalysts. Thus, the catalyzed oxidation of ammonia would occur at an even faster rate.

Design Connection Students' responses may vary. Possible advantages include that both copper and iron are inexpensive, they are easy to work with because they are solids, and they are neither toxic nor hazardous to use. Possible disadvantages are that they eventually become poisoned, they must be disposed of once they are poisoned, and heat is required in conjunction with the catalysts in order for the oxidation reaction to occur.

I Wonder

To stimulate questioning, you might have students make a list of various sources of air pollution. Ask them to consider whether it would be practical to use metal catalysts at those sources to help degrade the pollutants as they are being produced or released.

[side notes]

Discussing the Quote

Ask students what "truth" they learned from doing the activity. (Under the conditions of the activity, copper works better than iron in catalyzing the oxidation of ammonia.) Then discuss possible causes for this truth. In other words, why does copper work better? Accept all reasonable answers to the question. Students will learn the answer when they read the Expanding on the Concepts on page XX.

Discussing the Quote

Ask students if the results of the activity were what they expected, or predicted. Explain that scientists make predictions when they form hypotheses. When they test their hypotheses, scientists sometimes get unexpected results, which may lead them to form and test new hypotheses. Point out to students that making hypotheses, testing hypotheses, and changing the hypotheses when the results don't support them are all part of the scientific method.

Estimated Time

- ?? minutes to set up the apparatus
- 50 minutes to do the activity

To Save Time

Set up the apparatus for the students, or have students set up the apparatus the day before they do the activity.

Suggested Grouping

Groups of three or four

Activity Objectives

Students will:

- observe that more than one kind of metal can catalyze a particular reaction
- compare the effectiveness of copper and iron as catalysts for the oxidation of ammonia under the conditions of the activity
- compare the rate of inactivation (poisoning) of the copper and iron catalysts

Assessment Tip

As students do the activity, ask them why the liquid in each successive beaker becomes less pink. (More of the ammonia gas that is passing through the catalyst tube is being oxidized. Thus, less ammonia flows into the beaker.)

Troubleshooting

Remind students that the tip of the medicine dropper should be inside the liquid in the beaker, so that no ammonia gas is released into the air.

Summary of Experiment Results

The copper filings begin to catalyze the oxidation of ammonia sooner than the steel wool does. The steel wool stops catalyzing the oxidation of ammonia sooner than the copper filings do, indicating that the steel wool becomes poisoned faster. **[ED. NOTE: Can we give approximate times for each, or does it vary widely?]**

Note About the Use of Ammonia in Household Cleaners

Ammonia is widely used to clean glass and many other surfaces. Because ammonia is a base, it neutralizes greasy stains, which tend to be acidic. This reaction produces soap, through the process of saponification. The soap helps emulsify (break down) fats and oils. Ammonia is an effective glass cleaner because it evaporates quickly.

Vapor Pressure of Ammonia

Dissolved ammonia exhibits a significant vapor pressure. This means that when water containing dissolved ammonia is in contact with a gas phase, e.g., air, the equilibrium partial pressure (p_{NH3}) of ammonia in the gas phase is proportional to the aqueous ammonia concentration (C_{NH3}), in accordance with Henry's Law:

$$p_{\mathrm{NH3}} = {}^{C_{\mathrm{NH3}}}\!\big/_{K_{\mathrm{H,NH3}}}$$

where $K_{\mathrm{H,NH3}}$ is the Henry's constant for ammonia.

When air is bubbled into the flask containing ammonia, the air bubbles initially contain no ammonia. The system is therefore not in equilibrium. The system moves toward equilibrium via the transfer of ammonia from the dissolved phase into the gas phase; that is, ammonia leaves the water and enters the bubble. This transfer of ammonia into the bubble will continue until either (1) the equilibrium condition specified by Henry's law is reached or (2) the bubble leaves the water.

Engineers call this process "stripping," and it is widely used to transfer volatile dissolved species into the gas phase. For example, air can be bubbled through groundwater polluted by gasoline to remove volatile components, which can then be captured aboveground and treated. The smaller the bubbles, the greater is their surface area. By using very small bubbles, you can maximize the transfer of ammonia or any volatile components out of solution and into the gas phase (bubble).

Connection to Chemistry

Discuss with students how acid-base indicators work. Explain that these indicators are weak-acid or weak-base dyes whose colors change over a narrow pH range. For example, the indicator phenolphthalein changes from colorless to pink over a basic pH range of 8.2 to 10.0. Have students research acid-base indicators to make a chart that shows indicator color changes from pH 0.0 (acidic) to 12.0 (basic).

4

Expanding on the Concepts

This article explains why under the conditions of the activity, the copper filings were more effective than the steel wool in catalyzing the degradation of ammonia by oxidation.

Introducing the Topic

Give each student a ball of modeling clay, which will represent a sample of a material. Challenge students to demonstrate how they can increase the total surface area of the material. Students should recognize that this can be accomplished by dividing the ball into smaller balls, poking holes (pores) into the ball, or pulling the clay to form spikes on the surface of the ball.

How to Use This Article

After students read the article, have them make flow charts that illustrate the cycling of the copper and iron catalysts in the oxidation of ammonia. The flow charts should include the reactions that are involved.

Connection to Mathematics

You may wish to have students calculate the surface area-to-volume ratios of different-sized cubes and other three-dimensional shapes, as well as compare the ratios for different shapes of equal volume. They should find that a sphere has the smallest surface area-to-volume ratio of any shape.

Oxidation-Reduction Reactions

For an explanation of oxidation-reduction reactions, see the Background Information for Activity 1 on page XX.

Enhancing Catalyst Specificity and Selectivity

A catalyst that is highly active tends to react with a lot of chemicals. In addition, unwanted reactions occur when chemicals other than the desired reactants are present. In an industrial setting, the specificity and selectivity of a catalytic reaction are enhanced by using very pure reactant mixtures and by removing the products from the catalyst before they can undergo further reaction. The latter is much easier to do with a heterogeneous catalyst than a homogeneous one. Alternatively, the reaction conditions can be varied to find those conditions under which the desired reaction occurs much faster than the undesired reactions. In other words, finding the right catalyst for a desired reaction often involves playing a kinetics game that maximizes the desired reaction and minimizes the undesirable ones. Usually, this cannot be predicted; rather, many experiments must be performed to find the interactions and effects of the many reaction parameters.

Catalytic Synthesis of Ammonia

Besides being used to degrade ammonia, catalysts are used to synthesize ammonia for the purpose of making various products, including household cleaners, fertilizers, and explosives. The process used today for producing ammonia commercially, called the Haber-Bosch process, was developed in the early 20th century. Working for the German military before World War I, German chemist Fritz Haber developed a process for combining gaseous nitrogen (N_2) and hydrogen (H_2) to form ammonia (NH_3). The reactants are subjected to very high pressure and heat (500^oC, or 932^oF) in the presence of porous iron catalyst. Carl Bosch, Haber's brother-in-law, refined this process into a form for industrial use.

Like many industrial processes, the Haber-Bosch process has its disadvantages. The extreme conditions of high heat and pressure needed to catalyze the reaction between hydrogen and nitrogen demand expensive fossil fuels (e.g., gasoline, oil, natural gas). Also, these fuels generate nitrogen- and sulfur oxides (air pollutants) and carbon dioxide (a greenhouse gas thought to contribute to global-climate change).

[Ed. Note: I don't think the following TE notes relate closely to the content of the Expanding on the Concepts and should be deleted. Perhaps we should include them in a separate background article, using more of the text that Katie wrote. However, if we do this, we won't be able to include a Biology Connection here, in which students research the nitrogen cycle. Please advise.]

Ammonia, Fertilizers, and Pollution

The high yield of ammonia by the Haber-Bosch process has greatly increased the availability and use of commercial fertilizers over the past 50 years. Ammonia can be liquefied and applied directly to the soil. Alternatively, ammonia (NH_3) is reacted with nitric acid (HNO_3) to form ammonium nitrate (NH_4NO_3), an effective solid fertilizer.

Fertilizers greatly enhance crop yields by providing nitrogen, an essential nutrient, to plants; unfortunately, they can also cause air and water pollution. For example, the manufacturing and use of fertilizers releases ammonia into the atmosphere. Ammonia is a respiratory irritant and at high enough concentrations can cause tightness in the chest, difficulty breathing, and even death.

The use of fertilizers has also created a glut of nitrates in the ground and in surface waters, which are sources of drinking water. Nitrates are detrimental to human health. For example, nitrates may cause bladder cancer and such human disorders as methemoglobinemia, or "blue baby syndrome." Methemoglobinemia occurs when nitrate interacts with hemoglogin in red blood cells, forming methemoglobin, which lacks hemoglobin's oxygen-carrying capacity. Compared to adults, infants have a lower concentration of the enzyme that converts methemoglobin back to hemoglobin. Thus, infants with high levels of methemoglobin have insufficient oxygen delivered to their cells and as a result may appear blue around the mouth, hands, and feet.

Nitrates are also detrimental to the environment. High levels of nitrates in the surface waters flowing to the Mississippi River Basin have resulted in hypoxia (low oxygen levels) in the Gulf of Mexico, due to eutrophication (excessive algal production). As a result, fish and other marine organisms may not be able to survive.

Biology Connection

Many scientists think the answer to the problems (environmental and health effects, energy costs) associated with fertilizers is *Rhizobia* — bacteria that live in nodules that form on the roots of leguminous plants such as soybeans, peanuts, sweet clover, and alfalfa. *Rhizobia* convert nitrogen (N_2) from the air into ammonia (NH_3), a form of nitrogen that the plants can easily use. This conversion process, called nitrogen fixation, requires a complex enzyme that contains iron.

Instead of using fertilizers, scientists advocate rotating non-leguminous crops with legumes to add nitrogen to the soil. This process of crop rotation involves plowing under the leguminous crop, forming so-called green manure. When the legumes decompose, they release their stored nitrogen in the form of nitrates (NO_3^-), a form of nitrogen that non-leguminous plants can take up from the soil through their roots and use easily.

Rhizobia are one part of the earth's nitrogen cycle, which includes various pathways for nitrogen to enter ecosystems. For example, certain free-living bacteria in the soil fix gaseous nitrogen into ammonia. Because most soil is acidic, the ammonia picks up a hydrogen ion (H^+) to form ammonium ($NH4^+$), another form of nitrogen that plants can easily use. Have interested students research the nitrogen cycle and make a diagram illustrating it.

5

Planning Guide
Using Photocatalysis to Degrade a Water Pollutant

Links

TO THE PREVIOUS ACTIVITY In the previous activity, students used heat in addition to a catalyst to speed up the degradation of an air pollutant. In this activity, students learn about the process of photocatalysis, in which light is used in conjunction with a catalyst to increase the rate of a chemical reaction. They will use UV light and titanium dioxide to catalyze the degradation of an organic dye, methylene blue, dissolved in water. They will also test the effects of three variables – catalyst concentration, UV light intensity, and pH – on the rate of photocatalytic degradation of methylene blue.

TO THE DESIGN PROJECTS [TK]

Purpose

To have students observe the degradation of methylene blue by photocatalysis and test the effects of catalyst concentration, UV light intensity, and pH on the photocatalytic degradation rate of methylene blue

Summary of the Activity

In Part A, students expose a mixture containing the dye methylene blue and the catalyst titanium dioxide to UV light over a period of 30 minutes. They monitor the degradation of the dye by observing changes in the color of the mixture at 5-minute intervals. By comparing the color of the mixture with the colors of mixtures of known methylene blue concentrations, students infer the concentration of methylene blue in their mixture at each time interval. Using their data, students make a graph that shows the rate of photocatalytic degradation of methylene blue.

In Part B, each group tests the effect of catalyst concentration, UV light intensity, or pH on the photocatalytic degradation rate of methylene blue. Groups share their data, graph the class data, and use their graphs from Parts A and B to draw conclusions about the effects of the different variables tested.

Advance Preparation

Part A

Make 1 L of a stock methylene blue solution (100 mg/L) by dissolving 100 mg of methylene blue in 1 L of distilled water in a 1-L volumetric flask, using a stir plate and stir bar. ***Caution:** Methylene blue is an eye and skin irritant. Avoid inhalation and contact with eyes, skin, and clothing. Wear safety glasses, apron, and gloves, and work under a fume hood or in a well-ventilated place.* The stock solution can be used to make the various solutions needed for Parts A and B.

To make 100 mL of each of the standard methylene blue mixtures (X mg/L), where *X* equals the number of milligrams per liter of methylene blue desired, transfer *X* mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add 100 – *X* mL of distilled water to the beaker. Make standards for *X* = 0, 2, 4, 6, 8, and 10.

To make 100 mL of each of the standard methylene blue (X mg/L)-titanium dioxide (1 g/L) mixtures, where *X* equals the number of milligrams per liter of methylene blue desired, transfer *X* mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add 100 – *X* mL of distilled water to the beaker. Mix in 100 mg of titanium dioxide. This will create a suspension, because the titanium dioxide will not dissolve. Make standards for *X* = 0, 2, 4, 6, 8, and 10.

You might wish to provide each group with a set of each series of six standard mixtures, or if two or more groups will be working at the same workbench, they can share both sets of standards. To make a set of standards, use six small vials (8 mL) with screw caps or use six Pyrex (borosilicate) test tubes (13 mm × 100) with stoppers. Dispense about 5 mL of mixture into each vial/test tube. Be sure to stir the mixtures containing titanium dioxide before dispensing them. Label each vial/test tube with the mixture's concentrations of methylene blue and titanium dioxide. The standards, which will also be used in Part B, should be kept in the dark – in a box or wrapped in foil – between classes. Fresh standards should be made before each running of the module.

To make 500 mL of the methylene blue (10 mg/L) mixture, transfer 50 mL of the stock methylene blue solution (100 mg/L) to a 600-mL beaker and add 450 mL of distilled water. After using this solution for Part A, there should be enough remaining to use for Part B.

To make 500 mL of the methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture, transfer 50 mL of the stock methylene blue solution (100 mg/L) to a 600-mL beaker and add 450 mL of distilled water. Mix in 0.5 g of titanium dioxide. This will create a suspension, because the titanium dioxide will not dissolve. Stir the mixture before each use. After using this mixture for Part A, there should be enough remaining to use for Part B. The mixture should be kept in the dark – in a box or wrapped in foil – between classes. A fresh mixture should be made before each running of the module.

Part B

Testing Catalyst Concentration

To make 100 mL of each of the standard methylene blue (X mg/L)-titanium dioxide (3 g/L) mixtures, where *X* equals the number of milligrams per liter of methylene blue desired, transfer *X* mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add 100 – *X* mL of distilled water to the beaker. Mix in 300 mg of titanium dioxide. This will create a suspension, because the titanium dioxide will not dissolve. Make standards for *X* = 0, 2, 4, 6, 8, and 10.

You might wish to provide a set of the six standard mixtures to each group that is testing the effect of catalyst concentration, or if two or more groups testing catalyst concentration will be working at the same bench, they can share one set. To make a set of standards, use six small vials (8 mL) with screw caps or use six Pyrex (borosilicate) test tubes (13 mm × 100) with stoppers. Dispense about 5 mL of mixture into each vial/test tube. Be sure to stir the mixtures containing titanium dioxide before dispensing them. Label each vial/test tube with the mixture's concentrations of methylene blue and titanium dioxide. The standard mixtures should be kept in the dark – in a box or wrapped in foil – between classes. Fresh standards should be made before each running of the module.

To make 500 mL of the methylene blue (10 mg/L)-titanium dioxide (3 g/L) mixture, transfer 50 mL of the stock methylene blue solution (100 mg/L) to a 600-mL beaker and add 450 mL of distilled water. Mix in 1.5 g of titanium dioxide. This will create a suspension, because the titanium dioxide will not dissolve. Stir the mixture before each use. The mixture should be kept in the dark – in a box or wrapped in foil – between classes. A fresh mixture should be made before each running of the module.

Testing UV Light Intensity

The following mixtures which you made for Part A can also be used by students to test the effect of UV light intensity.

- Sets of standard methylene blue mixtures
- Sets of standard methylene blue-titanium dioxide (1 g/L) mixtures
- Methylene blue (10 mg/L) mixture
- Methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture

Testing pH

Prepare or purchase 0.1*M* NaOH. To make 100 mL of 0.1*M* NaOH, add 0.4 g of NaOH to 100 mL of distilled water. ***Caution:*** *The NaOH solution is extremely caustic and should be handled with care. Wear safety glasses, apron, and gloves, and work under a fume hood or in a well-ventilated place.*

Standards containing NaOH need to be prepared, because the base affects the color of methylene blue solution, making it purplish. To make 100 mL of each of the standard methylene blue (X mg/L)-NaOH mixtures, where *X* equals the number of milligrams per liter of methylene blue desired, transfer *X* mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add $100 - X$ mL of distilled water and 20 drops of 0.1*M* NaOH to the beaker. Make standards for $X = 0, 2, 4, 6, 8$, and 10.

To make 100 mL of each of the standard methylene blue (X mg/L)-NaOH-titanium dioxide (1 g/L) mixtures, where *X* equals the number of milligrams per liter of methylene blue desired, transfer *X* mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add $100 - X$ mL of distilled water to the beaker. Mix in 100 mg of titanium dioxide and 20 drops of 0.1*M* NaOH. This will create a suspension, because the TiO_2 will not dissolve. Make standards for $X = 0, 2, 4, 6, 8$, and 10.

You might wish to provide a set of each series of standard mixtures to each group that is testing the effect of pH, or if two or more groups testing pH will be working at the same bench, they can share the two sets of standards. To make a set of standards, use six small vials (8 mL) with screw caps or use six Pyrex (borosilicate) test tubes (13 mm × 100) with stoppers. Dispense about 5 mL of mixture into each vial/test tube. Be sure to stir the mixtures containing titanium dioxide before dispensing them. Label each vial/test tube with the mixture's concentrations of methylene blue and titanium dioxide and the base added to the mixture. The standard mixtures should be kept in the dark – in a box or wrapped in foil — between classes. Fresh standards should be made before each running of the module.

The following mixtures which you made for Part A can also be used by students to test the effect of pH.

- Methylene blue (10 mg/L) mixture
- Methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture

Safety

Discuss safety issues students should be aware of, including:

- wearing UV safety glasses, apron, and gloves while doing the activity
- using caution when handling the methylene blue mixtures, as methylene blue is an eye and skin irritant and can stain clothing
- not exposing themselves or anyone else to UV light
- using caution when handling the base solution, as it is caustic
- handling all materials carefully to avoid spills
- not eating or tasting any of the materials
- handling glassware carefully
- wiping up spills with paper towels or a mop as soon as possible
- safety issues of particular concern in your classroom

Curriculum Connections

Relating Photocatalysis to Different Subjects

Connecting to Your Curriculum on page TXX suggests ways in which you can fit the Environmental Catalysis module into your general curriculum. The chart below provides areas for connecting the concepts introduced in this activity with different disciplines. The page numbers in the chart refer to teaching tips in the margin that you can use to make connections to the listed subject.

Chemistry
Mixtures p. XX
Acids and bases p. XXX

Biology
Photosynthesis

Physics
Electromagnetic radiation

Mathematics
Graphing p. XX

Background Information

[Kim please provide. The information here should not duplicate the information provided in the Intro and Expanding on the Concepts in the PE.]

Tips from the Trenches

[TO COME]

Using the Internet

You might wish to direct students to the following Web sites to learn about practical uses for photocatalysis:

www.technogadgets.com/archive/Sep.Oct.Nov01/TG9501ppg.html
self-cleaning windows

www.kesmist.com/scrub3.htm
ethylene removal system for florists

www.sciam.com/article.cfm?articleID=0001D4EB-EDAD-1CC5-B4A8809EC588EEDF&catID=2
paving blocks that break down pollutants

www.aist.go.jp/aist_j/event/ev2003/ev20030407/eng/air.html
air purification systems

Portfolio Project

As students search the Internet for practical uses for photocatalysis, have them print out the information they find and add the printouts to their portfolio.

Alternative As an Open Activity

In Part B of the activity, you might wish to have students decide on their own how to test the effect of each variable – catalyst concentration, UV light intensity, and pH – on the photocatalytic degradation rate of methylene blue. For example, with regard to catalyst concentration, students can choose whether to increase or decrease the catalyst concentration used in Part A and to what degree. Direct students to write a detailed procedure with numbered steps, record and graph their data, and share their findings with the class.

Cross-Curricular Teaching

This activity can be assigned to coincide with a unit on reaction kinetics in chemistry class. After graphing their data in this activity, students can analyze the shapes of the graphs to gain information as to the kinetics of the photocatalytic reactions that cause the degradation of methylene blue. **[KIM/ALEX: Does this note make sense?]**

5

Introduction

To Inspire Questioning and Learning

Before students read the Introduction article, ask them to speculate about the meaning of the word *photocatalysis.* Based on their understanding of the meaning of the prefix *photo-,* most students will probably correctly say that *photocatalysis* refers to a catalytic process that involves light. At this time, you might wish to point out that photosynthesis is an example of photocatatalysis in nature. Explain that chlorophyll and other plant pigments absorb sunlight and that various catalysts (enzymes) drive reactions in which the captured light energy is converted to chemical energy that is required to make organic materials, such as sugars, proteins, fats, etc. Tell students that humans have found ways of utilizing photocatalysis to improve technology. Then have them read the Introduction article to learn about some of these technologies.

Focusing on Study Skills

Have students write three questions that can be answered from information in the Introduction article, and tell them to include the answers. Then have students write three questions that stem from the text but cannot be answered by it. Encourage students to revisit their questions and attempt to answer them after they have done the activity and read the Expanding on the Concepts article on page XX.

Note About Titanium Dioxide

Titanium dioxide does not exist in nature in pure form; it is mined and processed from deposits of ilmenite and leuxoceneores ores. The appearance of titanium dioxide depends on the size of its particles. Micrometer-sized titanium particles look like a white powder because the particles scatter nearly all the visible wavelengths of light. In fact, this form of titanium dioxide is the whitest substance known. It is used as a pigment to provide whiteness, brightness, and opacity in paints, cosmetics, paper, toothpaste, false teeth, and other products.

Titanium dioxide appears white as long as its particles are larger than the wavelengths of visible light, usually 400–700 nanometers. When titanium dioxide is ground to nanoparticles, which are smaller than those wavelengths, the nanoparticles do not scatter visible light and therefore appear transparent. For that reason, titanium dioxide nanoparticles are used in sunscreens. The nanoparticles absorb UV light but do not form a white layer on the skin.

Photoactivity of Titanium Dioxide

During the 1940s and 50s, because of its toxicity, white lead pigment in paint was replaced with titanium dioxide. There was, however, a downside to adding titanium dioxide to paint: When exposed to UV light over a period of time, the white paint turned to dust. This process is called paint chalking and is caused by the photocatalytic activity of the titanium dioxide. The catalyst degrades the organic components in paint that bind it to the surface, causing the powdery catalyst to fall off as dust. The paint industry solved this problem by finding forms of titanium dioxide that are less photoactive. There are three mineral forms of titanium dioxide — rutile, anatase, and brookite — that vary in their crystal structure. Rutile, the least photoactive form, which absorbs wavelengths of up to about 410 nm, is presently used as white pigment in paint, as well as in foods, cosmetics, and sunscreens. Anatase, the most photoactive form, which absorbs wavelengths of up to about 385 nm, is used in the self-cleaning and self-sterilizing applications discussed in the Introduction article.

Connection to Biology

Have students prepare a report or diagram that describes the reactions involved in the conversion of light energy to chemical energy during photosynthesis, including both photosystem I and photosystem II.

5
Activity

[bottom notes]

Leading In to the Activity

Have students read the first two paragraphs on this page. Ask them to give examples of other ways industries and people in their homes pollute water supplies. Discuss whether photocatalysis might be used to degrade those pollutants.

Show students a sample of titanium dioxide and a vial containing an aqueous solution of methylene blue. Tell them that solid methylene blue dye is dissolved in the water, giving it a blue color. In the activity, methylene blue will represent a water pollutant. Titanium dioxide, the catalyst that will be used in the activity, is a white powdery solid that is sometimes used as a white pigment in paint. Next, add some of the titanium dioxide to the vial and shake. Lead students to recognize that unlike the methylene blue, the titanium dioxide does not dissolve in the water but rather is suspended. Because it is white, the titanium dioxide lightens the mixture's blue color. Have students observe that eventually, the titanium dioxide settles to the bottom of the vial, but the methylene blue does not. Explain to students that during the activity, they will have to periodically mix their methylene blue-titanium dioxide mixtures to keep the catalyst suspended. (At this time, you might wish to discuss the meanings of the terms *mixture, solution,* and *suspension.*)

Write on the chalkboard the chemical formulas for methylene blue ($C_{16}H_{18}N_3SCl$) and titanium dioxide (TiO_2). Ask students to identify the kinds and numbers of atoms that make up each molecule. Tell students that in addition to carbon dioxide and water, nitrate, ammonium, and sulfate ions are produced when methylene blue is degraded by photocatalysis. **[ED. NOTE: Students will wonder how water can form if there is no oxygen atom in a molecule of methylene blue.]** Emphasize to students that because titanium dioxide is a catalyst it is not used up in the degradation reaction.

Use the questions in the gray box to focus students' thinking as they do the activity. To reinforce study skills, you might suggest that students copy these questions in their notebook, leaving space after each question so they can write the answers after doing the activity.

Part A

Predictions

The first paragraph on this page should help students predict that the methylene blue-titanium dioxide mixture that was exposed to UV light will become decolorized because it will have undergone photocatalytic degradation.

Recording Data

Activity-Log Sheet 7 is available for photocopying, if you wish to provide a sheet on which students can record their predictions, observations, and data from Part A. They can graph their data on Activity-Log Sheet 8.

Materials (per group)

The following is a partial list. Refer to page X of the Student Edition for other materials needed.

- four 13-mm × 100-mm Pyrex test tubes
- 10 mL methylene blue (10 mg/L) mixture
- 10 mL methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- 10-mL graduated cylinder

See Advance Preparation on page X for information regarding the preparation of the mixtures students will need.

Procedure, Data, and Observations

1. Before beginning the activity, you might wish to have students observe a sample of titanium dioxide. Point out to them that the sample is a white powder because the titanium particles are micrometer-sized, i.e., the particles are not nanoparticles. Explain that some of the mixtures they will be working with in the activity were made by adding the white titanium dioxide powder to a solution of methylene blue, which makes the solution a lighter blue.

The use of standard mixtures will allow students to collect quantitative data by inferring the actual concentrations (milligrams per liter) of methylene blue in their experimental mixtures at successive time intervals. The quantitative data will allow students to graph their data and draw certain conclusions about the photocatalytic degradation rate of methylene blue. However, if you prefer to simplify the activity and not have to make the standard mixtures, students can collect qualitative data by simply observing whether the methylene blue in the experimental mixtures appears to degrade with time, as evidenced by a decolorization of the mixtures.

Make sure students compare the colors of the standard mixtures within the same set, as the presence of titanium dioxide in a mixture makes it lighter blue. Remind students to swirl the mixtures containing titanium dioxide so as to thoroughly suspend it.

Students should conclude from observing both sets of standards that the higher the concentration of methylene blue in a mixture, the darker blue the mixture appears.

2. It is important that students use Pyrex (borosilicate) test tubes in order to ensure the transmission of UV light through the glass in step 4.

3. Students should recognize that the initial concentration of methylene blue in each mixture is 10 mg/L.

4. Swirling the mixtures that contain titanium dioxide maximizes contact between the methylene blue and titanium dioxide molecules by preventing the titanium dioxide from settling to the bottom of the test tubes. The mixtures that do not contain titanium dioxide are swirled as a control.

Caution students to swirl the mixtures carefully so that none of the mixtures spills out of the test tube.

5. Make sure students compare their experimental mixtures with the correct set of standards. That is, experimental mixtures that contain no titanium dioxide should be compared with standards that contain no titanium dioxide. Likewise, experimental mixtures that contain titanium dioxide should be compared with standards that contain titanium dioxide. You may wish to ask students to explain why. (The presence of titanium dioxide affects the color of the mixture.)

To make accurate color comparisons, students should hold their test tubes next to the standard mixtures.

Lead students to understand that an observed decolorization of a mixture indicates a decrease in the concentration of methylene blue in that mixture, due to the degradation of methylene blue molecules.

Students may have to interpolate the concentration of methylene blue in an experimental mixture if the color of that mixture is between the color of two consecutive standard mixtures. For example, if the color of an experimental mixture is darker than the 4 mg/L methylene blue standard but lighter than the 6 mg/L methylene blue standard, students can infer that the concentration of the experimental mixture is about 5 mg/L methylene blue.

7. Students may need help with graphing their data. Direct them to plot time (independent variable) on the x-axis and concentration (dependent variable) on the y-axis. Help groups select appropriate units for the axes, based on the concentration data and time periods involved. The graph should have four lines plotted, one for each experimental mixture. Suggest that students use a different colored pencil for each mixture.

Some students may need help with interpreting their graphs. Ask them to explain what a horizontal line, a line that slopes upward, and a line that slopes downward would indicate. (Horizontal line: no change in the concentration of methylene blue over time; upward sloping line: increase in the concentration of methylene blue; downward sloping line: decrease in the concentration of methylene blue)

At this time, you might want to discuss the meaning of the term *rate.* (A ratio between two quantities) Point out to students that their graph shows the rate of degradation of methylene blue. The ratio is between the concentration of methylene blue in a mixture and the amount of time that has passed.

Interpretations of the Data

1. Methylene blue should have degraded in the mixture that contained titanium dioxide and was exposed to UV light, as evidenced by a decrease in the blue color (i. e., methylene blue concentration) of the mixture.
2. The UV light and the titanium dioxide together helped to speed up the degradation of methylene blue. Neither the UV light alone nor the titanium dioxide alone was sufficient to catalyze the reaction.
3. Answers may vary, but students should see a decrease in methylene blue concentration after the first 5 minutes of irradiation.
4. By the end of the 30-minute time period, the mixture that underwent photocatalysis should appear white (methylene blue concentration = 0 mg/L), indicating the apparent absence of methylene blue.
5. Answers may vary depending on the data students collected and the accuracy with which they plotted the data on their graphs. Students' graphs should show that the photocatalytic degradation rate slows down over time, as evidenced by a downward line that curves. In other words, the concentration of methylene blue concentration decreases a smaller amount during each successive time interval. A straight downward line would indicate that photocatalytic degradation occurs at a constant rate. The amount of decrease in the concentration of methylene blue doesn't change with time.

Reflections

5. The standard mixtures allowed students to infer the actual concentration of methylene blue in each experimental mixture at each time interval, rather than simply observing a decrease in concentration over time. Knowing the methylene-blue concentration as a function of time allowed students to determine its rate of photocatalytic degradation.
6. The mixtures in the three test tubes labeled *dye + no UV, dye + UV,* and *dye + catalyst + no UV,* respectively, were the controls. The first test tube showed that methylene blue did not degrade on its own. The second test tube showed that UV light alone was not sufficient to cause the degradation of methylene blue. The third test tube showed that titanium dioxide alone was not sufficient to cause the degradation of methylene blue.
7. Answers will vary, depending on students' predictions. Some students might have predicted that the non-irradiated methylene blue-titanium dioxide mixture would show decolorization because the catalyst alone would be sufficient for the degradation of methylene blue to occur.

Part B

Assign one variable to each group. If there are more than three groups in your class, assign one or more of the variables to multiple groups. Alternatively, you may wish to have all groups test all three variables.

Testing Catalyst Concentration

Prediction

To help students make predictions, have them think about what they learned in Part A. What conditions were required for the degradation of methylene blue to be observed? Remind students that the concentration of titanium dioxide in the mixtures they worked with in Part A was 1 g/L. In this part of the activity, they will be tripling the concentration of the catalyst to 3 g/L. Ask students whether they think increasing the concentration of catalyst will cause the methylene blue to degrade faster.

Recording Data
Activity-Log Sheet 9 is available for photocopying, if you wish to provide a sheet on which students can record predictions, observations, and data regarding catalyst concentration. If more than one group tested this variable, provide each group with as many photocopies of Activity-Log Sheet 9 as needed.

Materials (per group)
The following is a partial list. Refer to page X of the Student Edition for other materials needed.

- two 13-mm × 100-mm Pyrex test tubes
- 10 mL methylene blue (10 mg/L)-titanium dioxide (3 g/L) mixture
- 10-mL graduated cylinder

See Advance Preparation on page X for information regarding the preparation of the mixtures students will need.

Procedure, Data, and Observations
1. The use of standard mixtures will allow students to collect quantitative data by inferring the actual concentrations (milligrams per liter) of methylene blue in their experimental mixtures at successive time intervals. The quantitative data will allow students to graph their data and draw certain conclusions about the photocatalytic degradation rate of methylene blue. However, if you prefer to simplify the activity and not have to make the standard mixtures, students can collect qualitative data by simply observing whether the methylene blue in the experimental mixtures appears to degrade with time, as evidenced by a decolorization of the mixtures.

Be sure students use the standards that contain 3 g/L (not 1 g/L) titanium dioxide for this part of the activity, because the additional titanium dioxide affects the color of the mixtures.

You might also wish to have students test the effect of decreasing the concentration of titanium dioxide to, for example, 0.5 g/L. To make 500 mL of 10 mg/L methylene blue-0.5 g/L titanium dioxide mixture, transfer 50 mL of the stock methylene blue solution (100 mg/L) to a 600-mL beaker. Then add 450 mL of distilled water and 0.25 g of titanium dioxide to the beaker.

To make 100 mL of each standard (X g/L) methylene blue-(0.5 g/L) titanium dioxide mixtures, where X equals the number of milligrams per liter of methylene blue desired, transfer X mL of the stock methylene blue solution (100 mg/L) to a 150-mL beaker. Then add $100 - X$ mL of distilled water and 50 mg of titanium dioxide to the beaker. Make standards for $X = 0, 2, 4, 6, 8, 10$.

2. It is important that students use Pyrex (borosilicate) test tubes to ensure the transmission of UV light through the glass.

Ask students to identify the test tube that will contain the control mixture and explain what the purpose of the control is. (The control will be the mixture that is not exposed to UV light. Its purpose is to show whether high catalyst concentration alone affects the degradation of methylene blue.)

4. Swirling the mixtures maximizes contact between the methylene blue and titanium dioxide molecules by preventing the titanium dioxide from settling to the bottom of the test tubes.

Caution students to swirl the mixtures carefully so that none of the mixtures spills out of the test tube.

5. To make accurate color comparisons, students should hold their test tubes next to the standard mixtures.

Make sure students understand that an observed decolorization of a mixture indicates a decrease in the concentration of methylene blue in that mixture, due to the degradation of methylene blue molecules.

Students may have to interpolate the concentration of methylene blue in an experimental mixture if the color of that mixture is between the color of two consecutive standard mixtures. For example, if the color of an experimental mixture is darker than the 4 mg/L methylene blue standard but lighter than the 6 mg/L methylene blue standard, they can infer that the concentration of the experimental mixture is about 5 mg/L methylene blue.

7. If more than one group is testing the effect of catalyst concentration, have the groups record their data in separate tables on the chalkboard.

Instead of having groups record their data on the chalkboard, you might have them provide photocopies of their data to other groups.

Testing UV Light Intensity

Prediction

Have students think about their observations of the mixtures in Part A that were exposed to UV light and those that were not. In which mixture did the methylene blue degrade? What effect would increasing the intensity of UV light have on how fast the methylene blue degrades?

Recording Data

Activity-Log Sheet 10 is available for photocopying, if you wish to provide a sheet on which students can record predictions, observations, and data regarding UV light intensity. If more than one group tested this variable, provide each group with as many photocopies of Activity-Log Sheet 10 as needed.

Materials (per group)
The following is a partial list. Refer to page X of the Student Edition for other materials needed.

- two 13-mm × 100-mm Pyrex test tubes
- 5 mL methylene blue (10 mg/L) mixture
- 5 mL methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- 10-mL graduated cylinder

See Advance Preparation on page X for information regarding the preparation of the mixtures students will need.

Procedure, Data, and Observations
1. The use of standard mixtures will allow students to collect quantitative data by inferring the actual concentrations (milligrams per liter) of methylene blue in their experimental mixtures at various time intervals. The quantitative data will allow students to graph their data and draw certain conclusions about the photocatalytic degradation rate of methylene blue. However, if you prefer to simplify the activity and not have to make the standard mixtures, students can collect qualitative data by simply observing whether the methylene blue in the experimental mixtures appears to degrade with time, as evidenced by a decolorization of the mixtures.

You might also wish to have students test the effect of decreasing the intensity of UV light. They can hold a UV lamp, for example, 30 cm away from the mixtures.

2. It is important that students use Pyrex (borosilicate) test tubes to ensure the transmission of UV light through the glass.

Ask students to identify the test tube that will contain the control mixture and explain what the purpose of the control is. (The control will be the mixture that does not contain titanium dioxide. Its purpose is to show whether high UV light intensity alone affects the degradation of methylene blue.)

4. The surfaces of the UV lamps should be next to the test tubes.

5. Swirling the mixture that contains titanium dioxide maximizes contact between the methylene blue and titanium dioxide molecules by preventing the titanium dioxide from settling to the bottom of the test tube. The mixture that does not contain titanium dioxide is swirled as a control.

Caution students to swirl the mixtures carefully so that none of the mixtures spills out of the test tube.

6. Make sure students compare their experimental mixtures with the correct set of standards. That is, experimental mixtures that contain no titanium dioxide should be compared with standards that contain no titanium dioxide. Likewise, experimental mixtures that contain titanium dioxide should be compared with standards that contain titanium dioxide. You may wish to ask students to explain why. (The presence of titanium dioxide affects the color of the mixture.)

To make accurate color comparisons, students should hold their test tubes next to the standard mixtures.

Be sure students understand that an observed decolorization of a mixture indicates a decrease in the concentration of methylene blue in that mixture, due to the degradation of methylene blue molecules.

Students may have to interpolate the concentration of methylene blue in an experimental mixture if the color of that mixture is between the color of two consecutive standard mixtures. For example, if the color of an experimental mixture is darker than the 4 mg/L methylene blue standard but lighter than the 6 mg/L methylene blue standard, they can infer that the concentration of the experimental mixture is about 5 mg/L methylene blue.

8. If more than one group is testing the effect of UV light intensity, have the groups record their data in separate tables on the chalkboard.

Instead of having groups record their data on the chalkboard, you might have groups provide photocopies of their data to other groups.

Testing pH

Prediction

Before students make their predictions, ask them what they know about acids and bases and to give common examples of each. (Acids: lemon juice, vinegar; bases: household ammonia, milk of magnesia) You may wish to review the pH scale at this time, pointing out the numbers that correspond to neutral solutions (pH 7), acid solutions (pH < 7), and base solutions (pH > 7). Lead students to understand that the lower the pH of an acidic solution, the more acidic it is; the higher the pH of a base solution, the more basic it is. You might wish to discuss the caustic nature of very acidic and very basic solutions.

Recording Data

Activity-Log Sheet 11 is available for photocopying, if you wish to provide a sheet on which students can record predictions, observations, and data regarding pH. If more than one group tested this variable, provide each group with as many photocopies of Activity-Log Sheet 11 as needed.

Materials (per group)
The following is a partial list. Refer to page X of the Student Edition for other materials needed.

- eight 13-mm × 100-mm Pyrex test tubes
- 20 mL methylene blue (10 mg/L) mixture
- 20 mL methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- 10-mL graduated cylinder
- 1 mL NaOH (0.1*M*) solution

See Advance Preparation on page X for information regarding the preparation of the mixtures students will need.

Procedure, Data, and Observations

1. The use of standard mixtures will allow students to collect quantitative data by inferring the actual concentrations (milligrams per liter) of methylene blue in their experimental mixtures at various time intervals. The quantitative data will allow students to graph their data and draw certain conclusions about the photocatalytic degradation rate of methylene blue. However, if you prefer to simplify the activity and not have to make the standard mixtures, students can collect qualitative data by simply observing whether the methylene blue in the experimental mixtures appears to degrade with time, as evidenced by a decolorization of the mixtures.

As noted under Advance Preparation on page XX, the addition of 0*.1M* NaOH to methylene blue solution causes it to appear purplish. Thus, students need to be given standards containing NaOH to ensure that in step 6, they correctly infer the concentration of methylene blue in the experimental mixtures that contain NaOH.

2. It is important that students use Pyrex (borosilicate) test tubes to ensure the transmission of UV light through the glass.

Ask students to identify the test tubes that will contain control mixtures and explain what the purpose of each control will be. (The non-irradiated mixture that contains methylene blue and NaOH will show whether NaOH alone causes the methylene blue to break down. **[KIM and/or Alex: Can you please explain the rest of the controls?]**

3. The pH of the mixtures will be about 5.

4. You may wish to tell students that the pH of the NaOH (0.1*M*) solution is 13. The addition of the NaOH solution to the mixtures will increase their pH to about 10.

5. Swirling the mixtures that contain titanium dioxide maximizes contact between the methylene blue and titanium dioxide molecules by preventing the titanium dioxide from settling to the bottom of the test tubes. The mixtures that do not contain titanium dioxide are swirled as a control.

Caution students to swirl the mixtures carefully so that none of the mixtures spills out of the test tube.

6. Make sure students compare their experimental mixtures with the correct set of standards. For example, experimental mixtures that contain titanium dioxide should be compared with standards that contain titanium dioxide. Experimental mixtures that contain NaOH should be compared with standards that contain NaOH. You may wish to ask students to explain why. (Both titanium dioxide and NaOH affect the colors of the mixtures.)

To make accurate color comparisons, students should hold their test tubes next to the standard mixtures.

Be sure students understand that an observed decolorization of a mixture indicates a decrease in the concentration of methylene blue in that mixture, due to the degradation of methylene blue molecules.

Students may have to interpolate the concentration of methylene blue in an experimental mixture if the color of that mixture is between the color of two consecutive standard mixtures. For example, if the color of an experimental mixture is darker than the 4 mg/L methylene blue standard but lighter than the 6 mg/L methylene blue standard, they can infer that the concentration of the experimental mixture is about 5 mg/L methylene blue.

8. If more than one group is testing the effect of pH, have the groups record their data in separate tables on the chalkboard.

Instead of having groups record their data on the chalkboard, you might have groups provide photocopies of their data to other groups.

Graphing Class Data

Students can graph the class data for catalyst concentration, UV light intensity, and pH on Activity-Log Sheets 12, 13, and 14, respectively.

Students may need help with graphing their data. Direct them to plot time (independent variable) on the *x*-axis and concentration (dependent variable) on the *y*-axis. Help groups select appropriate units for the axes, based on the concentration data and time periods involved.

If more than one group tested a given variable, students should plot the multiple sets of data on the same sheet of graph paper. Suggest that students use a different colored pencil to plot data from each group.

Interpretations of the Data

1. Students should compare each graph they made in Part B with the graph they made in Part A, focusing on the slopes of the lines on the graphs. They should recognize that the steeper the slope, the faster the rate of photocatalytic degradation of methylene blue. Graphs should show that high catalyst concentration, UV light intensity, and pH all increase the photocatalytic degradation rate of methylene blue. In contrast, low pH has the opposite effect.

Reflections

2. Answers will vary, depending on students' predictions. Some students may have predicted that the conditions tested in Part B would have no effect on the photocatalytic degradation rate of methylene blue because the conditions tested in Part A produced a maximum effect. Other students may have predicted that the conditions tested in Part B would decrease the rate of photocatalytic degradation by reasoning that it is possible to have "too much of a good thing."

Putting It All Together

1. Photocatalysis
2. Accept all reasonable answers at this time. After reading the Expanding on the Concepts article for this activity, students can compare their explanations with those given in the article.
3. Students will probably choose a combination of high catalyst concentration, high UV light intensity, and high pH to produce the highest photocatalytic degradation rate of methylene blue. Testing would be necessary to verify the combination of conditions because the effects of the separate conditions may not be additive and may negatively impact one another.
4. Students' answers will vary. A possible advantage of using UV light is that it is found in sunlight and therefore can be used to degrade outdoor pollutants at low cost. A possible disadvantage is that UV light is harmful to humans and other organisms.

Design Connection [TO COME]

I Wonder

Students might ask questions about photocatalysis in general, such as whether it can be used to degrade air pollutants, or specifically about the photocatalytic degradation of methylene blue, such as the actual series of steps by which methylene blue is degraded during photocatalysis. Suggest that students find answers to their questions by doing research or by designing and performing experiments.

[side notes]

Estimated Time

Part A

- 50 minutes to do the activity
- 15 minutes to graph the group data

Part B

- 50 minutes to do the activity
- 30 minutes to copy and graph the class data

To Save Time

Instead of making multiple sets of the same series of standard mixtures, make only one set and photograph it. Be sure that the colors of the mixtures in the photo match the actual colors. You can then give each group a copy of the photo.

Instead of having students collect quantitative data by comparing the colors of their experimental mixtures with the colors of standard mixtures of known concentrations, they can collect qualitative data by simply observing changes in the colors of their mixtures over time.

Suggested Grouping

Groups of three or four

Activity Objectives

Students will:

- observe the photocatalytic degradation of methylene blue
- determine the photocatalytic degradation rate of methylene blue under given conditions of catalyst concentration, UV light intensity, and pH
- determine how changing those conditions (i.e., increasing catalyst concentration, UV light intensity, and pH affects the photocatalytic degradation rate of methylene blue

Connection to Chemistry

Have students research the meanings of the terms *mixture, solution,* and *suspension* and give an example of each from the activity.

Connection to Chemistry

Use this part of the activity as a review of acids and bases. After students determine the pH of the mixtures in steps 3 and 4, ask them to calculate the mixtures' hydrogen-ion and hydroxide-ion concentrations.

Connection to Math

[ED NOTE: Would anyone like to write a note that deals with the slope of a line in Math (rise/run, or $\Delta y/\Delta x$) and relate it to the activity? Perhaps students can determine the slopes of the lines they graphed? Can we get into the equation of a line?]

Assessment Tip for Part A

After students complete their graph, ask them to explain what each line on the graph shows.

Discussing the Quote

After students read the quote, ask them why they think making observations would be important to a writer, such as Ben Jonson, as well as to a scientist. Then discuss the importance of making observations during the activity. Tell students that by carefully observing and comparing the colors of different mixtures that contain a dye, they will be able to infer the concentration of the dye in those mixtures.

Discussing the Quote

Ask students how the quote applies to the activity. Lead them to recognize that the activity was informative as a result of their descriptive graphs and their analysis of the graphs.

Troubleshooting

Remind students to swirl the mixtures containing titanium dioxide before observing their colors.

Troubleshooting

Have plenty of citric acid ($C_6H_8O_6$) powder to clean up spilled NaOH solution.

Portfolio Project

Have students place their graphs into their portfolio. They might want to refer to their graphs when they do the Design Projects.

Summary of Experimental Results for Part A

Only the mixture that contains methylene blue and titanium dioxide and is exposed to UV light shows a decrease in concentration of methylene blue (decolorization) over time, indicating the degradation of the methylene blue by photocatalysis. The photocatalytic degradation of methylene blue does not occur at a constant rate, but rather slows down with time.

Summary of Experimental Results for Part B

High catalyst concentration, UV light intensity, and pH all increase the photocatalytic degradation rate of methylene blue.

Enriching Science Experience

Students might wish to test the effects of other variables, such as temperature, type of catalyst, and type of light, on the photocatalytic degradation rate of methylene blue. For example, they might wish to repeat Part A using zinc oxide as the catalyst or test the effects of sunlight, incandescent light, or fluorescent light. To test the effect of temperature, students can place mixtures in the refrigerator or heat them in a water bath prior to exposing them to UV light.

5
Exanding on the Concepts

Introducing the Topic

Bring a solar-powered device, such as a calculator, to class. Ask a volunteer to explain how the device is powered by light. (A solar cell in the device converts light energy to electrical energy.) Point out that a catalyst is involved in the process. Tell students that light energy can also be converted to other forms of energy, such as heat and chemical energy, and that catalysts may be involved in these conversions. For example, during photosynthesis, chlorophyll and other plant pigments absorb sunlight. Various catalysts (enzymes) drive reactions in which some of the captured light energy is converted to chemical energy that is needed to make nutrients, such as sugars, proteins, and fats, for the plants. The rest of the captured light energy is converted to heat.

Efficiency of Photocatalysis

The efficiency of photocatalysis in photosynthesis is approximately 30%, which means that for every 100 photons of sunlight hitting chlorophyll, 30 of them are used in photocatalysis. Human efforts in harnessing the energy of sunlight fall short of nature's highly efficient ability in photosynthesis. Solar cells, which convert sunlight to electrical energy, have an efficiency of about 15%. The efficiency of titanium dioxide is from 3 too 10%, depending on its crystalline form.

5
Introduction

In the previous activity, you worked with catalysts that are activated by heat. You learned that under a given set of conditions, different catalysts speed up a reaction at different rates and that catalysts become inactivated at different rates as well. In this activity, you will work with a catalyst that is activated by light. You will explore some of the conditions, such as concentration, temperature, and pH, that may affect the rate of catalyzed reaction.

Photocatalysis

Cleaning windows can be quite a chore. First you have to scrub the windows with detergent, then rinse them with water, and finally dry them, in hope that no streaks form. Wouldn't it be great if there were windows that could clean themselves? Well, there are, thanks to catalysis. Researchers have developed self-cleaning windows, using the catalyst titanium dioxide (TiO_2), which is usually in the form of a white powder. In this case, however, the catalyst is ground into nanometer-sized particles, which makes it transparent. The window glass is coated with the titanium dioxide nanoparticles during the manufacturing process. When exposed to sunlight, the titanium dioxide catalyzes the breakdown of dirt on the windows, which loosens the dirt and allows it to be washed away easily by rainwater. Because the coating on the glass is attracted to water, rain runs down the glass in a continuous sheet instead of beading. This sheeting action prevents streaks from forming on the glass when the rain evaporates.

[Insert photo showing water beading on regular window and water running off self-cleaning window. See photo at http://popularmechanics.com/home_improvement/smart_consumer/2002/12/self_cleaning_glass/]

Titanium dioxide and other catalysts that are activated by light are called photocatalysts, from the Greek word *phos*, meaning "light." While catalysts lower the initial energy barrier that a chemical reaction must overcome in order to proceed, they don't eliminate it. In fact, many catalysts commonly used in industry require very high temperatures and pressures, which, unfortunately, consume a lot of energy and are therefore expensive to use. The ideal catalyst, from the combined perspective of industry and the environment, is one that is activated by renewable energy, such as sunlight. Titanium dioxide is one such catalyst.

Titanium dioxide is a crystalline mineral that is obtained from certain ores. Titanium dioxide is plentiful, inexpensive, nontoxic, and stable under environmental conditions. Different crystalline forms of titanium dioxide are activated by different wavelengths of light. Some forms are activated by UV light only, whereas others are also activated by wavelengths in the visible range.

Over the past 30 years, a lot of research has been conducted on photocatalysis by titanium dioxide. It has been found, for example, that when titanium dioxide is exposed to light, powerful oxidizing molecules are formed that can degrade organic materials to carbon dioxide and water. Today, manufacturers are producing self-sterilizing, self-cleaning bathroom tiles, sinks, and toilets that are coated with a thin layer of titanium dioxide nanoparticles. **[ED. NOTE: The following sentence will be added here if the last paragraph of the article is deleted:** Not only are the nanoparticles transparent, their high total surface area increases the rate of the photocatalytic reaction.] When exposed to light, the coating breaks down organic molecules, thereby reducing odors and killing bacteria and other microorganisms. The coating also prevents dirt from settling on the fixtures. Because of their anti-microbial properties, titanium dioxide-coated tiles may be used in hospitals and other places where sanitary conditions are necessary.

Titanium dioxide also photocatalyzes the degradation of inorganic materials, such as nitrogen oxides. Recall that nitrogen oxides, which are emitted by cars and other gas-burning vehicles, contribute to smog and acid rain. In Hong Kong, for example, concrete paving blocks coated with titanium dioxide degraded more than 80% of nitrogen oxides in the air to nitrogen and oxygen.

Titanium dioxide is presently used in air filters in automobiles, homes, and buildings to help remove odors, smoke, and toxic chemicals from indoor air and to disinfect it. The ability to photocatalytically treat air, in addition to filtering it, allows for a greater degree of air recycling in buildings, which, in turn, saves energy. That is because when indoor air is recycled, it doesn’t need to be heated or cooled as often. Concerns about energy efficiency, health, and security against chemical and biological terrorist threats are all factors that are stimulating the use of photocatalysis to treat indoor air.
[ED. NOTE: I feel uncomfortable about referring to terrorism so matter of factly. Any opinions???]

[ED. NOTE: Per Prof. Chang’s request, the following nano-related paragraph has been added. Please advise whether it is too extraneous to the topic of the Intro article.]

All of the products described above utilize nanometer-sized particles of titanium dioxide. Not only are the nanoparticles transparent, their high total surface area increases the rates of the photocatalytic reactions. The products are examples of nanotechnology, a field of research that deals with nanoparticles for the purpose of developing practical applications. Researchers think that because of the unique properties of nanoparticles, they may in the future be used in ways that will significantly impact the field of pollution treatment, as well as other fields such as medicine and electronics.

Concepts Behind Environmental Catalysis

Photocatalysts are activated by light energy. The photocatalyst titanium dioxide can be used to help break down harmful organic and inorganic materials in the environment into harmless products.

5
Activity

Using Photocatalysis to Degrade a Water Pollutant

Many people today include T shirts as part of their wardrobe. T shirts are sold just about everywhere — in stores, schools, museums, and sports events — and they often have colorful images printed on them. The images are produced by a process called screen printing, in which a screen is used to transfer a pattern of dyes onto the shirt. During the process, wastewater is produced that includes excess dye. Researchers have found that photocatalysis (using UV light and the catalyst titanium dioxide) can be used to help degrade the pollutant dyes in the colored wastewater. The dyes are degraded to carbon dioxide and water in a series of steps, which decolorizes the water.

Part A
Observing the Degradation of Methylene Blue by Photocatalysis

In this part of the activity, you will use photocatalysis to degrade the dye methylene blue in a mixture that also contains water and the catalyst titanium dioxide. You will monitor the degradation of the dye by observing changes in the color of the mixture over time.

Think about these questions as you do the activity:
? How do the standard methylene blue mixtures provided by your teacher vary in color?
? How can you tell whether the methylene blue in a mixture is degrading?
? What is needed for photocatalysis to occur?
? How does catalyst concentration affect the photocatalytic degradation rate of methylene blue?
? How does light intensity affect the photocatalytic degradation rate of methylene blue?
? How does pH affect the photocatalytic degradation rate of methylene blue?

Design Connection [To come]

[Quotes]

I do love to note and to observe.
Ben Jonson
English playwright

Science is analytical, descriptive, informative.
Eric Gill
British writer and sculptor

Prediction

After you read the procedure, predict which methylene blue mixture(s) will become decolorized. Record your prediction and your reason for making it.

Make a data table with space to record:

- prediction about which methylene blue mixture(s) will become decolorized and your reason for making the prediction
- relationship between the color of a mixture and its concentration of methylene blue
- concentration of methylene blue in each test tube at the beginning of the activity
- inferred concentration of methylene blue in each test tube after each 5-minute time interval

Gather these materials:

- UV safety glasses, apron, and gloves
- set of six standard methylene blue mixtures that vary in the concentration of the dye
- set of six standard methylene blue-titanium dioxide (1 g/L) mixtures that vary in the concentration of the dye
- 4 Pyrex test tubes
- test tube rack
- marker
- methylene blue (10 mg/L) mixture
- methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- graduated cylinder
- aluminum foil
- UV lamp
- stopwatch, or watch with second-counting ability
- graph paper

Procedure, Data, and Observations

Safety Note: *Wear UV safety glasses, an apron, and gloves.*

1. Obtain from your teacher two sets of "standard" methylene blue mixtures. Each set consists of six mixtures that vary in the concentration of the dye. Notice that the mixtures that make up one of the sets also contain the catalyst titanium dioxide, but all in the same concentration, 1 g/L. Compare the colors of the mixtures within each set. The mixtures containing titanium dioxide should be swirled gently before comparing their colors. ***CAUTION:*** *Methylene blue is an eye and skin irritant. Flush with plenty of water should any contact occur. Avoid contact with clothing.* Based on your observations, record in your data table the relationship between the color of a mixture and its concentration of methylene blue. Save the two sets of standard mixtures for step 5. You will use them to infer the concentration of methylene blue in unknown mixtures.
2. Label four Pyrex test tubes as shown below and place them in a test tube rack next to a wall.

[Insert illustration showing four labeled test tubes: *dye + no UV; dye + UV; dye + catalyst + no UV; dye + catalyst + UV]*

3. Your teacher will provide a mixture containing methylene blue (10 mg/L) and a mixture containing methylene blue (10 mg/L) plus titanium dioxide (1 g/L). Add 5 mL of each mixture to each appropriately labeled test tube. Gently swirl the mixture containing titanium dioxide before dispensing it. Record in your data table the concentration of methylene blue in each test tube.
4. Cover the two test tubes labeled *no UV* with aluminum foil. Then use a UV lamp to irradiate the other two test tubes for 5 minutes. Hold the lit surface of the lamp up against the test tubes, making sure the UV light is pointed at the wall behind the tubes. ***CAUTION:*** *Be sure the UV light is pointed away from everyone in the room.* Gently swirl the mixtures in all the test tubes about once per minute.
5. After 5 minutes, turn off the UV lamp and remove the aluminum foil from the non-irradiated tubes. Compare the colors of the mixtures in your test tubes with the colors of the appropriate set of standard mixtures you observed in step 1. Gently swirl the mixtures containing titanium dioxide before comparing them. From your comparisons, infer the concentration of methylene blue in each of your test tubes. Record the concentrations in your data table.
6. Repeat steps 4 and 5 five more times, for a total of 30 minutes.
7. Using your data, make a graph that shows the concentration of methylene blue in each of your test tubes over the 30-minute time period.
8. Return the two sets of standard mixtures to your teacher. The mixtures in your test tubes can be disposed of by pouring them down the sink drain and flushing with plenty of water.

Interpretations of the Data

1. In which mixture did the methylene blue degrade? How do you know?
2. Why did the methylene blue degrade in that mixture but not in the others?
3. After how much time did you first observe a change in the concentration of methylene blue?
4. Did all the methylene blue in the mixture appear to have degraded at some point? Explain.
5. Does the photocatalytic degradation of methylene blue proceed at a constant rate or does it slow down with time? Use your graph to support your answer.

Reflections

6. How was it helpful to use the standard mixtures?
7. Which mixtures in your test tubes were the controls? What did they show?
8. Was your prediction correct? If not, explain why you think you made an incorrect prediction.

Part B
Testing Variables That May Affect Photocatalysis

In this part of the activity, the groups in your class will test the effects of three variables – catalyst concentration, UV light intensity, and pH – on the photocatalytic degradation rate of methylene blue. Each group will test one variable (as assigned by your teacher), share their data with other groups in the class, graph the class data, and then use the graphs along with their graph from Part A to draw conclusions about the effect of each variable.

Testing Catalyst Concentration

Prediction

Predict the effect of high catalyst concentration on the photocatalytic degradation rate of methylene blue. Record your prediction and your reason for making it.

Make a data table with space to record:

- prediction about the effect of high catalyst concentration on the photocatalytic degradation rate of methylene blue and your reason for making the prediction
- concentration of methylene blue in each test tube at the beginning of the activity
- inferred concentration of methylene blue in each test tube after each 5-minute time interval

Gather these materials:

- UV safety glasses, apron, and gloves
- set of six standard methylene blue-titanium dioxide (3 g/L) mixtures that vary in the concentration of the dye
- 2 Pyrex test tubes
- test tube rack
- marker
- methylene blue (10 mg/L)-titanium dioxide (3 g/L) mixture
- graduated cylinder
- aluminum foil
- UV lamp
- stopwatch, or watch with second-counting ability

Procedure, Data, and Observations

Safety Note: *Wear UV safety glasses, an apron, and gloves.*

1. Obtain from your teacher a set of standard methylene blue-titanium dioxide mixtures that vary in the concentration of the dye but have the same concentration of the catalyst, 3 g/L. You will use the standards in step 5.
2. Label two test tubes as shown below and place them in a test tube rack next to a wall.

[Insert illustration showing four labeled test tubes: *dye + catalyst 3 g/L + no UV; dye + catalyst 3 g/L + UV.*]

3. Your teacher will provide a mixture containing methylene blue (10 mg/L) and titanium dioxide (3 g/L). Gently swirl the mixture and transfer 5 mL to each test

tube. ***CAUTION:*** *Methylene blue is an eye and skin irritant. Flush with plenty of water should any contact occur. Avoid contact with clothing.* Record in your data table the concentration of methylene blue in each test tube.

4. Cover the test tube labeled *no UV* with aluminum foil. Then use a UV lamp to irradiate the other test tube for 5 minutes. Hold the lit surface of the lamp up against the test tube, making sure the UV light is pointed at the wall behind the tube. ***CAUTION:*** *Be sure the UV light is pointed away from everyone in the room.* Gently swirl the mixture in both test tubes about once per minute.
5. After 5 minutes, turn off the UV lamp and remove the aluminum foil from the non-irradiated tube. Compare the colors of the mixtures in your test tubes with the colors of the standard mixtures you obtained in step 1. Gently swirl all mixtures before comparing them. From your comparisons, infer the concentration of methylene blue in each of your test tubes. Record the concentrations in your data table.
6. Repeat steps 4 and 5 five more times, for a total of 30 minutes.
7. Record all your data on the chalkboard for other groups to copy.
8. Return the set of standard mixtures to your teacher. The mixtures in your test tubes can be disposed of by pouring them down the sink drain and flushing with plenty of water.

Testing UV Light Intensity

Prediction

Predict the effect of high UV light intensity on the photocatalytic degradation rate of methylene blue. Record your prediction and your reason for making it.

Make a data table with space to record:

- prediction about the effect of high UV light intensity on the photocatalytic degradation rate of methylene blue and your reason for making the prediction
- concentration of methylene blue in each test tube at the beginning of the activity
- inferred concentration of methylene blue in each test tube after each 5-minute time interval

Gather these materials:

- UV safety glasses, apron, and gloves
- set of six standard methylene blue mixtures that vary in the concentration of the dye
- set of six standard methylene blue-titanium dioxide (1 g/L) mixtures that vary in the concentration of the dye
- 2 Pyrex test tubes
- test tube rack
- marker
- methylene blue (10 mg/L) mixture
- methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- graduated cylinder
- aluminum foil

- 2 UV lamps
- 2 file folders
- stopwatch, or watch with second-counting ability

Procedure, Data, and Observations

***Safety Note:** Wear UV safety glasses, an apron, and gloves.*

1. Obtain from your teacher the two sets of standard mixtures you used in Part A. You will use both sets in step 6.
2. Label two Pyrex test tubes as shown below and place them in a test tube rack.

[Insert illustration of two test tubes labeled: *dye + 2 UV lamps; dye + catalyst + 2 UV lamps*]

3. Your teacher will provide a mixture containing methylene blue (10 mg/L) and a mixture containing methylene blue (10 mg/L) plus titanium dioxide (1 g/L). Add 5 mL of each mixture to each appropriately labeled test tube. Swirl the mixture containing titanium dioxide before dispensing it. ***CAUTION:** Methylene blue is an eye and skin irritant. Flush with plenty of water should any contact occur. Avoid contact with clothing.* Record in your data table the concentration of methylene blue in each test tube.
4. Position two UV lamps on opposite sides of the test tubes as shown below. While the lamps are UNPLUGGED, turn on the switch on each lamp. ***CAUTION:** Use file folders to form a protective screen that completely encloses the UV lamps, as shown below. The screen will prevent you and others in the room from being exposed to the UV light.*
5. Turn on both lamps by plugging them into an electrical outlet. Irradiate both test tubes for 5 minutes. Gently swirl the mixtures in the test tubes about once per minute. Be careful not to knock down the screen when you reach over it to swirl the mixtures.

[Insert illustration of how to set up the screen.]

6. After 5 minutes, turn off both UV lamps by unplugging them. Do not turn off their switches. Compare the colors of the mixtures in your test tubes with the colors of the appropriate set of standard mixtures you obtained in step 1. Gently swirl all mixtures containing titanium dioxide before comparing them. From your comparisons, infer the concentration of methylene blue in each of your test tubes. Record the concentrations in your data table.
7. Repeat steps 5 and 6 five more times, for a total of 30 minutes.
8. Record all your data on the chalkboard for other groups to copy.
9. Return both sets of standard mixtures to your teacher. The mixtures in your test tubes can be disposed of by pouring them down the sink drain and flushing with plenty of water.

Testing pH

Prediction

Predict the effect of high pH on the photocatalytic degradation rate of methylene blue. Record your prediction and your reason for making it.

Make a data table with space to record:

- predictions about the effect of high pH on the photocatalytic degradation rate of methylene blue and your reason for making each prediction
- concentration of methylene blue in each test tube at the beginning of the activity
- inferred concentration of methylene blue in each test tube after each 5-minute time interval

Gather these materials:

- UV safety glasses, apron, and gloves
- set of six standard methylene blue-NaOH mixtures that vary in the concentration of the dye
- set of six standard methylene blue-NaOH-titanium dioxide (1 g/L) mixtures that vary in the concentration of the dye
- 4 Pyrex test tubes
- test tube rack
- marker
- methylene blue (10 mg/L) mixture
- methylene blue (10 mg/L)-titanium dioxide (1 g/L) mixture
- graduated cylinder
- pH paper
- medicine dropper
- base (NaOH) solution
- aluminum foil
- UV lamp
- stopwatch, or watch with second-counting ability

Procedure, Data, and Observations

Safety Note: *Wear UV safety glasses, an apron, and gloves.*

1. Obtain from your teacher two sets of standard methylene blue mixtures. One set is made up of mixtures that contain methylene blue and the base sodium hydroxide (NaOH), in varying concentrations of the dye. The other set is made up of mixtures that contain methylene blue, titanium dioxide, and NaOH, in varying concentrations of the dye. You will use both sets of standards in step 6.
2. Label four Pyrex test tubes as shown below and place them in a test tube rack.

[Insert illustration of eight test tubes labeled: *dye + base + no UV; dye + base +UV; dye + catalyst + base + no UV; dye + catalyst + base + UV*]

3. Your teacher will provide a mixture containing methylene blue (10 mg/L) and a mixture containing methylene blue (10 mg/L) plus titanium dioxide (1 g/L). Add 5 mL of each mixture to each appropriately labeled test tube. Swirl the mixture containing titanium dioxide before dispensing it. ***CAUTION:*** *Methylene blue is an eye and skin irritant. Flush with plenty of water should any contact occur. Avoid contact with clothing.* Use pH paper to measure the pH of the mixture in each test tube. Record the pHs in your data table. Also record in your data table the concentration of methylene blue in each test tube.
4. Add 1 drop of NaOH solution to each test tube. ***CAUTION:*** *The NaOH solution is caustic. Handle it with care. Flush with plenty of water should any contact with eyes or skin occur. Avoid contact with clothing.* Gently swirl the mixture in each tube. Use pH paper to determine the pH of each mixture. Record the pHs in your data table.
5. Cover the two test tubes labeled *no UV* with aluminum foil. Then use a UV lamp to irradiate the other two test tubes for 5 minutes. Hold the lit surface of the lamp up against the test tubes, making sure the UV light is pointed at the wall behind the tubes. ***CAUTION:*** *Be sure the UV light is pointed away from everyone in the room.* Gently swirl the mixtures in all the test tubes about once per minute.
6. After 5 minutes, turn off the UV lamp and remove the aluminum foil from the non-irradiated tubes. Compare the colors of the mixtures in your test tubes with the colors of the appropriate set of standard mixtures you obtained in step 1. From your comparisons, infer the concentration of methylene blue in each of your test tubes. Record the concentrations in your data table.
7. Repeat steps 5 and 6 five more times, for a total of 30 minutes.
8. Record all your data on the chalkboard for other groups to copy.
9. Return both sets of standard mixtures to your teacher. The mixtures in your test tubes can be disposed of by pouring them down the sink drain and flushing with plenty of water.

Graphing Class Data

Copy onto separate data tables the data that the different groups in your class recorded on the chalkboard. On a separate sheet of graph paper, graph the data that relates to the effect of catalyst concentration on the photocatalytic degradation rate of methylene blue. Do the same for the effect of UV light intensity and the effect of pH. Use these graphs in conjunction with the graph you made in Part A to help you interpret your data.

Interpretations of the Data

1. What was the effect of high catalyst concentration on the photocatalytic degradation rate of methylene blue? Effect of high UV light intensity? Effect of high pH? Explain your answers based on your graphs.

Reflections

2. How did the class results compare with your predictions? Did any of the results surprise you? Explain.

Putting It All Together

1. What is required for methylene blue to degrade?
2. What do you think is the reason each variable – catalyst concentration, UV light intensity, and pH – had the effect you observed?
3. Based on the results of the activity, what combination of conditions do you think would produce the highest rate of photocatalytic degradation of methylene blue? Would more testing be needed to verify the combination you chose? Explain your answer.
4. What would be an advantage of using UV light to degrade a pollutant? A disadvantage?

Design Connection [TO COME]

I Wonder

What new questions do you have about photocatalysis? Write down three or more questions you have. Give a reason for asking each question.

Research and Educational Activities

Catalysis is the essential process technology for the production of most chemicals and for the treatment of emissions in the United States. Its importance for reducing human impact on the environment was emphasized in the reports from two workshops cosponsored by NSF and DOE: "Basic Research Needs for Environmentally Responsive Technologies of the Future" and "Basic Research Needs for Vehicles of the Future."

The scientific focus for the IEC derives from the recognition that the understanding and improvement of one type of reaction, the selective catalytic oxidation of organic compounds, could reduce the environmental impact of a broad range of industrial activities. The removal of NOx from combustion exhaust, the more efficient use of fossil fuels for energy production, the "clean" production of many useful chemicals, the removal of pollutants from waste water streams, and the transformation of pollutants to biodegradable forms can all be improved by advances in the controlled catalytic oxidation of organic compounds. In the report from a workshop held March 1997 and sponsored by the Council for Chemical Research, the U.S. Department of Energy, and the American Chemical Society: "Catalyst Technology Roadmap Report", selective oxidation was ranked as the most important catalyst technology for the improvement of catalytic processes.

Catalysis also plays a major role in the cleanup of aqueous waste streams. Transformations of organic and inorganic contaminants are dominated by microbial catalysis. The microorganisms can be viewed as microscopic reactors that contain a host of enzyme catalysts and are self-propagating. As hosts of catalysts, microorganisms catalyze a suite of reactions, often leading to full detoxification and recycling of the elements. The overall process of organic waste detoxification is oxidation to CO_2 or insoluble carbonates. Thus, oxidation catalysis also plays a major role in biologically based contaminant removal.

The Institute for Environmental Catalysis (IEC) was established to:

1) Understand catalytic oxidation at the molecular level as it occurs both in chemicals and emissions processing and in the natural environment;

2) Work closely with industry in the application of this new knowledge to make commercial processes more environmentally friendly;

3) Train scientists and engineers with an integrated, interdisciplinary approach to research and problem solving;

4) Establish a national resource for catalytic solutions to environmental problems;

5) Educate the public about the role of catalysis in manufacturing and environmental preservation.

The research activities of IEC involve 21 Northwestern University faculty in five academic department and comprise 12 projects organized into 4 Collaborative Research Groups (CRG). The education and outreach components include 3 major programs for industrial outreach, high school and secondary school science teacher training, and development of a “hands-on” kit for K-12 science education.

These activities are summarized in the remainder of the document.

CRG: Molecular Science of Catalytic Oxidation

Project: *In-situ* Characterization and Atomic Structure

The objective is to provide experimental characterization of structure, chemical composition, reaction pathways, and theoretical interpretation required for a molecular level understanding of the chemistry studied in the IEC projects. This project encompasses a number of separate activities.

X-ray Synchrotron Methods:

Chemical and physical interactions at oxide surfaces control the oxidation activity and selectivity of metal oxide catalysts. The same statement can be made with regard to the transport behavior and bioavailability of hazardous metal contaminants and radionuclides in soils and groundwater systems. Atomic-scale structural information on metal speciation and reaction mechanisms at the oxide-gas and mineral-water interfaces is required to achieve a fundamental understanding of these interactions. Synchrotron-based measurement techniques, including X-ray absorption spectroscopy (XAS), X-ray standing wave (XSW), X-ray reflectivity and grazing incidence X-ray scattering, are utilized to provide *in-situ* atomic-scale information about ion adsorption at single-crystal oxide-gas and mineral-fluid interfaces. These techniques can also be applied to study the complex surface phases of organic molecules adsorbed on metal-oxide surfaces.

X-ray scattering studies of the UHV prepared (0001) surface of α-Fe2O3 (hematite) were performed in combination with LEED, AES, and XPS. The goal of this investigation was to characterize the atomic-scale structure of the Fe-terminated and O-terminated (0001) surfaces of hematite and to relate this structural information to catalytic activity on these two surfaces. X-ray crystal truncation rod (CTR) data was collected along several rods for the Fe-terminated surface.

The site-specific valence electronic structure of α-Fe_2O_3 was measured using a spatially modulated X-ray standing wave as the excitation source to separate valence band photoemission from iron and oxygen atoms. Contributions to valence band density of states from oxygen and iron ions are separated by this technique.

In-situ XSW measurements pin pointed the adsorption sites on $TiO_2(110)$ of Rb^{+1}, Sr^{+2}, Zn^{+2}, and Y^{+3} ions from an aqueous solution.

Ultraviolet Raman Spectroscopy:

Ultraviolet Raman spectroscopy is a powerful tool for measuring the vibrational spectrum of samples under *in-situ* reaction or environmental conditions. A new reaction cell based on a fluidized bed has been used to study the molecular state of oxygen in selective oxidation catalysts based on iron-oxo dimers in H-MFI zeolite. A new, low-temperature fluidized bed Raman cell was designed and constructed in order to study the formation of superoxide ions in the Fe/MFI system. This cell makes it possible to perform fluidized bed measurements at liquid nitrogen temperature. The results of this study are described in the section on lean NOx reduction. Experiments have also been conducted to determine the feasibility of detecting changes in atomic structure on metal oxide surfaces using UV Raman spectroscopy. Measurements on $SrTiO_3$ crystals with surface reconstructions but identical bulk structures have been performed as a proof-of-concept of this approach.

Broadband Sum Frequency Generation:

The BBSFG studies are carried out using an 800-nm 120-femtosecond regeneratively amplified Ti:Sapphire system (Hurricane, Spectra Physics) operating at a kilohertz repetition rate. The Hurricane system pumps an optical parametric amplifier (OPA-800CF, Spectra Physics) containing a β-barium borate (BBO) crystal for signal and idler generation and an $AgGaS_2$ crystal for difference frequency generation. The BBO crystal generates a signal beam between 1.1 and 1.6 μm and an idler beam between 1.6 and 2.6 μm that are mixed in the DFG crystal to produce infrared radiation between 3 and 10 μm. Figure 4 illustrates the layout of the BBSFG system.

To overcome the challenges associated with BBSFG spectroscopy of transparent insulating substrates with negligible non-resonant contributions to the SFG signal, a step-by-step experimental approach was taken. First, the BBSFG spectrum of thin gold samples was recorded since this metal surface has high non-resonant contributions to the SFG signal, which make them optimal for initial alignment. Then, the BBSFG spectrum of octadecanethiol (ODT) on gold was taken in order to optimize alignment and signal delivery (Fig. 5). Subsequently, the BBSFG spectra of dimethylsulfoxide (DMSO) and of polymethylmethacrylate (PMMA) on glass were recorded. This allowed for the optimization of the BBSFG setup for transparent substrates and provided a spectral calibration standard. Further, the relatively strong SFG signals from these samples enabled us to improve the signal-to-noise ratio using binning and signal averaging techniques, and to assess the spectral resolution of the experiment. Finally, the BBSFG spectra of various functionalized siloxanes on glass were recorded.

High-Resolution Electron Microscopy:

Ultrahigh vacuum, atomic resolution transmission electron microscopy provides surface and subsurface atomic structural information. The objective of this project is to study the surface structures of various catalytic transition metal oxides using Transmission Electron Diffraction (TED) and High-Resolution Electron Microscopy (HREM). We have studied the surface reconstructions of α-Fe_2O_3 (0001) and $SrTiO_3$ (111) using Direct Methods applied to X-ray diffraction data. The atomic surface structure of $SrTiO_3$ has been solved for two of the reconstructions observed in oxidizing conditions. More reconstructions have been observed and are in the process of being solved. Interesting similarities and trends have been observed among the reconstructions, providing insight into how oxide surfaces behave and what their structures are under various temperatures and atmospheres.

The reduction of bulk $Mg_3V_2O_8$ has been investigated, and we have observed single crystals transform from the oxidized phase to the reduced phase. We have shown that the transformation occurs via cation migration among a nearly stationary oxygen lattice. In addition, we have performed preliminary oxidation/reduction experiments in attempt to modify surfaces and determine changes in chemistry. Further oxidation/reduction experiments are to be carried out using a unique UHV surface science system (SPEAR) and a UHV H-9000 microscope.

A new chamber for gas exposures, integrated into the UHV HREM instrument to allow structural studies without sample contamination by either exposure to air or poor microscope vacuum, is currently near completion. The chamber will allow us to perform oxidation/reduction experiments *in-situ* on various catalytic transition metal oxide systems. The chamber includes 2 different sample locations: (a) chemical adsorption with low-pressure gas dosing (10^{-5} torr range); (b) high-pressure (up to 1 atm.) gas treatment. Both locations include heating of samples up to 1200ºC. Various gases (H_2, O_2, CO_2, H_2O, light alkanes, etc.) may be introduced into the chamber using a gas manifold. TEM samples of $Mg_3(VO_4)_2$, suitable for oxidation/reduction experiments, are also currently being prepared.

Scanning Probe Microscopy

The objective of this effort was to study the morphology and atomic step structure on hematite (α-Fe_2O_3) surfaces with atomic force microscopy (AFM). In particular, mineral hematite and chemical vapor transport (CVT) grown hematite samples were studied following a variety of annealing conditions in an effort to identify atomically flat hematite (0001) surfaces suitable for subsequent studies. Following annealing in oxygen-rich environments, the CVT hematite (0001) surface was observed to develop large (tens of microns in spatial extent) atomically flat terraces bounded by highly stepped regions. The atomically flat terraces possess circular depressions that are hundreds of nanometers in diameter and only 2.2 ± 0.2 Å deep. This unique surface morphology is exceptionally stable in air at room temperature as determined by AFM images taken before and after storage in ambient conditions for several months.

Following this work on hematite (0001), analogous studies were performed on $SrTiO_3$ and TiO_2 surfaces. On samples with low miscut angles, similar step morphologies were observed following annealing in oxygen-rich environments, thus suggesting that this phenomenon may be a general feature of oxide surfaces. Discussions have been initiated with Prof. Mark Asta of the Materials Science and Engineering Department regarding theoretical models that may explain these interesting experimental observations.

Transient Infrared Spectroscopy

Time resolved laser based techniques, particularly time resolved infrared spectroscopy, are used to probe kinetic and dynamical properties of systems. The IEC work focuses on the application of these and related techniques to processes taking place in zeolites and on titania surfaces. The projects in this area are part of work in the Emissions Treatment CRG and are described in detail in the relevant sections of this report.

In-situ NMR Spectroscopy

The pulsed field gradient (PFG) NMR technique is a reliable and convenient method for measuring molecular diffusivities of various systems. We have made an improvement on our PFG-NMR system in both hardware and software. We installed air and water cooling lines to utilize the full capacity of our PFG-NMR probe, which will be very important in measuring smaller diffusivities. The system is also equipped with an improved pulse sequence to minimize the side effect of eddy currents caused by short delays between RF pulses and field gradient pulses.

PFG-NMR has been employed along with MAS-NMR to address some aspects of diffusion in 1-hexene epoxidation catalyzed by titanium silicalite-1 (TS-1) as part of the project on selective oxidation of olefins to epoxides.

Project: Surface Science of Catalytic Oxidation

The objectives of this project are 1) determine the geometric and electronic structure of single crystal metal oxide surfaces that are active for hydrocarbon oxidation; 2) study the adsorption of alkyl radicals on these surfaces; 3) elucidate the oxidation reaction pathways for the adsorbed alkyl groups; and 4) understand the relationship between the physical and chemical properties.

Experiments

Experiments at Northwestern make use of an ultrahigh vacuum surface science instrument that has been modified for studies of methyl and ethyl group oxidation on oxide surfaces. Experiments at the Advanced Photon Source make use of the UHV MBE Surface Chamber at the DND-CAT undulator beamline.

The research has focused on the (0001) surface of α-Fe_2O_3. Two types of hematite samples have been obtained for these studies: an MBE grown Fe_2O_3 film from Scott Chambers at EMSL, and a natural single crystal of mineralogical origin.

High-resolution x-ray scattering and standing wave measurements have been performed on the UHV prepared (0001) surface of a mineralogical α-Fe_2O_3 single crystal in combination with LEED, AES, and XPS as alluded to above. High resolution UHV HREM measurements have begun to establish the relationship between low pressure surface exposure to atomic oxygen and the surface atomic structure. The objective is to determine if an oxygen terminated surface, which is normally only produced by surface annealing in atmospheric pressure oxygen, can be obtained using an atomic oxygen exposure.

This year has seen the culmination of several years' work resulting in a coherent understanding of methyl group surface chemistry. Hematite (0001) surfaces with several termination structures, Fe/O stoichiometries, and containing added chlorine and uranium atoms have been exposed to gas phase methyl radicals in order to produce adsorbed methyl groups. The surfaces were then heated to produce chemical reactions and desorption of reaction products.

Theory

In support of experimental programs, theory seeks to analyze surface structural configurations and their associated electronic structures by a hybrid mix of classical atomistic simulations and quantum mechanical Density Functional methods. Second-generation Order(N) Divide & Conquer (DAC) schemes are being developed to facilitate study of nanoscale features, and to form part of a feedback loop including parametrized interatomic potentials.

(1) The relaxed and defected hematite (0001) surface has been used as a 'test bed' for study of oxide interactions with atoms and small molecules, including H, OH, H_2O, and CH_3

(2) The substitution of iron, zinc and lead in hydroxyapatite (HAP) have been modeled. Lattice relaxation around the impurity has been calculated using semiempirical potentials, and resulting electronic structure has been evaluated. Charge distributions, spin densities, X-ray absorption profiles and Mössbauer hyperfine parameters have been calculated and compared with available experiment.

(3) The reconstructed (001) surface of $SrTiO_3$ observed by Marks et al. with TiO_2 termination has been studied in a collaborative effort involving Direct Methods of X-ray surface analysis (L. Marks, NU), atomistic simulations to determine positions of 'invisible' atoms, DF pseudopotential band structures (M. Asta, NU), and DAC embedded cluster studies of local electronic distributions. We have extended band structure studies of a number of the possible reconstructions of TiO_2 – rich $SrTiO_3$ (001) surfaces, in an effort to extract systematic stability rules and to understand the role of oxygen vacancies,defects, and vibrational entropy in determining surface free energies.

(4) Further coding of a more efficient DAC II scheme has been carried out; as a benchmark, electronic densities, atomic configurations, electrostatic potential maps, and Fukui indices were calculated for the 1AAG protein with 3365 atoms.

(5) Generalized Simulated Annealing techniques have been extended to better treat reactive bonding and film growth at surfaces. The role of oxygen vacancies in setting structural patterns for TiO_2 has been been studied in a preliminary analysis. Defect structures of bulk and nanoparticulate Indium Tin Oxide (ITO) were analyzed in conjunction with X-ray and neutron experiments, setting the stage for future studies on ITO surface chemical composition and structure.

CRG: Chemical Processing

Project: Synergistic Multimetallic Oxidation Catalysts

Crystal Growth

One objective of this research is to grow single crystals of Fe_2O_3, $Mg_3V_2O_8$, $Mg_{2.5}VMoO_8$, and $MgMoO_4$, and to characterize their surfaces in order to understand the process of oxidative dehydrogenation, which occurs in some unknown way when alkanes react with these oxides. After annealing the crystals in O_2 at 500°C to reduce the damage of the surface caused by the sample preparation, the surface structure can be studied using TEM, XPS, Raman, and FTIR. The adsorption and reaction of various gases (hydrogen, oxygen, and methyl radicals) on the crystal surface can be studied again using XPS, Raman, and FTIR. The spectra obtained will be examined to see if peak shifts occur after the reaction. The XPS data should show which atoms on the surface bind the adsorbed species, while the Raman and FTIR should show shifts in the metal-oxygen bonds. Recently, high quality single crystals of $Mg_3V_2O_8$ have been prepared using a floating zone furnace. Polycrystalline samples of $Mg_3V_2O_8$ have been prepared, and several alternative preparation methods are under development.

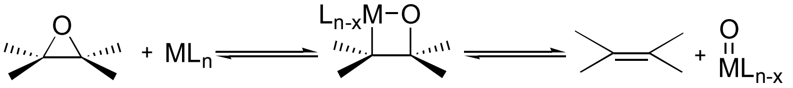
Catalytic and Surface Studies

Surface science techniques (XPS, Raman, TPD, TEM, etc.) are used to elucidate the reactions between the surface of the oxide, the alkane, and the oxidant.

A second area of research involves preparing high-surface area, polycrystalline powders of the above crystals. Propane oxidation over seventeen samples of Mo, Mo-V, or V catalysts from the MgO-V_2O_5-MoO_3 system have been measured under industrial conditions at Dow Chemical Corporation and BP Amoco. The product selectivity was examined and insight gained on the function of acidic molybdenum and how the selectivity of the alkenes is affected. TEM specimens of $Mg_3(VO_4)_2$ with two different orientations (100) and (20-1) have been obtained and characterized through a series of annealing experiments and subsequent TEM observations. Finally, many UV-Raman experiments have been conducted to study the surfaces of $Mg_3(VO_4)_2$.

Catalytic Epoxidation Mechanism

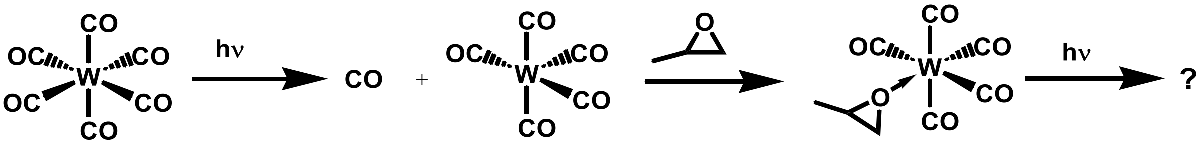
A third project is focused on the identification and characterization of the intermediates that occur in the transition metal promoted epoxidation of olefins, and in the reverse reaction, the deoxygenation of epoxides back to olefins (eq 1). A metallaoxetane has been proposed as a possible intermediate in such a reaction. We have focused on investigating the deoxygenation of epoxides using transition metal carbonyl compounds. The carbonyls serve as spectroscopic handles for monitoring reaction progress in the infrared, as well as providing a labile ligand for photochemical reactions, and a useful ligand for insertion reactions. The goal is to obtain spectroscopic evidence for the intermediate(s) in this type of reaction and, if a metallaoxetane intermediate is found and isolated, to study other chemical reactions involving this species.



(1)

Previous work has focused on examination of a variety of transition metal carbonyl complexes, primarily focusing on those of molybdenum and tungsten. Both their reactivity towards epoxides, and the practicability of working with the compound and obtaining data from it were examined. The result of this portion of the project was the discovery of a number of isolable carbonyl complexes showing reactivity toward epoxides. Equipment and methods were designed to study these compounds, and using these methods to perform studies on one of the reactive compounds, tungsten hexacarbonyl. $W(CO)_6$ was chosen as the first compound to be studied because, in addition to its inexpensiveness and ease of handling, it has a relatively high vapor pressure at room temperature. This is necessary to study the compound in a low temperature matrix. For compounds other than those with a formula $M(CO)_6$ (M = Cr, Mo, W) the vapor pressures are generally too low for quality matrix study and a system was designed to study these compounds in low temperature glasses.

An objective is to examine photochemically activated reactions of $W(CO)_6$ with propylene oxide (po) in a low temperature (60K) propylene oxide matrix (ratio of $W(CO)_6$:po = ~1:1000)

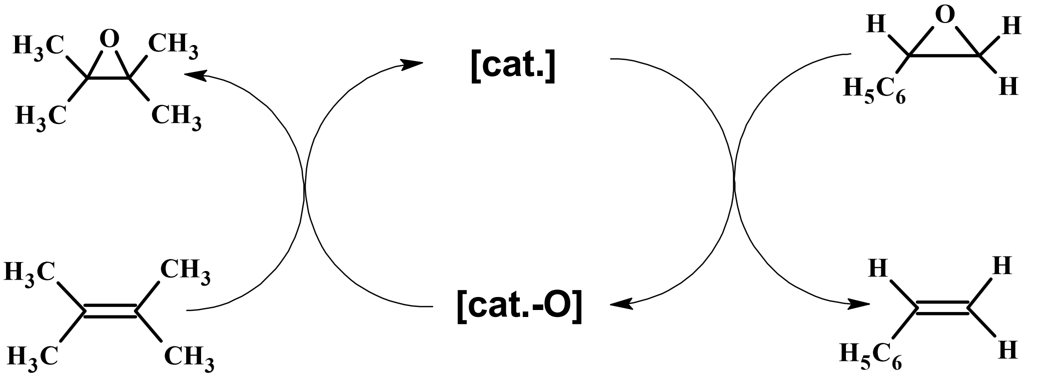


Equation 2. Reaction of propylene oxide with $W(CO)_6$ in a matrix

Trans-Epoxidation

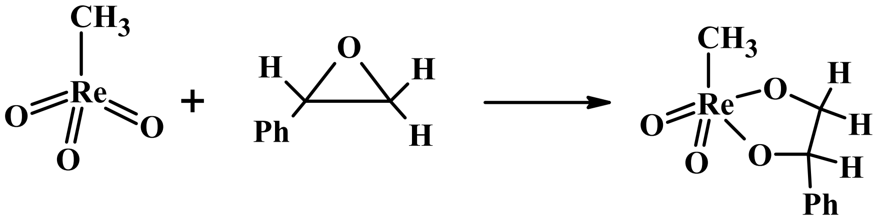
An alternate synthesis strategy for epoxides is to use a readily available epoxide as a source of oxidant. Thus the objective of this work is to investigate this trans-epoxidation approach using methyltrioxorhenium(VII) (abbreviated as MTO). The overall trans-epoxidation reaction, as depicted in scheme 1 as an example, can be viewed as a two-step process: oxygen transfer from an epoxide to the catalyst and its subsequent incorporation into an alkene to form another epoxide.

In the first phase of this investigation, we studied the interaction of styrene oxide with MTO. It has been shown that the reaction of MTO with styrene oxide is very slow in dried chloroform. However, in wet chloroform a Re(VII)-diolate complex formed quantitatively. It is assumed that styrene oxide is hydrolyzed to diol before it reacts with MTO, and trace amount of H_2O is the catalyst for this reaction. We investigated the possibility of releasing styrene from the Re(VII)-diolate complex. We found that the Re(VII)-diolate complex cannot release styrene by the means we have tried, including warming in chloroform solution for a couple of days, adding a coordinating reagent such as pyridine, heating the solid to 120 °C. Therefore, for the purpose of deoxygenation, formation of diolate complex should be prevented.



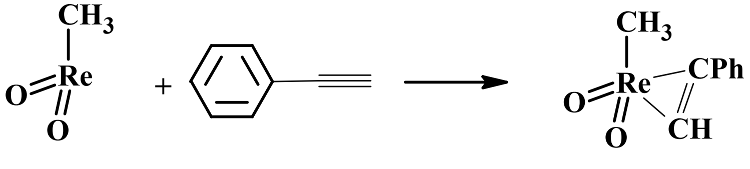
Scheme 1

Further studies revealed that, in the presence of a pyridine derivative in dried chloroform, formation of Re(VII)-diolate has been prevented and styrene oxide is deoxygenated by MTO. Since deoxygenation is an important part of the overall trans-epoxidation reaction, we investigated the mechanism of deoxygenation reaction.



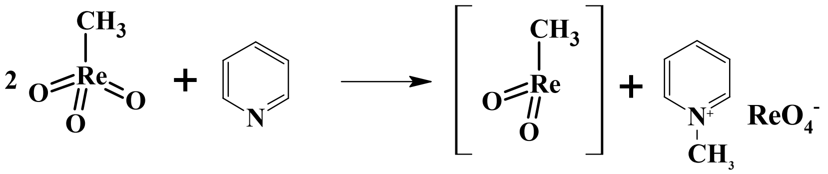
(1)

Deoxygenation of epoxides reported in literature were generally associated with Re(V) species. To verify the role of Re(V) in the deoxygenation of styrene oxide by MTO, phenylacetylene was introduced into the reaction. In the presence of phenylacetylene, formation of styrene was blocked, and a methyl dioxo rhenium-phenylacetylene adduct was formed, as shown in eq. 2. This clearly indicated that methyl dioxo rhenium (MDO) is an intermediate in the deoxygenation reaction.



(2)

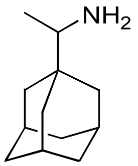
Re is in the +7 oxidation state in MTO, MDO originated from transfer of methyl group from MTO to pyridine to form methyl pyridinium ion and perrhenate. (eq. 3). The formation of methyl pyridinium has been confirmed by comparison with methylpyridinium iodide NMR spectrum. The formation of perrhenate was confirmed by FT-IR.

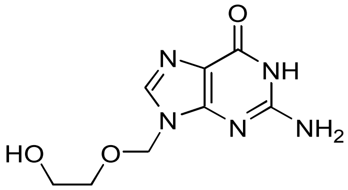


(3)

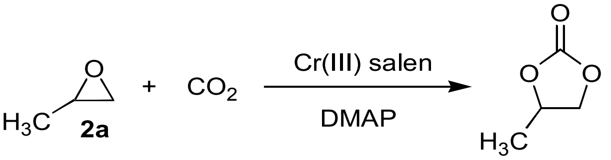
Cyclic Carbonate Formation

A fourth area focuses on the catalytic reaction of CO_2 with epoxides to form cyclic carbonates and/or polycarbonates (eq 3) is a rare example of an efficient and economical utilization of an alternative carbon source. During the past several decades, numerous catalyst systems have been developed for this transformation, and while the advances have been significant, all suffer from low catalyst stability/reactivity, air sensitivity, the use of solvent, the requirement for high pressure and/or high temperatures.





Equation 3



(2)

Project: Selective Oxidation in Zeolites

Cobalt Clusters

The general objective of this project is to use computational chemistry to better understand oxidation catalysis on metal-exchanged zeolites. Together with our experimental collaborators, we hope to contribute to better catalysts, particularly for automotive NOx emissions reduction.

Lean burn automobile engines are up to 50% more fuel efficient than engines operating near the air/fuel stoichimetric point. However, the current three-way catalytic converter cannot control nitrogen oxide (NOx) emissions from lean burn engines. The selective reduction of NOx in oxygen-rich exhaust gases can be catalyzed by metal-exchanged zeolites, such as cobalt-ferrierite, but without further improvements these catalysts are not commercially viable.

We are attempting to explain the role of the local zeolite environment on the catalytic activity of cobalt. The increase in the rate of NOx conversion to N_2 per cobalt atom with increasing cobalt loading is well known. This indicates that multiple forms of cobalt exist when exchanged into a zeolite. Recently, Wichterlova and co-workers have proposed three extra-framework sites for cobalt in the zeolite ferrierite. Each site was proposed to correspond in a one-to-one manner with a spectroscopic signature determined from multiple spectroscopic techniques. We have investigated cobalt siting and activity with quantum chemical calculations.

Quantum chemical calculations were performed to investigate the role of the metal-zeolite coordination environment on the catalytic activity for NOx reduction. The properties of divalent cobalt cations in two ferrierite extraframework sites were calculated and compared to experiment. Specific cobalt-ferrierite environments were proposed based on the relative agreement between theory and experiment. The infrared spectra of ferrierite exchanged with six additional divalent metals were also calculated to resolve the general characteristics of metal-induced infrared bands in ferrierite.

Molecular adsorption is the first step in a catalytic reaction. NO adsorption was examined in detail to elucidate the differences in the cobalt-nitrosyl structures, adsorption thermodynamics, and temperature programmed desorption profiles as a function of the local zeolite environment. Two primary factors were identified that control the preferential adsorption of molecules to cobalt in the ferrierite B site over the G site: the relative coordinative unsaturation of cobalt and the degree of adsorbate-induced strain on the cobalt-zeolite environment. The ability of the zeolite environment to promote secondary hydrogen bonds as well as the electrostatic field of the cobalt-zeolite environment were also identified as factors influencing preferential adsorption. Hence, the local zeolite environment near cobalt has a strong influence on the molecular adsorption properties of cobalt-ferrierite. This suggests that the catalytic activity of cobalt-exchanged zeolites for the selective catalytic reduction of NOx depends on the same general factors.

Liquid Phase Oxidation

It has been known for some time that the reactivity and selectivity of olefin epoxidation catalyzed by zeotype catalysts in the liquid phase can be significantly affected by solvent properties. The solvent can influence the observed catalysis by affecting 1) the intrinsic kinetics, 2) the partitioning of species between the fluid phase and the adsorbed phase, thus affecting the concentrations near the active sites, and 3) the rates of diffusion for reactants and products. Typical kinetic measurements are not able to deconvolute the contributions of each of these effects. The objectives for the project are:

- to determine how solvents affect reactivity and selectivity for liquid-phase oxidation reactions in Ti-substituted molecular sieves and other catalysts
- to quantitatively break down the solvents' effects on 1) intrinsic kinetics, 2) the partitioning of species between the fluid phase and the adsorbed phase, and 3) the rates of diffusion for reactants, products, and solvent species
- to compile the knowledge obtained into a comprehensive modeling scheme
- to generalize our results to guide the choice of optimal solvents for other catalytic systems.

In previous years, we synthesized and characterized TS-1 catalysts and demonstrated that our samples are comparable to those in the literature for test reactions. In the past year, we have done the following.

I. Catalyst Synthesis: We synthesized several additional batches of TS-1 in order to obtain samples with varying amounts of titanium. Samples were characterized as before to ensure that the titanium was incorporated into the MFI framework with a negligible amount of undesired extraframework titanium. Primary characterization tools were elemental analysis, XRD, SEM, UV-Vis, and catalytic test reactions. By luck, we also found a route to synthesize samples with larger crystal size. These may be useful to test the effect of diffusion.

II. Batch Kinetic Experiments: We carried out an extensive set of batch reaction studies on the epoxidation of 1-hexene with H_2O_2 and various solvents in TS-1 catalyst systems. The solvents we focused on were methanol, acetonitrile, and acetone. Special attention was paid to getting good initial rate data, which are lacking in the literature. Initial rate data are crucial for understanding the kinetics without the complications of deactivation. Over the course of the reactions, we tracked the compositions of 1-hexene and all products using a GC equipped with a FID. Cerimetric titration was used to track the concentration of H_2O_2. Product identification was carried out using GC-MS.

III. Liquid Phase Adsorption Measurements: We also studied the adsorption behavior of 1-hexene and 1,2-epoxyhexane in methanol, acetonitrile, and acetone. The compositions of the liquid phase before and after the addition of catalyst were measured, and the amount adsorbed was determined by mass balance. Difficulties with evaporation were solved by sealing the samples and using NMR to measure the liquid-phase compositions instead of removing liquid for GC analysis.

IV. Pulsed Field Gradient NMR Diffusion Measurements: We set up a Doty PFG NMR probe for diffusion measurements and thoroughly tested it on reference samples. We prepared a series of samples in NaX zeolites, containing mixtures of CF_4 and n-alkanes ranging from methane to octane. Self-diffusivities of both components in each sample were obtained using ^{19}F or ^{1}H NMR, respectively.

Results were used to test a Maxwell-Stefan scheme for estimating binary diffusion coefficients from single-component data. Samples of 1-hexene, n-hexane, and various solvents in MFI zeolites have been prepared. We also obtained self-diffusivities of both anion and cation species in a room-temperature ionic liquid being investigated as a "green" solvent by collaborators at the University of Notre Dame.

Project: Selective Oxidation over supported Au nano-particles

The overall objective of this project is to understand the nature of the high activity for low temperature CO oxidation on supported Au catalysts. In the last two progress reports, we reported that Au/alumina can be made nearly as active as Au/titania catalysts, and we have shown the importance of removing trace amounts of chloride ions from the catalyst, and the possible role of water on the support in determining the activity of alumina supported samples. Subsequently, we proceeded to probe the nature of the active site by studying the transformation of the Au species during activation of the catalyst.

Specifically, the objective of work during this period was to:

- Perform in-situ x-ray absorption spectroscopy to follow the changes in the oxidation state of Au during activation of the Au catalysts, and,
- Investigate the effect of the support (Al_2O_3 or TiO_2) on the transformation.

Major research findings

1. The ease of reduction of Au(III) complex deposited by the deposition-precipitation procedure depends strongly on the nature of the support. It is much more easily reduced on TiO_2 than on Al_2O_3. The difference could be due to the presence of stronger binding sites for the complex on alumina and/or higher concentration of chloride ions on alumina.

2. Adsorbed CO on Au can be detected at -60°C, but the majority is found not to be on the active sites. However, the mobility of adsorbed CO is rather high, and all of the adsorbed CO can be removed by reaction with adsorbed oxygen.

3. Evidence from XANES and FTIR suggests that the amount of adsorbed oxygen on Au/TiO_2 at -60°C is rather small, although the sample is active in CO oxidation.

Earlier, we found that a Au/Al_2O_3 catalyst, prepared by deposition-precipitation with $HAuCl_4$ at pH 7, was inactive at room temperature, but can be activated to a highly active state by a combination of H_2 and H_2/H_2O treatment at 100°C. In-situ XANES measurements showed that Au was in the (III) oxidation state, and was reduced in part to Au(0) after the treatment. However, the reduction was incomplete, and a small fraction of the Au remained in the cationic state. On the other hand, reduction in H_2 alone did not generate an active catalyst, although a portion of the Au was reduced. It was concluded that metallic Au is a necessary but insufficient condition for activity, because exposure of the catalyst to moisture is important for high activity.

In contrast, a Au/TiO_2 catalyst prepared by the same deposition-precipitation method was very active at room temperature without any prior treatment. Subsequent XANES measurements showed that nearly all of the Au was reduced to Au(0). Thus, the stability of the $Au(O)_x(OH)_y$ species on the support after deposition-precipitation differed for the two supports. These different reduction characteristics were confirmed using temperature programmed reduction with hydrogen. The Au complex on TiO_2 can be reduced starting at around 0^oC, whereas elevated temperature (above about 60^oC) is needed for the complex of Al_2O_3.

High resolution TEM collected by Steve Pennycook at Oak Ridge National Lab offered a picture for the difference. On TiO_2, after activation at room temperature, most of the Au exists in small particles of 2-3 nm. In contrast, a good fraction of the Au on Al_2O_3 after activation is dispersed in monoatomic species (probably ions) on the support, even after the sample had been heated to 100^oC. It appears that the surface of Al_2O_3 contains vacancies or defect sites that stabilize $Au(O)_x(OH)_y$ from migration.

The reductive activation of Au/TiO_2 was also studied using in-situ FTIR. The results are consistent with results using XAS. Exposure of an as-prepared sample to CO at -60^oC resulted in slow reduction of Au(III). A relatively broad IR band at about 2093 cm^{-1} appeared, which has been assigned to CO bound to Au(0). The intensity of this band increased with exposure to CO. Interestingly, when the sample with adsorbed CO was exposed to a mixture of CO and O_2, a shoulder at about 2100 cm^{-1} appeared. Removing the CO from the mixture caused disappearance of the adsorbed CO band at a rate faster than CO desorption in He. Thus, it appears all of the adsorbed CO can be oxidized. However, it appears that the various adsorbed CO bands disappear at different rates, which suggests that only a small fraction of the adsorbed CO was at or near the catalytic active site for oxidation, while the rest must migrate to the active site for reaction.

Another objective of our research program is to synthesize and characterize Au-based catalyst systems using physical vapor deposition (PVD) approach. PVD has several potential advantages over other (especially chemical) methods, and its application to Au-based catalyst systems may serve both as a model study as well as a practical one. The PVD approach we undertake is based on our innovative approach embodied in so-called JENDA (Jet-enhanced nanoparticle deposition apparatus) system, wherein the catalysts support (e.g., γ-Al_2O_3, TiO_2 etc.) are introduced as an aerosol and the active species (e.g., Au or alloys) are simultaneously evaporated to synthesize nanoscale well-dispersed and controlled loading of metal-catalyst, with potential for scale-up.

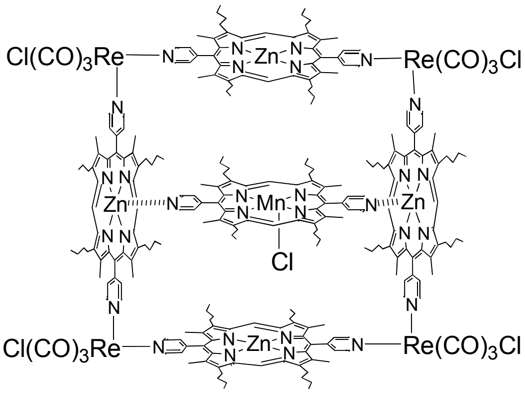
Major research activities in this period included two aspects of Au-catalyst system: novel aerosol-based synthesis and microstructural characterization. In synthesis, we demonstrated and confirmed that the physical vapor deposition technique can be utilized for heterogeneous catalyst synthesis and the resulting physical structure closely resembles those conventionally produced using chemical methods. However, physically produced heterogeneous catalysts showed reduced catalytic activity, causes of which were identified during the past period. The system was redesigned this year to eliminate these shortcomings, and revised synthesis yielded heterogeneous catalyst with the desired overall structural characteristics.

From characterization standpoint, many advanced characterization techniques were used to study both physically and chemically synthesized catalyst systems, including: transmission and scanning transmission electron microscopy (TEM/STEM), secondary ion mass spectroscopy (SIMS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

While supported gold catalysts are becoming worldwide interest due to the novel properties and potential applications in industries, the origin of the catalytic activity in gold nanoparticles is still not well understood. We applied the technique of time-of-flight secondary ion mass spectroscopy (TOF-SIMS) to investigate the nature of gold in Au (1.3wt%)/γ-Al_2O_3 and Au (2.8wt%)/TiO_2 catalysts prepared by deposition-precipitation method. SIMS found the existence of AuO^-, AuO_2^- and $AuOH^-$ ion species in supported gold catalysts. These measurements hint at potential direct evidence for oxidized gold on supported gold catalysts, and may be helpful for better understanding the origin of the catalytic activity.

Project: Biomimetic Oxidation Catalysts

Encapsulated Catalysts



1**Figure 1**

Robust, easily-functionalized nanoporous “molecular squares” have been used in the biomimetic encapsulation of Mn(III) porphyrin epoxidation catalysts. Complete isolation of the catalytically active Mn center within the cavity significantly stabilizes the catalyst by preventing bimolecular decomposition pathways. This encapsulated catalyst is exceptionally stable and gives up to 10,000-fold increase in catalyst turnover number. In addition, the interior cavities of the materials can induce size selectivity. The square-encapsulated manganese porphyrin system has been shown to induce significant size selectivity in the epoxidation of stilbene derivatives. This selectivity can be tuned predictably by ligation of pyridine-based compounds to the inside walls of the square. (Figure 1)

Salen/iron complexes were studied as catalysts for the selective oxidation and cyclopropanation of olefins. These catalysts work well for these reactions under air and also catalyze the oxidative cleavage of benzylic olefins using the environmentally friendly oxidant H_2O_2. This latter reaction provides an excellent environmental-friendly alternative to the use of ozone and heavy metal oxidants.

Porous, thin-film aggregates of molecular-square-encapsulated manganese-porphyrin catalysts have been studied. Previous work had shown that solution-phase encapsulation could stabilize catalysts, extending their lifetimes (turnover numbers) by close to two orders of magnitude in olefin epoxidation reactions. Catalyst lifetimes in aggregates could be extended by roughly another order of magnitude, i.e. to a few hundred thousand turnovers, when the catalysts were driven electrochemically. Under certain conditions, the porous thin-film aggregates were also observed to electro-catalyze the oxidation of water to hydrogen peroxide, with product detection and identification being accomplished using an interdigitated dual-microelectrode array measurement method (generator/collector method).

Functionalized homogeneous catalysts such as metalloporphyrin and metallosalen were successfully immobilized them onto solid supports for recycling and/or for special applications (e.g. electrocatalysis, membrane reactor, and photocatalysis). Catalyst loading and stability on solid supports is highly dependent on chemical properties of an anchoring group (e.g. catechol, phosphate, silicate, or carboxylate) and morphology of solid supports. We have also learned that when properly modified, catalysts can be incorporated into multilayer construction, which allows control of the catalyst loading on the surface. We have learned that mesoporous anodized aluminum membrane has a great potential as a solid support for homogeneous catalyst anchoring.

Recyclable oxidation catalysts with high activity and stability have been developed and applied to environmental-friendly processes utilizing inexpensive sources like sun light, electricity, water, and oxygen. Porphyrin catalysts coated on ITO electrode can be electrochemically activated in basic aqueous solution and oxidize olefins using water as an oxygen source.

Mechanism

The general objective of this project is to determine the reaction kinetics and mechanism for olefin epoxidation reactions with manganese porphyrins as catalysts. In particular, we are interested in the effects of encapsulating the porphyrins within novel "molecular squares" developed by Hupp and Nguyen at Northwestern. Such encapsulated systems have the potential to achieve the selectivity and long life-time of artificial enzymes, but further development requires kinetic data.

Molecular squares have excellent characteristics as hosts for catalytic groups that catalyze the selective oxidation of olefins. They prevent catalyst deactivation by protecting the catalyst, and they can induce size exclusion selectivity through the surrounding structure that immobilizes the porphyrin. These catalysts have the potential to be implemented in various reaction systems, and with the appropriate functionality, they may be polymerized into self-supporting membranes. However, two important concepts have to be addressed in order to fully understand these reaction systems and optimize their performance: the mechanism for the reaction and the rate law. Experimental data and computational methods, such as quantum mechanics and microkinetic modeling, are complementary tools that can give us better insight into the reaction mechanism and the molecular interactions between the reactants and the catalyst. Knowledge of the kinetic properties of the catalyst will help to design molecular architectures and focus research on reliable applications. The goals and research activities of this research project include:

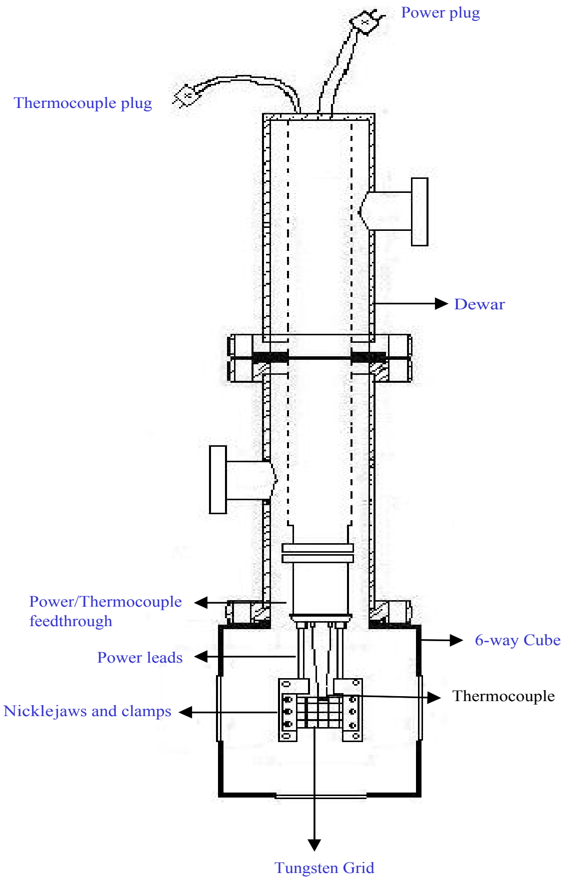
1. Collecting careful kinetic data for systems in which free porphyrins are used as catalysts for the epoxidation of styrene, as well as for the porphyrins encapsulated within molecular squares. This data will be used to examine how transferable the intrinsic kinetics are from free porphyrin systems to their encapsulated counterparts.

2. Performing quantum mechanical calculations to investigate the reaction mechanism. Computational quantum mechanics is a useful tool to obtain geometric and energetic information about stable structures and reactive intermediates.

3. Developing microkinetic models that capture the kinetics over a wide range of reaction conditions for different porphyrins as catalysts with and without molecular squares.

CRG: Emissions Treatment

Project: NO_x Emission Catalysis



NOx abatement in an oxidizing atmosphere (lean NOx reduction) remains a challenge, as no practical catalytic system is in place to meet the increasingly stringent environmental regulation. The objective of work by this group is to elucidate the reaction mechanism for the lean NOx reaction, to identify the nature of the active site on effective catalysts, and to investigate modification of these active sites. The group focuses on two types of catalysts: zeolite-based and alumina-based.

Zeolite-based Catalysts

A highly active, stable and selective catalyst for lean NOx based on iron in zeolite H-MFI has been developed and is under study in this project. The objective of these studies is to understand the mechanism of NOx reduction catalysis both from the point of view of the molecular reagents and from the catalyst. Coordinated chemical reaction experiments and UV Raman measurements have been carried out to determine the nature of chemical reaction intermediates and active iron-oxo species during the catalysis. A new, low-temperature fluidized bed reactor for in-situ UV Raman measurements has been fabricated. The reaction mechanism over the zeolite-based catalyst is being investigated using transient spectroscopy. Proof-of-concept studies on a simple model system, I_2 in silicalite, have been performed to test experimental design. Shown at left is a diagram of the "wire grid" reactor that we are fabricating to study hydrocarbon radical reactions in zeolite-based catalysts in an effort to determine the role of these radicals in NOx reduction chemistry. A "wire grid" reactor has been designed in which very thin films of zeolites can be formed on a tungsten wire grid that can be heated and cooled, and studied by IR spectroscopy. This apparatus has been used to study the mechanism of NOx reduction by acetaldehyde by Ba-NaY zeolite.

Alumina-based Catalysts

Studies of the bi-functional SnO_2/Al_2O_3 catalyst suggest that a potentially fruitful direction is to design a catalytic system where the hydrocarbon activation function and the nitrogen formation functions are separated. On SnO_2/Al_2O_3, the role of SnO_2 is to activate propene to form acrolein. On Al_2O_3 acrolein is quantitatively transformed to form acetaldehyde, which subsequently reacts with NO_x to form N_2. Activation of propene can also be achieved in a non-catalytic manner. Using non-thermal plasma (an alternative technology being explored for NO_x abatement), acetaldehyde is also formed from C_3H_6. Thus, efficient utilization of acetaldehyde may be a key towards realization of a practical NO_x abatement strategy.

Thus, one phase of lean NO_x catalysis research involves exploring suitable catalytic systems for (a) selective formation of oxygenates from alkene and (b) selective NO_x reduction by acetaldehyde. Non-thermal plasma technology is expensive and a catalytic solution is preferable. Currently we are looking for more selective and active catalytic systems than SnO_2 for C_3H_6 activation. Critical properties of this metal oxide catalyst must include thermal stability and low vapor pressure. V_2O_5 and/or MoO_3 are important components in most selective oxidation catalysts, but they have high vapor pressure and thus are not suitable for exhaust emission application. We have prepared GeO_2-SiO_2 mixed oxide using a co-gellation procedure. These preparations have high surface areas. The surface areas are 468 m^2/g and 330 m^2/g for samples with GeO_2 loadings of 34.5% and 50 wt. %, respectively. The GeO_2 are very well dispersed as no XRD peaks are detected for the 34.5 wt.% loading sample.

Concurrently, the NO_x reduction efficiency of various oxides when acetaldehyde is used as a reductant is under investigation. TiO_2 is being investigated, as we would like the catalyst to be more active than Al_2O_3 but less active than most transition metal oxides. The NO_x reduction efficiency appears to be dependent on the morphology of TiO_2. An anatase TiO_2 preparation is more active and selective than a mesoporous one. Impregnation of the mesoporous TiO_2 with Ba nitrate enhances the combustion of acetaldehyde. The properties of oxides that are important for the selective reduction of NOx using acetaldehyde as a reductant are being elucidated. We have also begun sol-gel preparation of mixed oxides for use in the selective oxidation of alkene to oxygenates for use in NO_x reduction.

To gain a deeper understanding of the observations from the steady-state reaction studies, we carried out in-situ infrared characterization to get information on the active species over anatase titania at the reaction temperature of 300^{o}C. Results of IR experiments concur with the high reactivity of adsorbed NO_2. Exposure of NO_2 produced peaks at 1608, 1583 and 1243 cm^{-1} that are assigned to a bidentate nitrate species. This nitrate species was stable and remained after 40 min purging at 300^{o}C. However, exposure of this nitrate species to acetaldehyde resulted in immediate and large decreases in peak intensities. The acetaldehyde was completely transformed (no C=O peak and C-H band was observed). The only C-containing species detected on the surface were carboxylate groups.

The IR results support the reaction studies in showing that the efficiency of the anatase titania catalyst is due to both the high coverage of its surface by nitrates and the high reactivity of these nitrate species with acetaldehyde. Presumably, nitrogen is formed in this reaction.

Project: Photobiocatalysis

The primary goal of the Photobiocatalysis project in the Emissions Treatment CRG is to determine if photocatalytic oxidation can be controlled to alter selectively organic structure, thereby enhancing the biodegradability of a chemical or chemical mixture. Related to this goal are three basic objectives. The first is to develop and apply molecular tools that allow us to probe the mechanism of photocatalytic oxidation. The second objective is to develop and apply the molecular tools that allow us to detail the response of a microbial community to chemical stress, in general, and photocatalytic oxidation products, specifically. The third objective is to determine how to couple the photo- and biocatalysis in a process that improves the effectiveness and efficiency of the single processes to achieve complete mineralization of a chlorinated organic chemical.

The work can be divided into 5 interconnected parts.

Development of new molecular tools to probe photocatalytic reaction.

The objective of this project is to detect reactants, intermediates and products of reactions on TiO_2 in a chemically specific fashion. One effort has focused on the development and application of methodologies for interrogating the energetics of photo-active semiconductor/solution interfaces, assessing molecular adsorption at semiconductor/solution interfaces, and building periodic, micropatterned semiconductor/biofilm arrays. A method was developed for fabricating high-quality and moderately high area micropatterned thin films of TiO_2 on transparent, conductive platforms. These films have been employed as photonic lattices, where the periodicity of the microstructure has been exploited to achieve efficient diffraction of coherent monochromatic visible light. The diffraction phenomenon, in turn, has been used to: 1) demonstrate the ability to detect and quantify binding of candidate pollutant molecules to TiO_2 (vapor-phase adsorption of chloroform; aqueous-phase adsorption of trichlorophenol), 2) assess interfacial energetics (environment-dependent conduction band edge energies for TiO_2 thin films), and 3) measure important electro-optical properties of TiO_2 thin films (wavelength-dependent and electrochemical-potential-dependent refractive indices).

The TiO_2 microfabrication and photonic lattice measurement techniques combined with infrared laser spectroscopy capabilities can accomplish at least two important things: a) extension of the adsorption detection limit of adsorbates hopefully by a few to several orders of magnitude, and b) introduction of chemical specificity in the adsorption assessment technique. The former is obviously important when the binding of candidate reactants to TiO_2 is weak, or when low-coverage photochemical intermediates are the target of the investigation. The latter is important for obvious mechanistic reasons - clearly molecules must interact with the TiO_2 surface before they can be degraded, and their binding constant should be an input to a complete model of surface photochemistry. The basis for the anticipated enhanced sensitivity is the ability to achieve wavelength-dependent (adsorbate molecular structure dependent) resonance enhancement of the diffraction response, and the ability to employ lock-in detection as a consequence of being able to frequency modulate the infrared laser used to achieve resonant enhancement of the diffraction response. Initially, this technique will be demonstrated for the adsorption of vapor phase species. Fabrication of TiO_2 "gratings" on InSnO coated on glass substrates has been accomplished. Learning how to form TiO_2 grating on a substrate(s) that transmits into appropriate regions of the infrared is in progress. A possible candidate is sapphire or metal coated sapphire surfaces.

Another focus is to better understand the mechanism(s) of photoinduced degradation processes taking place on TiO_2 surfaces. This understanding will allow the formulation of a more complete and accurate mechanistically-based model for such processes. Of particular interest are degradation pathways for halogenated hydrocarbons. An initial target molecule is trichlorophenol (TCP). The specific goals of our work include: the identification of initial steps in the photoinduced decomposition of such species, the identification of products formed as a result of subsequent reaction steps, the identification of intermediates formed during reaction, and the measurement of rates of reaction of species on TiO_2. In this area a focus of the work centers on the use of ATR (attenuated total reflection) spectroscopy to directly probe processes taking place on TiO_2 surfaces in the presence of water. We have designed and tested a cell that uses a CaF_2 ATR element. This element is transparent in the infrared to about 10 microns and to UV to below 200nm. CaF_2 is sufficiently insoluble in water that it can be in direct contact with water. The concept of the ATR cell is that we can deposit a film of TiO_2 directly on the ATR element. Using appropriate gasketing material, the ATR element is then sealed to a cell that contains water and the species to be studied. Alternatively, the species to be studied can be directly dosed onto the TiO_2 film which is then exposed to water. The UV or visible light is passed through the crystal and is incident on the surface of the film that can be in direct contact with water.

In evaluating the configuration delineated above we noted some interesting phenomena. With a number of organic solvents absorption signals were obtained that appeared to be greatly enhanced over the corresponding solution phase or gas phase absorptions. We also sometimes observed apparently new or displaced absorptions. We now believe these phenomena have their origin in the fact that the index of refraction of CaF_2 is close to the index of refraction of a number of common organic solvents. The index of refraction of a solvent is wavelength dependent and can change considerably at the wavelength of a strong absorption. ATR spectroscopy is based on the fact that when the index of the material the light is propagating in exceeds that of the index of the material on the other side of the optical interface, a critical angle can be achieved which leads to internal reflection. However, if the index of the material in contact with the ATR element approaches that of the ATR crystal, the internal reflection efficiency decreases. When an index match is achieved, transmission of the IR beam through the interface can occur. This will appear as an enhanced absorption since the beam is no longer detected at the infrared detector set up to monitor the internally reflected beam. Where the frequency dependence of the index of refraction is know we have been able to correlate new bands in the ATR spectrum with changes in the index of refraction that lead to index matching conditions with the CaF_2 ATR element.

There is also an alternative ATR configuration. Other researchers at Northwestern have succeeded in making thin films of TiO_2 with thickness less than 10 microns. With films of this thickness the evanescent wave that is generated at the crystal - film interface, in ATR spectroscopy, can penetrate through most if not all of the film. Thus, higher index ATR elements can be employed which are not UV transparent but where there is no problem with obviating the internal reflection conditions due to index matching with materials adsorbed on the film. The concept in the use of higher index, non-UV transparent ATR elements is to deposit very thin films of TiO_2 on the ATR elements. Infrared radiation would go through the ATR element, one surface of which (the one with the TiO_2 film) could be in contact with water. The UV or visible radiation would be directed onto the film through the solution. This would achieve the goals of using infrared radiation to probe UV (or visible light) initiated process (and their subsequent steps) taking place on and/or in TiO_2 films in an aqueous environment.

Use of established tools to provide new mechanistic insights into photocatalytic reactions.

This project studies the charge separation characteristics of an high activity mixed phase titania catalyst (Degussa P25) utilizing EPR spectroscopy. Typical titania catalysts are composed of the anatase phase or a mixture of anatase and rutile. The goal of this project is to understand why mixed phase formulations are highly active in comparison to pure phase anatase or rutile. With this knowledge we can improve catalyst design and control performance. It is known that the presence of rutile, inactive in pure phase, is critical to the activity of mixed phase TiO_2 formulations, but the mechanism is not well understood. Our EPR data show the clear presence of both anatase and rutile electron trapping sites in Degussa P25 under visible illumination. The same experimental conditions do not lead to charge separation in pure phase anatase. In order for these anatase trapping sites to be populated, electron transfer must occur from the rutile to the lower energy anatase sites. Further experiments confirm this process and show that the increased effectiveness of the mixed phase formulations of TiO_2 is due to electron transfer at the rutile-anatase interface. This electron transfer reduces the rate of recombination in the catalyst creating catalytic “hot spots” at the interface of the two phases. Subsequent migration of the electrons from the lattice trapping sites has also been monitored indicating that there are two distinct trapping sites on the surface. This migration further spatially separates the electron-hole pair and stabilizes the charge separation, leading to a more active catalyst.

Additionally it has been found that the relative size of the anatase and rutile particles is critical to this charge transfer. Rutile particles that are of the same approximate size as the anatase particles have been found to be most efficient in this charge transfer process. Further studies on the size dependence of the aggregated particles indicate that the aggregates with the smallest rutile particles are qualitatively the most active. Work is continuing to quantify this increase in activity and relate it to the size of the aggregates.

Probing the nature of surface reactions on TiO_2.

The objective of the research is to determine how illumination conditions affected the adsorption of the model pollutant 2,4,5-trichlorophenol (TCP) onto the surface of TiO_2. Light wavelengths above the bandgap of rutile and anatase are used so to study adsorptive phenomena in the absence of charge separation. Nevertheless, we have discovered intriguing effects of visible light on aqueous systems containing both TiO_2 and TCP. The focus of this project has been on characterizing the nature of the interaction and its mechanisms.

Prior experiments revealed that in aqueous suspensions of Degussa P25, a commercial preparation of TiO_2 consisting of about 80% anatase phase and 20% rutile phase, adsorption of TCP appeared to increase by as much as fourfold under visible light versus dark conditions. To ensure that trace UV in the fluorescent lighting was not the cause of the phenomenon, the experiments were repeated with an optical gel filter that removed all UV light (l<415). A significant light effect was still observed on P25. However, a light effect was observed on pure anatase only without the filter (in the presence of trace UV), and no light effect was observed on pure rutile under any conditions. Furthermore, total organic carbon (TOC) measurements of the bulk solution showed that TOC remained constant in unfiltered anatase experiments even though [TCP] decreased. This suggests the conversion of TCP to organic byproducts that remained in the aqueous phase and shows that the only light effect on anatase was in fact low-level photocatalytic transformation triggered by the small amount of UV in the fluorescent lighting. Conversely, on P25, the aqueous decrease in TOC corresponded to the decrease in [TCP], indicating that the organic carbon was likely adsorbed to the catalyst. However, the release of chloride (about 1 mol Cl^- per 3 mol TCP depleted from the aqueous phase) indicated some degree of transformation of TCP.

Experiments in the past year have focused on clarifying the fate (adsorption or reaction) of TCP in aqueous P25 slurries under visible light. Less than half of the TCP lost from solution is accounted for as adsorbed TCP. No products are detected in the solution phase of the TiO_2 slurries. Efforts to recover adsorbed products assuming that they were lighter and more polar than the parent compound, as photocatalytic oxidation products generally are, had proved fruitless. Assuming the opposite, that TCP might polymerize to form less polar products on the TiO_2 surface, led to a successful non-polar extraction technique using an acetone/hexane mixture and a desiccant. Analysis of concentrated extracts by GC/MS identified dimerized TCP species such as dioxins and dibenzofurans containing between four and six chlorines. Direct MS and LC/MS revealed the existence of much larger molecules, with molecular weights higher than 1200 D. These larger polymers have not been identified.

The identified products close the mass balance on carbon and illustrate that the P25 surface promotes sub-bandgap photochemistry. The products are formed only under visible illumination conditions. They are not typically produced in photocatalytic reactors and are themselves labile to photocatalysis. To demonstrate this, a sample of TiO_2 and TCP illuminated with visible light (and therefore containing dioxins and dibenzofurans) was then subsequently treated with high intensity UV light for 1 h in an annular photocatalytic reactor. The TiO_2 was extracted, and no fusion products were found in the extract.

It was hypothesized that the reaction of TCP on TiO_2 under visible illumination occurred via a charge-transfer complex. This hypothesis was confirmed using EPR and diffuse reflectance UV-vis spectroscopy. EPR spectra showed transfer of electrons from TCP to P25 under wavelengths as high as 495 nm, while no electron accumulation occurs on TiO_2 by itself under the same light conditions. The EPR findings were corroborated by the diffuse reflectance spectroscopy of P25 with and without dark-adsorbed TCP. P25 by itself does not absorb wavelengths above 410 nm, but with adsorbed TCP wavelengths as high as 550 nm were absorbed.

Excitation of the charge-transfer complex is consistent with the products formed. Direct transfer of an electron from TCP to TiO_2 results in a TCP radical species. If TCP molecules in close proximity to each other on the catalyst surface carry unpaired electrons, it is likely that they will combine to pair their electrons, resulting in the polymerized products. This mechanism differs from that of conventional photocatalytic degradation, where UV light activates the catalyst directly and the catalyst, in turn, reacts with water and/or hydroxide to form hydroxyl radicals, which then attack organic compounds at or near the surface. Thus under UV light, TCP molecules react not with each other but with $^{\cdot}OH$.

Future work includes exploring effects of varying the organic molecule or the illumination wavelength. Diffuse reflectance spectra will be taken of P25 bound to a series of chlorophenols. Trends will be sought based on number and location of chlorine atoms. Also, a Xe arc lamp has been set up with the necessary attachments to produce narrow band (10 nm) light, ranging from super-bandgap energy (360 nm) to the limit of the TCP/P25 charge transfer complex band (550 nm). Experiments will assess whether specific products or class of products can be selected by controlling the wavelength of irradiation.

Develop new and established molecular tools to probe microbial community dynamics.

The main objectives of the biological portion of the project are as follows:

1. To examine how the nature of the photocatalytic by-product mixture affects microbial diversity.

2. To understand how different photocatalytic product mixtures affect microorganisms at the genetic level.

3. To determine if microbial diversity can be correlated with the functional stability of the process.

Terminal restriction fragment length polymorphism (T-RFLP) is a fingerprinting technique to estimate microbial diversity in a complex environment. This technique is used to assess the microbial diversity present in the bioreactor as a result of exposure to different photocatalytic by-product mixtures. Much progress has been made in optimizing this technique for our system.

Similarly, denaturing gradient gel electrophoresis (DGGE) is also a fingerprinting technique used to estimate microbial diversity in complex environments. While it is generally not as sensitive (when compared to T-RFLP), for low density populations, it does offer the added advantage of being able to simultaneously sequence specific bands of DNA from the gel, which allows us to determine the genetic make-up of the species in the community. Progress has also been made in optimizing this technique for our system.

To understand how different photocatalytic by-products affect microorganisms at the genetic level, we developed a 2-D profiling technique that allows us to monitor gene expression in microorganisms under various environmental conditions. To test this technique, we grow a common soil bacterium (*Pseudomonas aeruginosa)* under aerobic and denitrifying conditions, and we then compare the resulting gene expression profiles. It is expected that denitrification genes, such as nitrate reductase (*narG*), nitrite reductase (*nirS*), and certain regulatory genes (*anr*, *dnr*), are expressed to a greater extent under denitrifying conditions as compared to aerobic conditions. The results from the profiling technique are validated using other techniques, such as primer extension. Several primer extension experiments have been completed with *narG*. In batch culture, *narG* expression was very similar between cultures that were open to the atmosphere and those from which oxygen was purposely excluded from the headspace. This indicated that oxygen was rapidly depleted from the "aerobic" batch culture, leading to *narG* expression. Therefore, *P. aeruginosa* was then grown in a chemostat that was sparged with pure oxygen (aerobic) or pure nitrogen (anoxic). As expected, *narG* expression was much higher in the anoxic chemostat. Due to the success of the primer extension experiment, it can be concluded that the experimental steps (e.g., isolating RNA to creating cDNA) are operating as they should. Thus, the 2-D profiling technique can be applied to aerobically- and anoxically-grown *P. aeruginosa,* and the expression of *narG* may be compared between the two growth conditions. Once the 2-D profiling technique has been validated with *narG*, it will be applied to important isolates from microbial communities degrading 2,4,5-TCP and/or its photocatalytic by-products. The results will show what genes, in addition to the obvious degradation genes, allow these isolates to survive in challenging environments.

Probing the stability and resilience of microbial communities as a function of carbon source.

The main objectives of portion of the project are as follows:

1: Demonstrate the need for photobiocatalysis through an analysis of the resistance to biodegradation of our model compound, 2,4,5-Trichlorophenol (TCP).

2: Demonstrate that combined photocatalytic-biological degradation of TCP is viable.

3: Explore the relationship between photocatalytic effluent composition and biological post-treatment performance.

We have completed both batch and continuous studies aimed at examining biodegradation of TCP. We have completed a theoretical kinetic analysis of TCP biodegradation that helps to elucidate the difficulties associated in its biodegradation. We have completed the chemical and biological analysis of our first combined treatment system. This included producing multiple batches of photocatalytic effluent from TCP and feeding this effluent into bioreactors to determine if the combined process was viable. We analyzed the reactors for TCP concentration, chemical oxygen demand (COD), dissolved organic carbon (DOC), and we used molecular biology techniques, denaturing gradient gel electrophoresis (DGGE) and terminal-restriction fragment length polymorphism (T-RFLP), to assess the community diversity of these reactors. Finally, we succeeded in producing batches of photocatalytic effluent that differed substantially in their chemical composition. We then fed these unique batches to different bioreactors to gauge how effluent composition affects the biological post-treatment. These experiments were completed, and all of the chemical work except for DOC is finished, and DNA was extracted and we are now in the process of using the aforementioned molecular techniques to determine how the community diversity is a function of effluent composition, and to correlate this information to bioreactor performance. We also used perturbation analysis on these reactors after they had reached steady state to determine which of these reactors is the most stable, or resistant and resilient to perturbation. This analysis is completed, save for the molecular techniques. To corroborate this data, we also ran bioreactors using single carbon sources as the input, with each carbon source intended to mimic a different type of photocatalytic effluent. For instance, we modeled a lightly degraded effluent with 4-chlorocatechol, a moderately degraded effluent with 2-chloromuconic acid, and a heavily degraded effluent with acetate. By using these model effluents we can further understand how substrate composition affects microbial diversity and process performance. These experiments are also finished, and we are currently finishing the molecular analysis.

CRG: The Natural Environment

The natural environment collaborative research group is focused on elucidating and understanding the mechanisms of microbial resistance to metal stress. It is organized into three highly inter-related sub-areas:

1. Metal speciation and bioavailability

2. Mechanisms of microbial metals resistance

3. Formation, structure, and reactivity of biologically produced manganese oxides.

While most of the research involves laboratory experiments and modeling to explore mechanisms at the molecular level, the group also takes advantage of a field site, Lake Depue, which has been highly contaminated with heavy-metal discharges. For comparison purposes, the group also investigates Lake Michigan, which is pristine with regard to metals contamination.

Project: Metal Speciation and Bioavailability

The determination of the chemical speciation of elements in the environment is key for determining the toxicity, bioavailability, and fate of metal contaminants. It has been shown that various chemical species of the same element lead to different toxic effects among a wide range of microorganisms, and that these species have contrasting mobility. If microbial species are sensitive to the chemical species to which they are exposed, they are also capable of changing the chemical speciation of elements to reduce their bioavailability and therefore their toxicity.

In natural systems, the molecular-scale processes having implications for the toxicity and bioavailability of heavy metals can interact in complex ways. One goal of this research is the development and computational implementation of a mathematical model that will allow us to unravel this complexity by explicitly connecting microbial reactions to geochemical speciation and reactivity. A closely related goal is to generate and interpret experimental results that emphasize key mechanisms of bioprotection—or the processes by which microbial communities avoid severe metal toxicity—, which we propose that bacteria accomplish at metal-contaminated sites. To effect bioprotection of all the community's members, the community must lower the concentration of the toxic forms of the metals to concentrations that do not impart serious toxic responses. To do so, the community must catalyze reactions that make the toxic forms of the metals biologically unavailable to them. Bioprotection can work in biofilms, in sediments, or in groundwater aquifers, although the time and space scales are very different among these settings.

At the level of biofilms, one of the main processes that we think limit metals' availability is the complexation or sorption of these elements at specific sites. It has been long recognized that biofilm bacteria are more resistant to various environmental stresses. It has been hypothesized that this is due to the extracellular polymeric substances (EPS) that protects biofilm organisms against abiotic and biotic influences from the environment. We are specifically interested in understanding how the EPS protect microbial organisms from metal toxicity. The goal of our research is to determine if the EPS structure affords specific biological protection, for instance, by complexing metals, or if the EPS simply creates diffusional barriers and chemical gradients. Related to this, we are also interested in determining if there are qualitative or quantitative changes in the EPS structure in response to metal exposure.

Model Development:

Our research so far has focused on expanding and exploiting a biogeochemical model (CCBATCH) developed here to understand the time and space scales over which the bioprotection mechanisms can be expected to act. The original CCBATCH model linked microbial reactions with acid/base and complexation reactions occurring in the aqueous phase. It also was set up to handle only batch reactions. In order to expand this model to address realistic bioprotection scenarios, we added these features:

I. An efficient sub-model to describe precipitation reactions as either kinetically or equilibrium controlled.

II. The formation of surface complexes, or complexation to ligands attached to surfaces.

III. The ability to model multiple microbial species.

IV. Advective and dispersive transport processes in one or two dimensions.

Great candidates to provide the necessary bioprotection from metals are sulfate-reducing bacteria because they are widespread naturally occurring microorganisms and provide passive metal protection by producing sulfide, which forms sparingly soluble precipitates with many toxic metals. Recent modeling of metal-toxicity experiments with *Desulfovibrio vulgaris* shows the detoxification potential of sulfate reducing bacteria. Even when exposed to severe metal stress, *Desulfovibrio vulgaris* continues respiring, and eventually produces enough sulfide to completely detoxify the metal.

Characterization of biofilm EPS material:

This research just started this past year and focused on the analysis of chemical composition of the EPS from *Pseudomanas aeruginosa* biofilms as a first step to characterize the EPS. EPS extracted from *P. aeruginosa* biofilms was characterized by Pyrolysis-GC-Mass spectrometry and conventional chemical assays to determine the chemical fingerprint and composition of the EPS matrix, respectively. Different chemical fingerprints were obtained for the EPS from wilde-type (PAO1) and mucoid strains (PDO300) of *P. aeruginosa*. EPS from PAO1 biofilms showed more complex chemical signatures and were more enriched in proteinous and lipid materials. EPS from PDO300 biofilms, however, showed simpler chemical signatures derived principally from highly acetylated carbohydrates (O-acetylated uronic acid). These results were further confirmed by wet chemical assays that uronic acid was the major fraction (> 95 %) of total carbohydrate in EPS from PDO300 biofilms, while the EPS from PDO300 biofilm was mainly composed of neutral and anionic carbohydrates and the fraction of uronic acid remained very low (≤ 5 %).

To further determine the chemical identities and compositions of the EPS matrix, experiments were conducted to cleave polysaccharide or oligosaccharide into their monosaccharides, derivatized to the volatile forms of trimethylsilyl (TMS) ether or ester derivatives, and followed by GC-Mass analysis. Results from TMS derivatization-GC-MS method showed significantly different monosaccharide compositions in the EPS from PAO1 and PDO300 biofilms. Glucose and rhamnose were the major components and variable amounts of other neutral sugars, including arabinose, galactose, mannose, and xylose, were determined in the EPS from PAO1 biofilms. EPS from PAO1 biofilms also contained amino acids such as leucine and phenylalanine as the minor components. EPS from PDO300 biofilms, however, was mainly composed of uronic acid derivatives and contained small amounts of neutral sugars such as glucose, rhamnose, and xylose. Both EPS from PAO1 and PDO300 biofilms also contained small amounts of lipid components which were identified to C10 ~ C12 fatty acid derivatives. Our results clearly showed that, contrary to conventional wisdom, alginate which is uronic acid-based polysaccharide is not the principal chemical component of the EPS from wild-type *P. aeruginosa* and rather EPS composed of alginate appears to only be a feature of mutant strains of *P. aeruginosa* biofilms.

Experiments were also conducted to determine changes in the chemical composition of the EPS in response to heavy metal stress, focusing especially on the determination of uronic acid which has a carboxylic functional group and thus has been considered as the important chemical identity along with the anionic forms of carbohydrate to bind free metal ions. Mucoid strains of *P. aeruginosa*, PDO300 were exposed to total Cu concentrations ranging from 1 to 2 mmol and the content of uronic acid in the EPS were compared.

Project: Mechanisms of Microbial Metal Resistance

Despite high concentrations of heavy metals in impacted environments, bacteria still thrive. One explanation might be that bacteria in the environment exist as surface-attached communities called biofilms that generally have greater resistance to toxic compounds than free-swimming cells.

One of the foci of our research is to understand how bacterial biofilms can offer a better protection mechanism for metal exposure.

Another component of this research is aimed at understanding bacterial mechanisms that provide resistance to lead (Pb) since it is a pervasive environmental contaminant, and one of the top ten most common contaminants in Superfund sites. In addition, lead poisoning afflicts 4-5% of children nationwideENRfu. Despite the prevalence of this problem, many questions about the molecular mechanism of lead's toxicity remain unanswered. These questions include: What proteins are targeted by lead *in vivo*? How does lead binding to these proteins related to the physiological response of an organism to lead? Recent studies by the Godwin laboratory reveal that lead can displace zinc from structural zinc-binding sites in proteins and alter their structure. These structural zinc-binding sites are found in a wide variety of proteins that regulate gene expression; lead's ability to disrupt these proteins could account for the developmental problems associated with lead poisoning.

Our primary objectives regarding the role of biofilms are to investigate:

1. Whether biofilm bacteria will be more resistant to heavy metals as compared to free-swimming bacteria. This was tested with the common environmental Gram-negative bacterium, *Pseudomonas aeruginosa*.

2. Determine if this phenomenon holds true for other representative environmental microorganisms.

3. Examine and determine the nature of the heavy metal resistance mechanisms of biofilm bacteria.

4. Specifically evaluate the role secreted polysaccharides play in the resistance of microbial biofilms to heavy metals.

In order to understand the mechanism of lead binding to transcription factors and the effects of lead on gene expression in microorganisms we want to find the answers to several intriguing questions:

1. Is the timescale required to displace zinc in structural zinc binding sites short enough to be physiologically and environmentally relevant?

2. Do these proteins have to release zinc prior to binding lead or does lead bind to the proteins via an associative mechanism?

3. How does the ability of lead to bind to these structural zinc-binding sites affect patterns of gene expression in microorganisms?

Project: Formation, Structure, and Reactivity of Biologically produced Manganese oxides.

Biologically produced manganese oxides -MnO_X- act as catalysts, reactants and products in a suite of sorption and electron transfer reactions that affect the fate, transport, and transformation of metal and organic contaminants in aquatic systems. These compounds can lead to the oxidation of As(III), Co(II), Cr(III), and Pu(III), and natural organic matter such as humic materials. Therefore they represent key compounds that we need to understand better in order to investigate many environmentally relevant catalytic processes. In addition to their environmental properties in natural systems, these biological produced manganese oxides may possess untapped catalytic properties that we want to investigate.

The oxidation of Mn(II) to MnO_x in aquatic systems is largely catalyzed by microbes, producing various chemical structures of nanophase MnO_X that remain poorly understood. Two key features of some of these manganese oxides are: (1) varied structural arrangements from open tunnel structures - that provide high scavenging properties – to layered formations, and (2) mixed valence states of manganese [Mn II-III-IV] that confer chemical reactivity.

As outlined in the previous yearly reports, our major efforts have been directed towards studying the morphology and the chemical structure of these oxides, as well as understanding the mechanism of Mn(II) oxidation.

The general goal behind this work is to gain molecular-scale knowledge of how manganese oxide formation is catalyzed by microbes. For that purpose, we used a combination of electron microscopy, x-ray absorption and UV-Raman spectroscopy to determine the morphology and the coordinative environment of Mn in these oxides.

Recently, we have focused on the synthesis of phase pure MnOx model compounds for more accurate spectroscopic comparison to biogenic MnOx. In addition, we have used these synthetic phases as analogs for biogenic MnO_x (primarily hexagonal K^+-Birnessite) to conduct a series of metal uptake experiments with Cd, Zn, Cu, Pb. The impetus for these experiments is to determine the role that biogenic MnO_x may play in transport and fate of heavy metals in the environment. Natural MnO_x would naturally form as very fine and widely dispersed material that is mixed with biologic material. The use of a sunthetic MnO_x analog phase allows us to more easily separate and specifically determine the metal sorption capacity of the Mn-phase, without complicating the experiments and interpretation with biosorption effects.

Several potential MnO_x model compounds were synthesized, characterized, and compared to biogenic MnOx using X-ray absorption spectroscopy, UV-Raman, and synchrotron X-ray diffraction. The following model compounds were synthesized:

- Bixbyite (Mn_2O_3)
- Hausmannite (Mn_3O_4)
- Todorokite (MnO_2 polymorph)
- Chalcophanite ($ZnMn_3O_7 \cdot 3H_2O$)
- colloidal MnO_2
- $Ca_2Mn_3O_8$
- $CaMn_3O_6$
- $CaMn_4O_8$
- $CaMn_3O_7$
- $CaMnO_3$
- Birnessite-type layered MnO_2 compounds
    - triclinic Na^+-birnessite
    - H^+-birnessite (*c*-disordered form)
    - hexagonal K^+-birnessite (crystalline *c*-ordered form)

Educational Program

Seminars:

The IEC inaugurated a new, informal seminar series in January 1999, held every Friday at noon. Lectures are given by outside visitors as well as IEC graduate students and postdocs. A number of Industrial Mentors for IEC have presented seminars including Paula Bogdan, Russell Johnson, Dennis Hucul, Bruce Rosen, and Joe Ray.

Short Course:

A one-day short course on "Experimental Design" was presented in June 2001 by Dr. James Hansen from Union Carbide as part of the Industrial Mentor Program.

Undergraduate Education:

Beginning in the summer of 2000 and in cooperation with the chemistry department undergraduate laboratory instructors, IEC began development of undergraduate laboratory modules in Environmental Catalysis. A module in organic chemistry was developed in the summer 2001 to show the advantages, in terms of separations and solvent use, of using solid acids compared to liquid acids for the Fischer esterification reaction. A new undergraduate, titled "Green Chemistry" was taught Spring Quarter 2002. The course introduces the concept and discipline of green chemistry and illustrates, by examples, its growth and expansion from its birth in the early 1990's through the most recent Presidential Green Chemistry awards of 2001. Particular emphasis is placed on innovative technology to development of "greener" routes to improve industrial processes and to produce important products.

Undergraduate Research:

During the summer 2000 IEC sponsored four undergraduates for summer research under the REU program.

Industrial Mentor Program:

Industrial scientists have been invited to act as outside mentors to graduate students and postdocs in the IEC. This program provides graduate students and postdocs with access to the knowledge, experience, and perspective of industrial scientists. Mentors participate intellectually in designing the research projects and guiding the conduct of experiments or calculations. Communication between mentors and students is facilitated by Electronic Notebook software developed by the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory. When appropriate, companies provide support for internships at industrial research laboratories. At the present time 27 scientists from 12 companies participate in the Industrial Mentor Program. Two went on internships in member company research laboratories in Summer 2001.

Semiannual Scientific Meetings:

The IEC conducts two scientific meetings each year. The meetings are intended primarily for the IEC participants, including industrial and national laboratory scientists, but they are open other members to the university community.

Materials World Modules:

The primary goal of this project is to develop a teaching module for high school students around the concept of environmental catalysis. Over the last year we have designed 3 sets of activities that allow students to discover the basic principles of catalysis and how catalysis can be applied to environmental protection. The modules are designed to first "hook" student interest with a simple, but impressive experiment. A combustion experiment using carbon black has been devised for this. A set of photocatalytic activities has been designed to show students how a catalyst can convert radiant energy to chemical energy and provides a simple chemical module for photosynthesis. We show students how the addition of TiO_2 to a solution of methylene blue can be decolorized rapidly if placed under a germicidal lamp. We then have students set up an experimental system to find the best catalyst and catalyst loading for methylene blue destruction. Another set of experiments is centered on the reaction of gas phase chemicals with an iron based catalyst under elevated temperature conditions.

These experiments have all been subjected to scrutiny by high school teachers and modified in accordance with their comments. In addition, we have visited a number of area schools (Lake Forest H.S., Evanston Township H.S., Schaumburg H.S.) and done the experiments in classroom settings. We also added two more activities to demonstrate biocatalysis and how catalysis is used in chemical synthesis to provide environmental benefit.

The final product is a module titled "Environmental Catalysis". The module is highly engaging and involves two weeks of hands-on activities, problem solving, and internet research on the topic of catalysis. The curriculum gives students a good understanding of how kinetic processes take place in chemical reactions that can be applied to catalysis, photochemistry, and the protection of our natural environment. Students analyze different types of catalytic systems, including homogeneous and heterogeneous catalysis, thermocatalysis, and photocatalysis. In their study, they explore concepts such as catalytic selectivity, specificity, poisoning, condition optimization, and waste minimization, which they apply in the design and construction of a unique catalytic deodorizing device.

Hands-On Science Program:

The Institute of Environmental Catalysis (IEC) at Northwestern University is involved in a highly innovative educational outreach activity for high school and middle school science teachers. A one-week workshop for middle and high school teachers has been conducted in partnership with the Educational Division at Argonne National Laboratories in summer 2000 and 2001. This June the Middle and High School Teachers workshop, Unlocking Nature's Secrets: Catalysis in the Environment and Industry, will take place at Argonne National Labs. This is the third year the workshop has been run and as in other years the workshop will provide instruction and teaching materials for 30 teachers. This summer program has established a very positive and popular reputation among teachers in the Chicago area. This year over 60 teachers applied to participate at which time the course was closed to any further applications. The goal of the workshop is to provide teachers with the knowledge and tools to enhance their students' inquiry and understanding about the world around them. Each day begins with a lecture that explains various principles and examples of catalysis in chemical production (e.g., catalytic cracking to produce gasoline and the synthesis of rubber), emissions treatment (e.g., catalytic converters on automobiles and biological degradation in wastewater treatment), and natural phenomena (e.g., stratospheric ozone depletion and the biogeochemistry of wetlands). After the lecture the teachers spend the rest of the day conducting a series of hands-on experiments designed to illustrate the lecture topics and to be easily incorporated into their existing curricula. Through this workshop, teachers discover how to use catalytic phenomena to provide exciting opportunities that could challenge AP students in high school and stimulate curiosity among middle school students.

Research Findings

CRG: Molecular Science of Catalytic Oxidation

Project: *In-situ* Characterization and Atomic Structure

The in-situ characterization results from the activities by this group are described under other projects.

Atomic Structure

Determination of the surface atomic structures of NiO and $SrTiO_3$ are major achievements of this project. Strontium titanate was studied because it is a simple, cubic, multi-component oxide of the perovskite structure which represents an extremely large class of materials that are used in the study of catalysis and also have application as substrates for the growth of superconducting thin films and piezoelectric micromechanical systems. Several terminations of the (111) surface have been found to adopt a distorted TiO_2 structure. These structures minimize dipolar fields at the surface. They would not have been found without the Direct Methods approach. Three new and previously unreported surface reconstructions on the (111) surface of $SrTiO_3$ have been found. These surfaces terminate in “truncated octapolar units”. Interesting similarities and trends have been observed among the reconstructions, providing insight into how oxide surfaces behave and what their structures are under various temperatures and atmospheres. A set of rules for predicting the nature of the surface structure are under development based on the fugacity of oxygen gas in which the sample is prepared. The reduction of bulk $Mg_3V_2O_8$ has been investigated, and we have observed single crystals transform from the oxidized phase to the reduced phase. The transformation occurs via cation migration among a nearly stationary oxygen lattice.

Surface atomic structure determination is a crucial step toward understanding the surface electronic and chemical properties. Hematite (0001) is reported to have a (1x1) Fe-terminated or (1x1) O-terminated surface, depending on the oxygen/annealing conditions. Both surfaces need be considered in environmental catalysis applications. Recent theoretical calculations predict large relaxations in the top several surface layers for both surfaces. Using surface X-ray scattering we found lateral displacements of the second layer oxygen atoms in Fe-terminated hematite (0001) surface in addition to vertical relaxations in the top four surface layers. By UHV HREM we have found that after Ar^+ ion bombardment the sample surface is reduced and covered by a spinel phase. After annealing these samples at 900°C and high partial pressures of oxygen, the sample has a (1x1) termination. However, we discovered that by annealing these samples in low oxygen partial pressures, a so-called bi-phase structure is formed wherein the surface consists of coexisting islands of Fe_2O_3 and another phase which is yet to be determined. As an alternative to annealing in O_2, initial experiments using a flux of atomic oxygen, produced by the thermal decomposition of N_2O, have shown promise as a low-pressure technique to produce oxygen-terminated hematite surfaces. TED experiments to confirm these findings are ongoing.

From the analysis of the α-Fe_2O_3 XSW VB spectroscopy we find both a bonding and nonbonding state originating from the oxygen ions. The valence densities of states from iron agree well with predictions based on configuration interaction cluster calculations, which considered charge transfer from ligand to metal. The effects of strong hybridization between Fe and O valence states to X-ray emission and resonance photoemission are also evident. In the future we plan to extend this method to surface valence states to study chemical reactions on surface.

In-situ XSW measurements were carried out to pin point the location of Rb^{+1}, Sr^{+2}, and Zn^{+2} ions adsorbed from aqueous solution on TiO_2 (110). Sr^{2+} and Zn^{2+} adsorb from aqueous solution up to 0.1 ML coverage at the Ti site with some inward contraction dependent on ionic radius.

Major research findings from scanning probe microscopy are:

(1) Atomically flat hematite (0001) surfaces were achieved on chemical vapor transport (CVT) grown hematite samples following annealing at 900ºC for 2 hours in air.

(2) The annealed CVT hematite (0001) surfaces showed step bunching with ~60 µm wide atomically flat terraces.

(3) On the atomically flat terraces, nearly circular pits were observed with a depth of 2.2 ± 0.2 Å in agreement with the spacing between equivalently terminated layers in the hematite unit cell.

(4) Attempts to achieve a comparable morphology on mineralogical hematite surfaces were unsuccessful and attributed to the increased impurity levels in these samples compared to the CVT samples.

(5) Analogous results were obtained on $SrTiO_3$ and TiO_2 surfaces with low miscut angles after annealing in oxygen-rich environments.

Project: Surface Science of Catalytic Oxidation

Experiment

The adsorption and bonding of methyl groups on hematite is a strong function of the surface structure. Our data shows that only when there exist oxygen anions with dangling bonds is there the possibility for methyl radicals to form surface bonds. Methyl radicals do not bond to iron cations in either the 2+ or 3+ oxidation state. When the hematite surface with methyl groups bonded to oxygen is heated, the carbon-oxygen bond is broken and free methyl radicals are generated at two different temperatures depending on the coordination of oxygen to the underlying iron cations. Some of the methyl radicals react with each other to generate ethane when their density is sufficiently high.

In the presence of chlorine or uranium additives to the surface the chemical picture changes significantly. The methyl groups are now reactive with chlorine to generate chlorinated methanes and with uranium oxide species to generate the partial oxidation product formaldehyde. These results demonstrate the importance of local atomic structures and impurities in determining the surface chemistry of metal oxides with simple hydrocarbons.

Theory

1. Density Functional force-field calculations for atoms and small molecules on the hematite surface show that embedding effects beyond second neighbor explicit bonding interactions are still important for determining equilibrium geometries and small-displacement energetics. While not surprising, in view of the dominant long-range electrostatics effects, this leads us to explore further the minimum size of clusters needed before simplified effective medium approximations can be used.

2. The uptake, retention, and release of transition and heavy metals by the bone analog HAP can begin to be understood, now that the primary bulk absorption sites are characterized. Correlation of theoretical modeling and electronic structure results with experimental iron Mössbauer data in the case of Fe:HAP (A. Rossi et al. , CBPF) and lead L-edge XANES (M. Bedzyk, NU) build confidence in the models we have developed.

3. The reconstructed $SrTiO_3$ (001) surface can now be understood in terms of a 'shear wave' phenomenon seen previously. From the perspective of surface reactivity, two terminal oxygen anions extend over the 'trench' and are more exposed to attack, exhibit reduced ionic charge and heightened covalency.

4. The oxygen-terminated and iron-terminated hematite (001) potential energy surfaces have been characterized, using an embedded cluster technique, where incoming molecular fragments interact with an unrelaxed substrate. Binding energies in atop, bridged, and pocket sites were obtained as ‘reference states’ for computationally intensive band structure studies on relaxed interacting surfaces.

5. Examination of a considerable number of possible reconstructions of TiO_2 – rich $SrTiO_3$ (001) shows that the relaxation of oxygen anions which are singly coordinated to metal, and thus ‘flexible’ is the dominant factor in determining relative energies. However, two-fold coordinated less-rigid oxygen atoms contribute significantly in second order. This observation permits the generation of simple predictive rules for structural energies at low temperature; entropic contributions to free energy evidently are decisive in determining observed structures at elevated temperature.

CRG: Chemical Processing

Project: Mixed Metal Oxide Catalysts

Crystal Growth

The single crystal growth of $Mg_3(VO_4)_2$ has been optimized to obtain single crystals of ~ 5.5cm in length. The largest and highest quality single-crystals are grown under an oxygen atmosphere at 0.5mm/h. The oxidizing atmosphere stabilizes the V^{5+} and prevents the formation of oxygen vacancies. Growth rates slower than 0.5mm/h do not improve the size or quality of the single crystal; however faster growth rates result in several smaller crystalline domains. The natural facets have been identified as the (100) and (20-1) orientations.

An Fe_3O_4 single crystal was grown and characterized by XRD. The natural facets, owing to their high symmetry, were easily characterized by the Laue technique to be (111) plane (six-fold symmetry). The growth direction was found not to contain high symmetry (neither 6 nor 4 nor 2-fold symmetry).

Fe_2O_3 was grown using a solvent zone initially composed of $CaFe_4O_7$, under 6.5 bars of O_2. The surface of the crystal was most likely not corundum Fe_2O_3. It is difficult to discriminate between Fe_3O_4 and maghemite, Fe_2O_3, but the surface is magnetic. It is possible that the surface is an intermediate phase, since the O sublattice is the same face centered cubic.

Catalytic and Surface Studies

Catalytic testing revealed that the seventeen catalysts from the MgO-V_2O_5-MoO_3 system can be divided into three groups, Mg-V-O, $Mg_{2.5-x}V_{1-2x}Mo_{1+2x}O_8$, and Mg-Mo-O. The vanadates are the most active catalysts at lower temperatures but are the least selective for the formation of propene. Catalysts of the $Mg_{2.5-x}V_{1-2x}Mo_{1+2x}O_8$ structure are the least active catalysts. The low activity corresponds to their low surface area ($<1m^2/g$). It was found that the incorporation of molybdenum increases the activity and selectivity of the reaction to propene for both systems. The molybdates were less active at low temperatures but are the most selective catalysts. The catalytic activity correlates to the ease of reduction of the catalyst; the vandates are easier to reduce and are more active at lower temperatures, whereas, the molybdates are harder to reduce and less active at lower temperatures. Interestingly, catalysts that are active at lower temperatures produce more CO_2 than CO, while the opposite trend is observed for the catalysts that are the least active.

It was found the most active (18.6%) and selective (61.8%) catalyst was $MgMoO_4$. As expected, the activities of the catalysts increase with increasing temperature, while the selectivities decrease with increasing temperature until the system becomes oxygen deficient. An important discovery is that once the system becomes oxygen deficient, the selectivity improves with increasing temperature. The enhanced selectivity occurs because additional propane converted is due solely to the oxidation of propane from the lattice oxygen of the catalysts.

The Mg-V-O family of single phase catalysts was tested for catalytic activity, specifically the oxidative dehydrogenation of propane, under an oxidative environment and compared to the previous experiments done under reducing conditions. It can be seen that the conversion is significantly higher due to the excess oxygen. However, the selectivity to propylene is lower. Catalysts were prereduced to simulate oxygen deficiency in the system, but showed little improvement. Work is ongoing with funding from the DOE.

Divalent mixed metal tungstates and molybdates were also tested for catalytic activity. Specifically, the oxidative dehydrogenation of propane to propylene and the ammoxidation of propane to acrylonitrile. It was found that the most active and selective catalyst for formation of acrylonitrile was $NiMoO_4$.

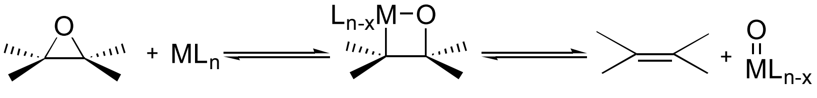
Studies on metal oxide surfaces have yielded varied results. For $Mg_3(VO_4)_2$ single crystal studies, TEM observations indicated the surfaces did not reconstruct under given experimental conditions. It was found that different crystallographic orientations gave unique Raman spectra. However, for $SrTiO_3$ samples it is difficult to obtain useful Raman spectra.

The oxidized surface of $SrTiO_3$ has been studied extensively by TEM. Single crystal TEM samples were annealed under oxidizing conditions, and different surface reconstructions were observed for various annealing temperature ranges. A similar experimental approach was used to study $Mg_3V_2O_8$ surfaces. Upon investigation by TEM, islands of MgO were observed. From information acquired from TEM and XPS, it is proposed that V_2O_5 sublimes from the surface of the $Mg_3V_2O_8$ at elevated annealing temperatures.

Currently, the studies of $SrTiO_3$ and $Mg_3V_2O_8$ have been extended to the reduced surface phases. Preliminary results for $SrTiO_3$ suggest surface reconstructions different to those seen in the oxidized state. Research is ongoing with funding from the DOE.

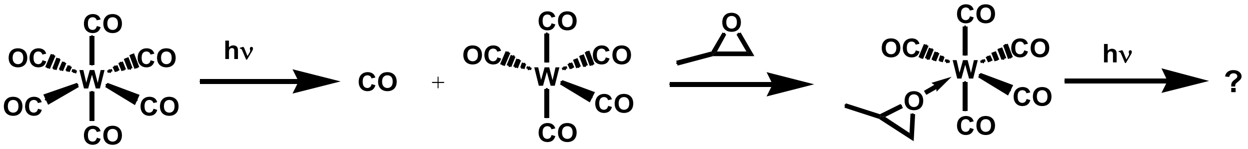
Catalytic Epoxidation Mechanism

A mechanistic focus is the identification and characterization of intermediates that occur in the transition metal promoted epoxidation of olefins, and in the reverse reaction, the deoxygenation of epoxides back to olefins (eq 1). A number of Mo and W compounds have been investigated so far. Three promising reactions have been discovered. One is



(1)

the photochemical reaction of $W(CO)_6$ and $Mo(CO)_6$ in propylene oxide at 350nm to form the coordinatively unsaturated species $[W(CO)_5]$ and $[Mo(CO)_5]$. An objective is to examine photochemically activated reactions of $W(CO)_6$ with propylene oxide (po) in a low temperature (60K) propylene oxide matrix (ratio of $W(CO)_6$:po = ~1:1000)



Equation 2. Reaction of propylene oxide with $W(CO)_6$ in a matrix

Irradiation with wavelengths longer than 300 nm leads to a change in the IR spectrum of the matrix. The single peak at ~1975 cm^{-1} , characteristic of $W(CO)_6$, decreases in intensity while a triplet of peaks at ~1933 (large), ~1870 (medium), and ~2005 (very small) grow in. These latter peaks are assigned to the matrix-isolated monosubstituted product, $W(CO)_5(po)$. The excess propylene oxide can then be removed via gentle heating to isolate this new molecule. Matrices of $W(CO)_6$ in xenon behave similarly -- lower energy (λ >300 nm) irradiation produces infrared absorptions assigned to $W(CO)_5Xe$

Irradiation of a $W(CO)_6$:po matrix with higher energy light (λ< 300 nm) results in a W complex which has undergone loss of multiple CO ligands and can react with epoxide. The products of this latter reaction can also be isolated by evaporation of the propylene oxide matrix. Continued irradiation of the resulting residue, for several hours, with higher energy UV light (λ <300 nm) results in the complete disappearance of the metal-carbonyl signal, although free CO is still observed. Again, matrices of $W(CO)_6$ in xenon behave similarly under identical reaction conditions.

Addition of CO to the matrix residue that remains after evaporation of the major matrix component (either xenon or propylene oxide) results in the generation of new products rather than regeneration of starting material. The carbonyl peaks that grow in upon addition of CO to this residue are shifted to higher energy than the peaks of either the starting material, the epoxide, or the xenon complex. The growth of these new peaks indicates that the photoinduced reaction between $W(CO)_6$ and po (or Xe) is not reversible beyond some degree of irradiation. A possible explanation for this behavior is that the W atoms, having been stripped of their CO ligands, and having the surrounding constraining matrix evaporated, aggregate to form W metal clusters. After additional CO is added, new CO stretches are observed that appear to be more characteristic of CO adsorbed on an amorphous W surface rather than those of a W-O complex.

Trans-Epoxidation

In the study of trans-epoxidation, we have extensively examined the reaction between styrene oxide and 2,3-dimethyl-2-butene over methyltrioxorhenium (MTO). We have studied the dependence of the product formation rate as well as their distribution on MTO concentration and the reaction temperature. In addition we have examined the interaction of styrene epoxide and 2,3-dimethyl-2-butene oxide with MTO separately. As a supplement we have also studied (1) influence of the presence of other alkenes on the interaction of styrene epoxide with MTO, (2) the solvent dependency of the interaction of styrene oxide with MTO, and (3) other epoxide interaction with MTO. The control experiments have been done to show that none of the products are present in the absence of MTO.

We found that styrene oxide is deoxygenated to form styrene in the presence of MTO. 2,3-Dimethyl-2-butene oxide, the expected trans-epoxidation reaction product, is not directly detected. However, the formation of the complex (2,3-dimethyl-2-butane diolate)dioxorhenium(VII) strongly suggests that 2,3-dimethyl-2-butene is oxidized.

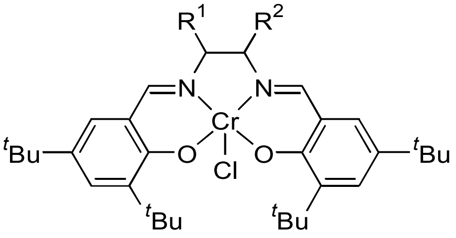
The reaction of MTO and epoxide is highly solvent dependent. The deoxygenation of epoxide occurs in acetonitrile. However, in chloroform and dichloromethane, epoxide reacts with MTO to form complex (diolate)dioxorhenium(VII) quantitatively.

Increase in MTO concentration enhances both the conversion of styrene oxide and the formation of styrene and the complex (2,3-dimethyl-2-butane-diolate)dioxorhenium(VII). Increase in temperature also accelerates the conversion and the formation of the products.

The alkene epoxidation is supposed to be a nucleophilic reaction. The more electron rich the alkene, the easier to be oxidized. Taking into account the epoxidation competition between the substrate alkene and the generated alkene (for example, for the reaction of styrene oxide and 2,3-dimethyl-2-butene, 2,3-dimethyl-2-butene is the substrate alkene and styrene is the generated alkene), the generated alkene should be more electron deficient than the substrate alkene. Therefore, some electron deficient epoxides, namely 4-nitrostyrene oxide, 2-(fluoromethyl)oxirane and cis-stilbene oxide, are used to take the place of styrene oxide. However, the experimental results indicated that the highly electron deficient epoxides are not good choices for the oxygen transfer reaction. The reaction rates between these epoxides and MTO are very slow, suggesting that the deoxygenation reaction is also a nucleophilic reaction and the strong electron withdrawing substituents slow down the reaction.

Cyclic Carbonate Formation

A very promising new catalyst system for the coupling of CO_2 and epoxides into cyclic organic carbonates has been discovered. Our system employs Cr salen metal complexes **1** in addition to an amine co-catalyst such as 4-dimethylamino pyridine N-oxide (DMAP) (eq 2). Our initial report has focused on the optimization of reaction parameters such as temperature, solvent, catalyst and co-catalyst concentrations, and CO_2 pressure in order to maximize catalytic activity and substrate scope. We have been able to attain very high (TOF of ca. 1000 h^{-1} for propylene oxide) and persistent (over 4 days lifetime) catalytic activity for the clean conversion of several α-substituted epoxide to the corresponding cyclic carbonate under mild reaction conditions. We were very pleased to discover that our catalysts system operates most efficiently at low CO_2 pressures (1-3 atm.), as the requirement for high CO_2 is the primary concern when considering the use of CO_2 as a reagent. We discovered that the catalyst with cis diphenyl backbone (**1d**) gives the highest catalytic activity, and interestingly, is twice as active as the trans analog (**1c**). Preliminary investigations into variations of the aldehyde moieties reveals that electron donating substituents in the 5 and 5' positions will increase activity in combination with sterically bulky *tert*butyl substituents in the 3 and 3' positions.



1a: R^1 and R^2 = *trans* -(CH_2)$_4$-
1b: R^1 = CH_3, R^2 = H
1c: *trans*, R^1 = R^2 = Ph
1d: *meso*, R^1 = R^2 = Ph

The substrate scope of our Cr-salen catalyst system is quite remarkable. All α-epoxide investigated yielded the desired cyclic carbonates in near quantitative yields with no side reactions. This reaction is truly "green" for it involves no side products and no waste.

We have also recently found that we are able to selectively couple other heterocumulenes such as isocyanates and isothiocyanates with propylene oxide using our DMAP/Cr^{III} salen systems as the catalyst. This reaction gives very good yield of the cyclic products with greater than 90% selectivity for one isomer under mild reaction conditions. Though we have yet to optimize the reaction conditions our catalyst system compares very favorably with other catalyst systems reported to date.

Project: Selective Oxidation in Zeolites

Cobalt Clusters

Any fundamental description of the catalytic ability of metal-exchanged zeolites must begin with an understanding of the metal active sites. One of the most basic properties of exchanged metals is the location of the cation in the zeolite channels. Ferrierite has a total of seven ion-exchange sites and it is not clear *a priori* which of these sites may be occupied by a given cation. Experimental work in the literature suggests that cobalt occupies three particular ferrierite sites based on indirect spectroscopic evidence.

To probe these siting of cobalt in these sites computationally, eight cluster models were extracted from the ferrierite framework for the purpose of computing the spectroscopic signature of cobalt in these environments. The computed cobalt signatures were found to depend on the relative arrangement of aluminum atoms in the extraframework site. The cobalt B-1,4, B-2,5, G-1,4, and G-2,5 clusters were all determined to have the α signature, while only the G-1,3 cluster produced the β signature. The B-2,6 and G-2,6 clusters were predicted to have inconsistent IR and EXAFS signatures, while the B-1,3 did not match any of the signatures well. Other, more indirect evidence suggests that the α signature is mainly due to cobalt in the B-1,4 site. This conclusion agrees with the original site/signature assignment proposed by Wichterlova and co-workers that the α signature is due to cobalt in the B site while the β signature arises from cobalt in the G site. However, the calculated results also show that the spectroscopic signature is not an intrinsic property of an extra-framework site, but rather a given signature could, in principle, correspond to cobalt in multiple extra-framework sites.

Based on similarities in the experimental infrared bands in the ferrierite transmission region (800 to 1,000 cm^{-1} for several divalent metal cations, the infrared signatures of other metal-ferrierites were calculated using the same set of ferrierite clusters. All of the calculated properties for a given environment, e.g., binding strength, exhibit a U-shaped trend over the manganese to zinc series as the number of d electrons increases. As observed for cobalt, the calculated infrared signatures were found to depend on the relative aluminum arrangement; however, they were not necessarily the same for different metals in the same environment. The other metal-ferrierites produce infrared signatures consistent with experiment, suggesting that these metals also occupy the B and G sites in ferrierite. However, unlike cobalt, the other metals do not have a second experimental signature available to further refine the assignment to specific relative aluminum environments. Metal cations weaken the T-O framework bonds for the oxygen atoms directly coordinated to the cation. This metal-induced structural perturbation is proposed to produce the infrared bands in the ferrierite transmission window. The common characteristics shared among nearly all of the calculated modes demonstrate that all of the divalent metals perturb the framework similarly.

We also examined the adsorption of NO to cobalt in all of the B and G ferrierite environments to begin to probe the effect of environment on catalytic activity for NO_x reduction. NO adsorption to cobalt in the B site is approximately 50 kJ/mol more favorable than to cobalt in the G site. Despite this large difference, the overall electron transfer between cobalt, the zeolite, and NO is similar for all of the sites investigated. The adsorption energy difference is partly attributable to the greater strain that adsorbed NO places on the G site than the B site. The remaining difference is due to the greater degree of coordinative unsaturation of cobalt in the B site compared to the G site.

The two factors identified as controlling NO preferential adsorption, cobalt coordinative unsaturation and adsorbate-induced metal-zeolite strain, were examined in more detail. The adsorption of several NOx molecules was investigated for multiple adsorbate configurations. For nearly all of the molecules examined here, adsorption is preferred for cobalt in the B ferrierite environment over cobalt in the G ferrierite environment. This preference arises primarily from two metal-zeolite properties. First, cobalt is more coordinatively unsaturated in the B environment than the G environment. As a result, adsorption is intrinsically favored by ~13 kJ/mol to cobalt in the B environment. The second characteristic is related to the strain that the adsorbate places on the cobalt-zeolite structure. Adsorbates pull cobalt away from the zeolite to different degrees. The two characteristics usually act in the same direction, making the B environment even more preferred for adsorption. However, in some cases, the strain effect reverses and negates the intrinsic preference of molecules for cobalt in the B environment. Ammonia and water deviate from the trends observed for the other molecules. Both of these molecules form a secondary hydrogen bond with the zeolite; hydrogen bond formation is more favorable in the G environment than the B environment. Additionally, long-range electrostatic forces in the zeolite are expected to more significantly affect ammonia and water than the other adsorbates. The electrostatic contribution to adsorption was estimated to be larger for the G environment than the B environment.

Hence, local zeolite framework heterogeneity near cobalt has a strong influence on the molecular adsorption properties on cobalt-ferrierite. This suggests that the catalytic activity of cobalt-exchanged zeolites for the selective catalytic reduction of NOx depends on the same general factors: induced strain and intrinsic metal coordination differences. In some specific cases where the reactants, intermediates, or products are highly polar, long-range electrostatic effects will also be important.

Liquid Phase Oxidation

A. We have obtained accurate initial rates for 1-hexene epoxidation in TS-1 over a wide range of 1-hexene concentrations in three solvents. We have also measured 1-hexene adsorption constants over a wide range of concentrations in the same solvents. The rate data track the adsorption data in a striking manner when plotted versus 1-hexene concentration in all three solvents. This supports one suggestion from the literature that differences in rate are largely governed by 1-hexene sorption. On the other hand, the results seem counter to many other literature suggestions that the solvent affects the rate by changing the intrinsic reaction kinetics. Quantitative modeling will now be used to further test this conclusion.

B. NMR in sealed sample tubes can be used to measure liquid-phase adsorption in zeolites for systems where evaporation is a problem.

C. Binary self-diffusivities of CF_4 and n-alkanes in faujasite zeolite depend on the combination of molecular size and mass in ways that are sometimes difficult to understand by simple intuition. The data obtained by PFG NMR will provide a good test of proposed schemes for predicting binary diffusivities from single-component data using the Maxwell-Stefan formulation of diffusion (in progress).

D. For the ionic liquid BMIM-BF_4, the anion moves faster than the cation above about 45 C, and they have similar diffusivities below this temperature. This is an interesting and unexpected behavior.

Project: Selective Oxidation over supported Au nano-particles

Supported Au catalysts are typically prepared with a chloride-containing precursor ($HAuCl_4$). It is well known that large amounts of residual chloride are correlated with low catalyst activity. It has been suggested that Cl^- present during calcination causes the agglomeration of Au particles and that these larger particles are responsible for the low activity, as many researchers have proposed that very small (3-5 nm) particle sizes are integral to generating highly active supported Au. When no attempt was made to remove Cl^- from a Au/γ-Al_2O_3 catalyst prepared at pH 4, the average Au particle size after calcination was 44.6 nm by TEM, and the catalyst activity for selective oxidation of CO in H_2 was very low (0.05 ± 0.03 mol CO mol Au^{-1} min^{-1}). If Cl^- was removed from the catalyst with Mg citrate prior to calcination, the average particle size was much smaller, 16.7 nm, and the SCO activity was much higher (1.2 ± 0.1 mol CO mol Au^{-1} min^{-1}). Additionally, Mg citrate can successfully remove Cl^- from the catalysts after calcination. The particle size of these catalysts remained large, 49.6 nm, but the activity was almost as high as that of the catalyst treated with Mg citrate before calcination (0.96±0.1 mol CO mol Au^{-1} min^{-1}). This confirms that Cl^- does facilitate the agglomeration of Au particles. Moreover, the relatively high activity of the catalyst treated with Mg citrate after calcincation suggests that small Au particle size cannot be the only necessary requirement for high activity. Cl^- has an additional inhibitive effect. It is possible that Cl^- poisons the active sites for CO oxidation, which have been proposed to consist of an ensemble of Au^+-OH^- and Au^0, by replacing the Au^+-OH^- with Au^+-Cl^-.

To further examine the potential of Cl^- to act as a poison for the active site, Cl^- was added to a catalyst prepared with a Au acetate precursor. By first impregnating the catalysts with phosphate anions, it is possible to suppress the Cl^- uptake by the Al_2O_3 support so that the Cl^- can be added directly to Au. The catalyst activity after phosphate impregnation is about one-third its original activity, suggesting that the phosphate anions can block some of the Au active sites. If Cl^- was added in the ratio Cl^-/Au of 0.01, the initial activity for SCO was almost completely suppressed, though the activity did increase slowly with time on stream until a steady state was reached at an activity approximately two-thirds that of the original, active catalyst. In fact, activity could be suppressed at a Cl^-/Au ratio as low as 0.0006, indicating that only a small amount of Au is associated with the active sites. This correlates well with Cl K edge XANES results for supported Au catalysts. When comparing the XANES of a catalyst prepared with Au acetate to that of a catalyst to which Cl^- has been added (Cl^-/Au = 0.15), the Cl^- on Au is not visible in the XANES spectrum. This suggests that the concentration of Au sites which are associated with Cl^- is too small to be detected, implying that these catalysts contain a very small number of active sites.

The observation that the activity of the Cl^--poisoned catalysts increases with time on stream supports the proposal that Cl^- acts as a poison for the active sites. During the SCO reaction, the H_2O produced by H_2 oxidation hydrolyzes the Au^+-Cl^- and restores the Au^+-OH^-, gradually increasing the catalytic activity. Thus, we have found that the role of Cl^- is twofold. It does cause Au particle agglomeration, but this is not the reason for the suppression of CO oxidation activity, as suggested in the literature. Cl^- acts as a poison for the catalytic active sites, which are present in very small concentrations.

The ease of reduction of Au(III) complex deposited by the deposition-precipitation procedure depends strongly on the nature of the support. It is much more easily reduced on TiO_2 than on Al_2O_3. The difference could be due to the presence of stronger binding sites for the complex on alumina and/or higher concentration of chloride ions on alumina.

Adsorbed CO on Au can be detected at -60°C, but the majority is found not to be on the active sites. However, the mobility of adsorbed CO is rather high, and all of the adsorbed CO can be removed by reaction with adsorbed oxygen.

Evidence from XANES and FTIR suggests that the amount of adsorbed oxygen on Au/TiO_2 at -60°C is rather small, although the sample is active in CO oxidation.

Earlier, we found that a Au/Al_2O_3 catalyst, prepared by deposition-precipitation with $HAuCl_4$ at pH 7, was inactive at room temperature, but can be activated to a highly active state by a combination of H_2 and H_2/H_2O treatment at 100°C. In-situ XANES measurements showed that Au was in the (III) oxidation state, and was reduced in part to Au(0) after the treatment. However, the reduction was incomplete, and a small fraction of the Au remained in the cationic state. On the other hand, reduction in H_2 alone did not generate an active catalyst, although a portion of the Au was reduced. It was concluded that metallic Au is a necessary but insufficient condition for activity, because exposure of the catalyst to moisture is important for high activity.

In contrast, a Au/TiO_2 catalyst prepared by the same deposition-precipitation method was very active at room temperature without any prior treatment. Subsequent XANES measurements showed that nearly all of the Au was reduced to Au(0). Thus, the stability of the $Au(O)_x(OH)_y$ species on the support after deposition-precipitation differed for the two supports. These different reduction characteristics were confirmed using temperature programmed reduction with hydrogen. The Au complex on TiO_2 can be reduced starting at around 0°C, whereas elevated temperature (above about 60°C) is needed for the complex of Al_2O_3.

High resolution TEM collected by Steve Pennycook at Oak Ridge National Lab offered a picture for the difference. On TiO_2, after activation at room temperature, most of the Au exists in small particles of 2-3 nm. In contrast, a good fraction of the Au on Al_2O_3 after activation is dispersed in monoatomic species (probably ions) on the support, even after the sample had been heated to 100°C. It appears that the surface of Al_2O_3 contains vacancies or defect sites that stabilize $Au(O)_x(OH)_y$ from migration.

The reductive activation of Au/TiO_2 was also studied using in-situ FTIR. The results are consistent with results using XAS. Exposure of an as-prepared sample to CO at -60°C resulted in slow reduction of Au(III). A relatively broad IR band at about 2093 cm^{-1} appeared, which has been assigned to CO bound to Au(0). The intensity of this band increased with exposure to CO. Interestingly, when the sample with adsorbed CO was exposed to a mixture of CO and O_2, a shoulder at about 2100 cm^{-1} appeared. Removing the CO from the mixture caused disappearance of the adsorbed CO band at a rate faster than CO desorption in He. Thus, it appears all of the adsorbed CO can be oxidized. However, it appears that the various adsorbed CO bands disappear at different rates, which suggests that only a small fraction of the adsorbed CO was at or near the catalytic active site for oxidation, while the rest must migrate to the active site for reaction.

For the synthesis of supported gold by jet-enhance-nanoparticle-deposition, we confirmed that the redesigned system improves the quality of the catalyst synthesized. By using resistant heating source, nano-sized metal particles can be successfully and efficiently evaporated onto oxide support. The end product has the desired physical morphology which is confirmed after characterization using advanced electron microscopy. More importantly, carbon contamination during synthesis has been completely eliminated and chlorine and sulfur contaminations which are know for catalytic site poisoning have been minimized.

We have demonstrated the use of SIMS as an effective catalyst characterization technique, which contributes greatly to the surface study of catalysts. For example, oxidation was found to have occurred at the surface of gold nanoparticles in our SIMS study of chemically prepared high activity catalysts. The amount of oxidation is extremely low and thus can only be detected by SIMS. Such finding points us to the further investigation of increased catalytic activity in associated with oxidized gold clusters.

Project: Biomimetic Oxidation Catalysts

Encapsulated Catalysts

Supramolecular-array-based catalysts for epoxidation display sharp substrate size cutoffs that are absent for free catalysts. The array based catalysts function at least 10,000 times longer (in terms of total turnovers) than do free catalysts.

Salen/iron complexes were studied as catalysts for the selective oxidation and cyclopropanation of olefins. These catalysts work well for these reactions under air and also catalyze the oxidative cleavage of benzylic olefins using the environmentally friendly oxidant H_2O_2. This latter reaction provides an excellent environmental-friendly alternative to the use of ozone and heavy metal oxidants.

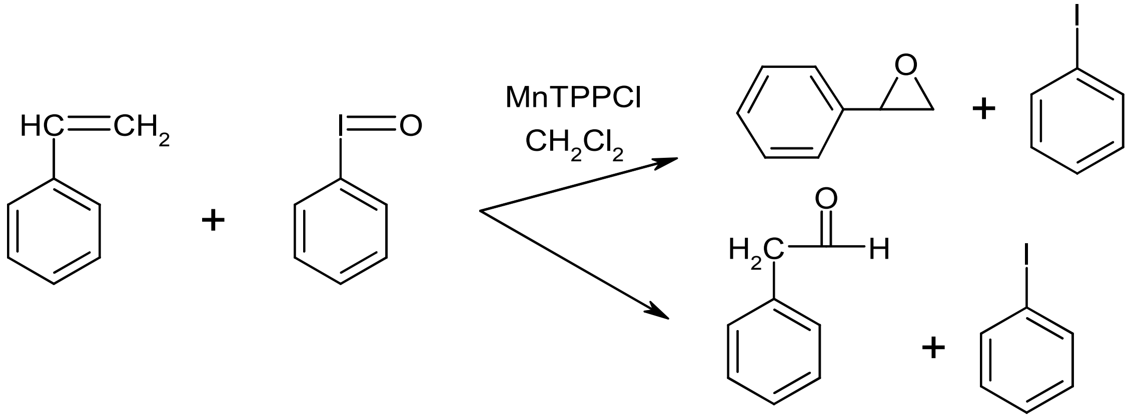
Porous, thin-film aggregates of molecular-square-encapsulated manganese-porphyrin catalysts have been studied. Previous work had shown that solution-phase encapsulation could stabilize catalysts, extending their lifetimes (turnover numbers) by close to two orders of magnitude in olefin epoxidation reactions. Catalyst lifetimes in aggregates could be extended by roughly another order of magnitude, i.e. to a few hundred thousand turnovers, when the catalysts were driven electrochemically. Under certain conditions, the porous thin-film aggregates were also observed to electro-catalyze the oxidation of water to hydrogen peroxide, with product detection and identification being accomplished using an interdigitated dual-microelectrode array measurement method (generator/collector method).

Functionalized homogeneous catalysts such as metalloporphyrin and metallosalen were successfully immobilized them onto solid supports for recycling and/or for special applications (e.g. electrocatalysis, membrane reactor, and photocatalysis). Catalyst loading and stability on solid supports is highly dependent on chemical properties of an anchoring group (e.g. catechol, phosphate, silicate, or carboxylate) and morphology of solid supports. We have also learned that when properly modified, catalysts can be incorporated into multilayer construction, which allows control of the catalyst loading on the surface. We have learned that mesoporous anodized aluminum membrane has a great potential as a solid support for homogeneous catalyst anchoring.

Recyclable oxidation catalysts with high activity and stability have been developed and applied to environmental-friendly processes utilizing inexpensive sources like sun light, electricity, water, and oxygen. Porphyrin catalysts coated on ITO electrode can be electrochemically activated in basic aqueous solution and oxidize olefins using water as an oxygen source.

Mechanism

Systematic experiments have been performed in order to obtain parameters to describe the kinetics of the oxidation of styrene with iodosylbenzene using Mn tetraphenyl porphyrin (MnTPP) or Mn dipyridyl porphyrin (MnDPyP) as catalysts as described in Equation 1. Two main products are observed in this reaction: styrene oxide and phenylacetaldehyde. By monitoring reactant disappearance and product formation in a batch reactor, the reaction rates can be quantified.



Initial rates have been fitted to a power-law rate equation, and kinetic parameters that describe initial reaction rates have been obtained for MnTPP-Cl and MnDPyP-Cl. For MnTPP-Cl the rate equation based on results to date was found to be:

$$-r_{styrene} = r_{products} = kC_{styrene}^{0.57}C_{PhIO}^{0.33}C_{MnTPPCl}^{1}$$

and for MnDPyP-Cl it is:

$$-r_{styrene} = r_{products} = kC_{styrene}^{0.46}C_{PhIO}^{0.29}C_{MnDPyPCl}^{0.61}$$

For both catalysts, the turnover number (TON) increases as the catalyst concentration decreases and as the styrene concentration increases. Finally, it has been observed that at similar experimental conditions, higher TONs were obtained for MnTPP-Cl.

Quantum mechanical calculations were carried out to obtain information about reaction energetics as a first step in quantifying rate constants for the reaction mechanism. Density functional theory (DFT) and quantum/classical ONIOM calculations were performed in order to obtain optimized geometries for MnTPP and the intermediates along the proposed reaction path. For the DFT calculations and for the high-level part of ONIOM, the PW91 exchange-correlation functional was used, along with the LANL2DZ basis set, which uses effective core potentials. UFF was used for the low-level part of the ONIOM calculations. Different spin states of the porphyrin and the intermediates were analyzed with both levels of theory. In all results, the porphyrin had a saddle conformation, and bond lengths obtained were in very good agreement with the crystal structure of MnTPP. The results from the quantum chemical calculations were incorporated into a microkinetic model that was able to capture the concentration dependence observed experimentally for both the reactant and the catalyst. The microkinetic model was more informative than power law rate equations regressed previously since it is applicable over a wider range of reaction conditions and provides insight into the concentrations of different intermediates and rates of controlling reaction steps.

CRG: Emissions Treatment

Project: NOx Emission Catalysis

Zeolite Catalysts

In Sachtler's group, the attempt to unravel the reaction mechanism of NO reduction with hydrocarbons over zeolite-based catalysts showed that 50% of the NO is converted to a surface complex which has the characteristic of an amine. These amine groups react with the other 50% of NO to form N_2. Every N_2 molecules thus contains two N atoms of different history. This important finding shows that there is an intimate chemical link between reduction of NO_x with hydrocarbons and the SCR of NO_x with ammonia. To verify this concept, the group did some studies of NOx reduction with ammonia over Fe/MFI and Cu/MFI catalysts.

The results of this work show that NO_x reduction with ammonia over Fe/MFI is much faster than NO_x reduction with hydrocarbons over the same catalyst. It was also found that for reduction with ammonia our Fe/MFI catalyst is much more active and selective than a Cu/MFI catalyst or an Fe/MFI catalysts prepared by wet ion exchange. See Table

Reduction with ammonia of NOx to N_2 (=N_2 yield) over three catalysts at three temperatures under identical conditions

Temperature\Catal.	Cu/MFI	Fe/MFI wet exch.	Fe/MFI sublim
200°C	------	------	30%
250°C	5%	9%	48%
300°C	20%	27%	80%

Unraveling of the reaction mechanism showed that NO is first oxidized, but unlike the situation with hydrocarbons, ammonia intercepts the molecules already in the state of N_2O_3, leading to the reaction:

$$2NH_3 + N_2O_3, = 2N_2 + 3H_2O.$$

Isotopic labeling revealed, that each N_2 molecule contains one N atom from ammonia, and one from NO_x .

Bimetal/zeolite combinations, such as (Pd+Co)/MFI or (Pd+Fe)/MFI have higher activity for NO_x reduction with hydrocarbons than physical mixtures of the mono-metallic counterparts. We have ascertained that with catalysts containing a majority of Co, introduced by sublimation, besides a small minority of Pd, introduced by ion exchange, a higher activity is achieved than with any physical mixtures of the monometallic catalysts. Formation of Pd(0) in the dynamic equilibrium is a likely cause of this enhanced activity, as the activation of the hydrocarbon will be increased by reduced metal sites.

The reactions of acetaldehyde, acetic acid and nitromethane with NO_2 on a BaNa-Y zeolite were studied using FTIR spectroscopy, temperature programmed reduction and in a flow reactor. Constant temperature studies were typically performed at 473 K. The mechanism that has been deduced for the reaction of NO_2 with acetaldehyde, the details of which principally come from FTIR work, is outlined schematically below:

$CH_3CHO \rightarrow CH_3COO^- \rightarrow CH_2NO_2^- \rightarrow O_2NCH_2NO_2^- \rightarrow CNO^- \rightarrow HNCO \rightarrow NH_3$

Exposure of a BaNa-Y zeolite to acetaldehyde leads to formation of acetate ions and subsequently the aci-anion of nitromethane. NO_2 can then react with the aci-anion of nitromethane, which is stabilized in the ionic environment of the zeolite, to form a proposed $O_2NCH_2NO_2^-$ intermediate. This intermediate is expected to rapidly decompose at 473K by loss of NO_2 and H_2O to yield the formonitrile oxide anion, CNO^-, which can then isomerize to NCO^-. This latter species can then react with a proton to form HNCO. NH_3 and CO_2 can then be formed from the reaction of HNCO with H_2O. Once NH_3 is produced, well known chemistry can lead to the formation of N_2 as a result of formation and decomposition of ammonium nitrite, which as discussed below, is facile at temperatures below 200K. Remarkably, in this system N_2 formation from the reduction of NO_x takes place in the absence of a transition metal.

The reaction channel outlined above takes place with acetic acid and results in a very high CO_2/CO ratio (>20:1). The reaction of either acetic acid or acetaldehyde with NO_2 gives a similar set of products, except that the CO to CO_2 ratio is higher *and* methanol formation is observed when acetaldehyde is the reactant. These observations suggest that a parallel reaction channel is operative when acetaldehyde is the added reactant, and that this channel could involve free radicals. Such a pathway could involve the initial abstraction of an H atom from acetaldehyde by NO_2. The resulting acetyl radical could then dissociate to CO and a methyl radical. Gas phase nitromethane is directly observed with acetaldehyde as the initial reductant but not with acetic acid as the reductant. Nitromethane could by produced by neutralization of an appropriate ionic precursor and/or it could be a product of the additional reaction channel for acetaldehyde alluded to above.

Another aspect of our work seeks to understand low activation energy pathways for the catalytic reduction of nitrogen oxides to N_2, with reductants other than ammonia. A general scheme to provide for facile reduction of NOx involves two sets of reaction steps. In the first set of reactions part of the NO_x is reduced to NH_3. The second set of reactions incorporates the ammonia thus formed into ammonium nitrite, NH_4NO_2, which is a product of the reaction of NH_3 and $NO + NO_2$ and water. The NH_4NO_2 thus formed will decompose either on the zeolite surface or on an inert support at ~100 °C to $N_2 + H_2O$. On the other hand, ammonium nitrate, NH_4NO_3, which can also be formed from NH_3 and $NO_2 + O_2$ and water, (or HNO_3), decomposes at a much higher temperature, 312 °C, yielding mainly N_2O. Application of Redhead's equation, which was developed for first order desorption, to the decomposition of ammonium nitrite, yields an activation energy of 22.4 kcal/mole for this process, which is consistent with literature data.

For the reaction path producing ammonium nitrite a consumption ratio of 1/1 for NO and NO_2 is predicted, and confirmed by injecting NO into a mixture of $NH_3 + NO_2$ flowing over a BaNa/Y catalyst. This leads to an increase in N_2 yield of one N_2 molecule per added molecule of NO. Little N_2 is produced from NH_3 + NO in the absence of NO_2.

It is well known that ammonia can act as a reductant for NOx. As such, the operative chemistry this system was studied with an emphasis on the role of NO in NOx reduction. In a system that involves NOx species, ammonium nitrate and surface nitrates can both form. Both of these species are more thermally stable than the corresponding nitrite. We have found that NO reduces HNO_3 to HONO and surface nitrates to nitrites on a BaNa-Y zeolite, and it reacts with NO_2 to form N_2O_3. Additionally, adsorbed NO^+ reacts with water to form HONO. In the presence of NH_3 and H_2O these reactions lead to the formation of ammonium nitrite that efficiently decomposes near 100 °C to give N_2 + H_2O. The overall reaction sequence thus provides a means for effecting the catalytic reduction of NOx to N_2. A criterion for this path is that the optimum yield of N_2 is obtained with an equimolar mixture of NO + NO_2. Since ammonium nitrate does not significantly decompose at 200°C, a typical temperature for diesel exhaust, the reduction of nitrate to nitrite serves to regenerate active sites on the BaNa-Y catalyst.

The formation of peroxide and superoxide in Fe/MFI, prepared by sublimation of $FeCl_3$ into H-MFI, was observed by UV Raman spectroscopy. Peroxide produced a distinct peak at ~730 cm^{-1}, while the presence of superoxide was identified by a complex band in the region 1050-1160 cm^{-1}. The position and intensity of these bands and their behavior as a function of temperature and O_2 pressure depend on the catalyst pretreatment history. Three types of pretreatment after $FeCl_3$ sublimation but prior to placing the catalyst into the fluidized-bed cell can be distinguished: 1) Oxidation at 823 K, designated Fe/MFI; 2) Treatment of Fe/MFI with NaOH solution followed by calcination at 823 K (to replace Fe-cations with Na^+) designated Fe,Na/MFI; 3) Re-exchange of Fe,Na/MFI with NH_4^+ followed by calcination (to replace Na^+ with H^+) designated Fe,H/MFI. After placement in the Raman cell the samples were oxidized at 773 K and then reduced in H_2 at 723 K. The Fe/MFI and Fe,H/MFI samples both exhibited bands due to peroxide and superoxide in contact with O_2 at room temperature and below with the bands being stronger for the Fe,H/MFI. Heating the samples to 543 K on O_2 or switching to He flow at 300 K caused the peroxide and superoxide bands to disappear. No peroxide or superoxide was detected on Fe,Na/MFI under any circumstances; neither were they seen on a sample prepared by incipient wetness impregnation of H/MFI with $Fe(NO_3)_3$. The iron in these latter samples has been shown to exist primarily as Fe_2O_3 crystallites. This result shows that the presence of binuclear iron clusters is required for peroxide and superoxide formation.

The formation of peroxide and superoxide on Fe,H/MFI compared to Fe/MFI also shows two distinguishing features. First, the amount of peroxide on Fe,H/MFI at room temperature is significantly greater than on Fe/MFI as judged by the peroxide peak intensity relative to the zeolite bands. Second, on Fe,H/MFI peroxide is converted to superoxide when the sample temperature is lowered to 93 K and then restored when the temperature is returned to 300 K; on Fe/MFI the relative peak intensities of peroxide and superoxide remain constant with temperature between 93 K and 300 K. (Note: A special variable temperature fluidized-bed Raman cell was constructed for these experiments.) Taken together the temperature behavior of Fe,H/MFI and Fe/MFI suggests 1) the peroxide state of adsorbed O_2 is higher in energy than the superoxide state (equilibrium favors peroxide at 300 K compared to superoxide at 93 K), and 2) the interconversion of these states is more facile on Fe,H/MFI than on Fe/MFI. Infrared spectroscopy has shown that the concentration of hydroxyl groups is higher on Fe,H/MFI than Fe/MFI. Since the reversible conversion of peroxide to superoxide corresponds to a reversible electron transfer between the O_2 anion and iron cations, these results suggest that the presence of hydroxyl ligands bonded to iron in the binuclear cluster facilitates redox changes in the iron.

An additional type of Fe/MFI material can be distinguished with respect to the temperature dependence of peroxide and superoxide formation by higher temperature H_2 reduction at 873 K instead of 723 K in the Raman cell and then reoxidation using N_2O at 523 K, designated HTH,Fe/MFI. This procedure mimics the treatment reported to produce exceptionally high activity Fe/MFI by Sachtler and coworkers. After this treatment peroxide and superoxide were found to be stable in He atmosphere at least to 523 K. In H_2 atmosphere more than 50% of the peroxide is removed between 413 K and 500 K (see Fig. 4, upper) where a pronounced and highly exothermic reaction was reported during H_2 temperature programmed reduction. These Raman spectroscopy results not only identify the culprit of this exceptional hydrogen reduction, but also demonstrate enhanced stability of peroxide and superoxide species to higher temperature following high temperature hydrogen reduction of Fe/MFI. When the hydroxyl content of this material is increased by exposure to water vapor, the highly active species in hydrogen TPR disappears. This consequence of added water to the HTH,Fe/MFI material is consistent with a picture where the addition of hydroxyl groups destabilizes the peroxide species so that it is no longer present on the surface at the temperatures where the highly active iron sites are observed. Taken together these data point to a picture where the redox activity of iron and hence the presence and reactivity of peroxide and superoxide are controlled by hydroxyl groups bonded to the iron.

Alumina-Supported Catalysts

For the alumina-based catalyusts, the study in Kung's group on the bi-functional SnO_2/Al_2O_3 suggest that a potentially fruitful direction is to design a catalytic system where the hydrocarbon activation function and the nitrogen formation functions are separated. On SnO_2/Al_2O_3, the role of SnO_2 is to activate propene to form acrolein. On Al_2O_3 acrolein is quantitatively transformed to form acetaldehyde, which subsequently reacts with NO_x to form N_2. Activation of propene can also be achieved in a non-catalytic manner. Using non-thermal plasma (an alternative technology being explored for NO_x abatement), acetaldehyde is also formed from C_3H_6. Thus, efficient utilization of acetaldehyde may be a key towards realization of a practical NO_x abatement strategy.

Thus, one phase of lean NO_x catalysis research in this our group involves exploring suitable catalytic system for (a) selective formation of oxygenates from alkene and (b) selective NO_x reduction by acetaldehyde. Non-thermal plasma technology is expensive and a catalytic solution is preferable. Currently we are looking for more selective and active catalytic systems than SnO_2 for C_3H_6 activation. Critical properties of this metal oxide catalyst must include thermal stability and low vapor pressure. V_2O_5 and/or MoO_3 are important components in most selective oxidation catalysts, but they have high vapor pressure and thus are not suitable for exhaust emission application. We have prepared GeO_2-SiO_2 mixed oxide using a co-gellation procedure. These preparations have high surface areas. The surface areas are 468 m^2/g and 330 m^2/g for samples with GeO_2 loadings of 34.5% and 50 wt. %, respectively. The GeO_2 are very well dispersed as no XRD peaks are detected for the 34.5 wt.% loading sample.

Concurrently, the Kung group is exploring the NO_x reduction efficiency of various oxides when acetaldehyde is used as a reductant. TiO_2 is being investigated, as we would like the catalyst to be more active than Al_2O_3 but less active than most transition metal oxides. The NO_x reduction efficiency appears to be dependent on the morphology of TiO_2. A rutile TiO_2 preparation is more active and selective than a mesoporous one. Impregnation of the mesoporous TiO_2 with Ba nitrate enhances the combustion of acetaldehyde. They are beginning to map out properties of oxides that is important for the selective reduction of NOx using acetaldehyde as a reductant. We have also begun sol-gel preparation of mixed oxides for use in the selective oxidation of alkene to oxygenates for use in NO_x reduction.

To gain a deeper understanding of the observations from the steady-state reaction studies, we carried out in-situ infrared characterization to get information on the active species over anatase titania at the reaction temperature of 300^oC. Results of IR experiments concur with the high reactivity of adsorbed NO_2. Exposure of NO_2 produced peaks at 1608, 1583 and 1243 cm^{-1} that are assigned to a bidentate nitrate species. This nitrate species was stable and remained after 40 min purging at 300^oC. However, exposure of this nitrate species to acetaldehyde resulted in immediate and large decreases in peak intensities. The acetaldehyde was completely transformed (no C=O peak and C-H band was observed). The only C-containing species detected on the surface were carboxylate groups.

The IR results support the reaction studies in showing that the efficiency of the anatase titania catalyst is due to both the high coverage of its surface by nitrates and the high reactivity of these nitrate species with acetaldehyde. Presumably, nitrogen is formed in this reaction.

Project: Photobiocatalysis

The major findings in each of the respective 5 areas explained in "Activities" are summarized.

Development of new molecular tools to probe photocatalytic reaction.

One area of effort in the photobiocatalysis group focused on the development and application of methodologies for interrogating the energetics of photo-active semiconductor/solution interfaces, assessing molecular adsorption at semiconductor/solution interfaces, and building periodic, micropatterned semiconductor/biofilm arrays. As part of this effort a method was developed for fabricating high-quality and moderately high area micropatterned thin films of TiO_2 on transparent, conductive platforms. These films have been employed as photonic lattices, where the periodicity of the microstructure has been exploited to achieve efficient diffraction of coherent monochromatic visible light. The diffraction phenomenon, in turn, has been used to: 1) demonstrate the ability to detect and quantify binding of candidate pollutant molecules to TiO_2 (vapor-phase adsorption of chloroform; aqueous-phase adsorption of trichlorophenol), 2) assess interfacial energetics (environment-dependent conduction band edge energies for TiO_2 thin films), and 3) measure important electro-optical properties of TiO_2 thin films (wavelength-dependent and electrochemical-potential-dependent refractive indices).

As a result of the work described above it seemed promising to explore the possibility that TiO_2 microfabrication and photonic lattice measurement techniques combined with infrared laser spectroscopy capabilities could accomplish at least two important things: a) extension of the detection limit of adsorbates, and b) introduction of chemical specificity in the adsorption assessment technique. The former is obviously important when the binding of candidate reactants to TiO_2 is weak, or when low-coverage photochemical intermediates are the target of the investigation. The latter is important for obvious mechanistic reasons - clearly molecules must interact with the TiO_2 surface before they can be degraded, and their binding constant should be an input to a complete model of surface photochemistry. The basis for the anticipated enhanced sensitivity was the ability to achieve wavelength-dependent (adsorbate molecular structure dependent) resonance enhancement of the diffraction response, and the ability to employ lock-in detection as a consequence of being able to frequency modulate the infrared laser used to achieve resonant enhancement of the diffraction response.

Adsorption of VOC's (volatile organic compounds) on such patterned substrates will cause the intensity of the diffraction pattern of the substrate to change as a result of the refractive index of the adsorbate. As alluded to above, because most VOC's have similar refractive indices in the visible region, a chemical sensor using this methodology with visible light laser light is not expected to be molecular specific. However, the refractive index of a material changes at the frequency of an absorption. Since all VOC's absorb in infrared region, moving the interrogation frequency into this region provided a potential route for developing a molecular specific chemical sensing method.

Experiments in infrared region showed that the diffraction intensity changed when a VOC was adsorbed on the patterned substrate. But, we determined that the contribution from the change in refractive index when the incident light was resonant with an absorption of an adsorbate was not as large as hoped for. Diode lasers were employed as the tunable infrared laser source. We found that variations in the intensity of the diode laser resulted in "noise" in our signals. Though there were ways that this noise could be mitigated, we had enough data to perform at least an approximate calculation of the sensitivity of this method and found it to be lower than other better developed sensing techniques for adsorbates. Thus, a decision was made not to pursue further developments of this methodology.

Use of established tools to provide new mechanistic insights into photocatalytic reactions.

This research disproves previous proposals that describe rutile as the electron sink serving to hinder charge recombination on anatase. Rather, rutile acts as an antenna to extend the photoactivity of the catalyst into visible wavelengths and stabilizes charge separation through electron transfer to lower energy anatase centers. This work illustrates the utility of EPR as a method to directly characterize catalyst activity. Not only does this research illustrate the mechanism for the enhanced activity observed in mixed phase TiO_2 photocatalysts, but it has also provides evidence for a structural model of the catalyst in which the two phases must be closely coupled in order for the rapid electron transfer observed to occur. Such information is important for future rational catalyst design.

Probing the nature of surface reactions on TiO_2.

The objective of the research is to determine how illumination conditions affected the adsorption of the model pollutant 2,4,5-trichlorophenol (TCP) onto the surface of TiO_2. Light wavelengths above the bandgap of rutile and anatase are used so to study adsorptive phenomena in the absence of charge separation. Nevertheless, we have discovered intriguing effects of visible light on aqueous systems containing both TiO_2 and TCP. The focus of this project has been on characterizing the nature of the interaction and its mechanisms.

Prior experiments revealed that in aqueous suspensions of Degussa P25, a commercial preparation of TiO_2 consisting of about 80% anatase phase and 20% rutile phase, adsorption of TCP appeared to increase by as much as fourfold under visible light versus dark conditions. To ensure that trace UV in the fluorescent lighting was not the cause of the phenomenon, the experiments were repeated with an optical gel filter that removed all UV light ($l<415$). A significant light effect was still observed on P25. However, a light effect was observed on pure anatase only without the filter (in the presence of trace UV), and no light effect was observed on pure rutile under any conditions. Furthermore, total organic carbon (TOC) measurements of the bulk solution showed that TOC remained constant in unfiltered anatase experiments even though [TCP] decreased. This suggests the conversion of TCP to organic byproducts that remained in the aqueous phase and shows that the only light effect on anatase was in fact low-level photocatalytic transformation triggered by the small amount of UV in the fluorescent lighting. Conversely, on P25, the aqueous decrease in TOC corresponded to the decrease in [TCP], indicating that the organic carbon was likely adsorbed to the catalyst. However, the release of chloride (about 1 mol Cl^- per 3 mol TCP depleted from the aqueous phase) indicated some degree of transformation of TCP.

Experiments in the past year have focused on clarifying the fate (adsorption or reaction) of TCP in aqueous P25 slurries under visible light. Less than half of the TCP lost from solution is accounted for as adsorbed TCP. No products are detected in the solution phase of the TiO_2 slurries. Efforts to recover adsorbed products assuming that they were lighter and more polar than the parent compound, as photocatalytic oxidation products generally are, had proved fruitless. Assuming the opposite, that TCP might polymerize to form less polar products on the TiO_2 surface, led to a successful non-polar extraction technique using an acetone/hexane mixture and a desiccant. Analysis of concentrated extracts by GC/MS identified dimerized TCP species such as dioxins and dibenzofurans containing between four and six chlorines. Direct MS and LC/MS revealed the existence of much larger molecules, with molecular weights higher than 1200 D. These larger polymers have not been identified.

The identified products close the mass balance on carbon and illustrate that the P25 surface promotes sub-bandgap photochemistry. The products are formed only under visible illumination conditions. They are not typically produced in photocatalytic reactors and are themselves labile to photocatalysis. To demonstrate this, a sample of TiO_2 and TCP illuminated with visible light (and therefore containing dioxins and dibenzofurans) was then subsequently treated with high intensity UV light for 1 h in an annular photocatalytic reactor. The TiO_2 was extracted, and no fusion products were found in the extract.

It was hypothesized that the reaction of TCP on TiO_2 under visible illumination occurred via a charge-transfer complex. This hypothesis was confirmed using EPR and diffuse reflectance UV-vis spectroscopy. EPR spectra showed transfer of electrons from TCP to P25 under wavelengths as high as 495 nm, while no electron accumulation occurs on TiO_2 by itself under the same light conditions. The EPR findings were corroborated by the diffuse reflectance spectroscopy of P25 with and without dark-adsorbed TCP. P25 by itself does not absorb wavelengths above 410 nm, but with adsorbed TCP wavelengths as high as 550 nm were absorbed.

Excitation of the charge-transfer complex is consistent with the products formed. Direct transfer of an electron from TCP to TiO_2 results in a TCP radical species. If TCP molecules in close proximity to each other on the catalyst surface carry unpaired electrons, it is likely that they will combine to pair their electrons, resulting in the polymerized products. This mechanism differs from that of conventional photocatalytic degradation, where UV light activates the catalyst directly and the catalyst, in turn, reacts with water and/or hydroxide to form hydroxyl radicals, which then attack organic compounds at or near the surface. Thus under UV light, TCP molecules react not with each other but with $^{\cdot}$OH.

Future work includes exploring effects of varying the organic molecule or the illumination wavelength. Diffuse reflectance spectra will be taken of P25 bound to a series of chlorophenols. Trends will be sought based on number and location of chlorine atoms. Also, a Xe arc lamp has been set up with the necessary attachments to produce narrow band (10 nm) light, ranging from super-bandgap energy (360 nm) to the limit of the TCP/P25 charge transfer complex band (550 nm). Experiments will assess whether specific products or class of products can be selected by controlling the wavelength of irradiation.

The use of new and established molecular tools to probe microbial community dynamics.

Using typical T-RFLP conditions from the literature, we demonstrated incomplete digestion of the 16S PCR amplicon. Complete digestion is a critical part of T-RFLP because incomplete digestion leads to overestimation of microbial diversity. Incomplete digestion was demonstrated through the use of a pure culture of *Pseudomonas aeruginosa*. Since the genome of *P. aeruginosa* has been sequenced, the theoretical terminal restriction fragment (T-RF) length can be calculated for different restriction enzymes. This was done for several enzymes, including *HhaI*. For *HhaI*, the T-RF length is 153, but the T-RFLP pattern showed strong bands at 153 and 564 bases. It is possible for an organism to have multiple copies of the 16S gene that differ in sequence. This is true for *P. aeruginosa*, which has 4 copies of the 16S gene, but these 4 genes do not differ in the location of the terminal *HhaI*-restriction site. A 564-base fragment can be generated from *P. aeruginosa* if *HhaI* does not cut the DNA at each *HhaI*-restriction site (i.e., incomplete digestion). To obtain complete digestion, many variations on the digestion procedure were tried. It was determined that complete digestion (> 98%)will be attained for *P. aeruginosa* if 300 ng of DNA are digested in a 20-mL reaction containing 40 U of *HhaI*.

Probing the stability and resilience of microbial communities as a function of carbon source.

Through our work on TCP biodegradation we have found that TCP is biorecalcitrant at concentrations greater then 40 μM. We found that TCP is strongly inhibitory to respiration and that the degree of inhibition is in direct proportion to TCP concentration, with maximum inhibition predicted at 200 μM. We determined mixed microbial communities adapted to TCP acted reproducibly at concentrations less then 40 μM but at concentrations greater then this the replicate reactor's behavior varied wildly, further indicating a threshold near 40 μM above which biodegradation is difficult. We ran continuous bioreactors using TCP as the sole carbon source, but these systems were found to be brittle and did not accumulate biomass even after manipulating reactor conditions for precisely this purpose. The reactors failed after about 45 days of operation, highlighting the difficulty associated with biodegradation of TCP. Kinetic analysis of TCP biodegradation was performed to try and understand why it cannot be biodegraded reliably. Through this analysis we predicted an approximate value, using some kinetic parameters from dichlorophenol biodegradation, that in order to sustain biomass in a continuous reactor you need to supply 266 μM TCP. However, this concentration is highly inhibitory and so the trade-off is well demonstrated. This work demonstrating the difficulty associated with TCP biodegradation shows why a photobiocatalytic system is warranted, providing that it can work reliably.

To demonstrate the viability of the photobiocatalytic system we produced multiple batches of heavily degraded photocatalytic effluent. We used 1.0 g/L Degussa P25® TiO_2 in 1-L of 500 μM TCP, and photodegraded the mixture for 30 minutes under an oxygen atmosphere. Using these same conditions we produced multiple batches of effluent, filtered off the catalyst, and added media components. We then fed this photocatalytic effluent with media components to 4 parallel bioreactors and monitored their performance. The overall effluent (coming out of the bioreactors) showed complete TCP removal, good biomass accumulation, and COD and DOC removal. Analysis of the microbial communities showed a 75% decrease in community diversity after reaching steady-state after which the diversity stabilized, and showed no discernible differences in diversity between the 4-parrallel reactors. This work demonstrates the capability of photobiocatalysis, which was able to completely remove 500 μM TCP whereas biodegradation alone could not remove even 75 μM TCP in the continuous reactors.

We now needed to examine how changing the photocatalytic reactor conditions affects what is produced in the effluent, and how these different effluent compositions can in turn affect biological reactor performance, and therefore overall system performance. To examine this relationship we chose 4 photocatalytic reactor conditions that would give us 4 unique effluent compositions, the conditions were (a-d); A - photolysis (no TiO_2) for 15 minutes with a quartz sleeve (all light with λ>190 nm allowed into the photoreactor), B – photocatalysis (with 1.0 g/L TiO_2) for 5 minutes with the quartz sleeve, C – photocatalysis for 30 minutes with the borosilicate sleeve (all light with λ>340 nm allowed into the photoreactor), and D – photocatalysis for 50 minutes with the borosilicate sleeve. Based on Mwende Lefler's masters work, and our own analysis of the effluents produced, the composition of each of these effluents is as follows; A – No remaining TCP, but primarily composed of chlorinated aromatics and some chlorinated aliphatics, B – roughly half of the input TCP remaining, mixture of chlorinated aromatics, chlorinated aliphatics, and non-chlorinated aliphatics, C – roughly 30% of the input TCP remaining, mixture of chlorinated aromatics, chlorinated aliphatics, and non-chlorinated aliphatics, but with much less aromatic character then batch B, D – roughly 25% of the input TCP remaining, majority of the remaining carbon is non-chlorinated aliphatics. We produced multiple batches of each of these effluents, filtered off the TiO_2, and then diluted each down appropriately to 40 mg/L of COD and added media components. We wanted to normalize by input COD so that any differences we see in the bioreactors would be a function of substrate composition.

We then fed each of these effluents to bioreactors, using the same activated sludge as the inoculum for each, and allowed them to come to steady state. We found that effluent A gave poor COD removal and biomass accumulation but of course had no TCP remaining (there was none going in). This shows that even though there was no TCP input to the bioreactors, by having the majority of carbon tied up in difficult to degrade chlorinated aromatics and chlorinated aliphatics we still have a poor treatment process. Effluent B gave better COD removal then A and much better biomass accumulation, furthermore it completely removed all of the input TCP which is interesting since it had the most TCP into the reactor of the 4 conditions tested. This shows that having some chlorinated aromatics and aliphatics can aid in TCP biodegradation, but since so much of the carbon was still tied up in TCP we did not have good biomass accumulation and COD removal. Effluent C gave the best biomass accumulation and had very good COD removal. There was a small but non-zero concentration of TCP remaining in the effluent from the bioreactor (this reactor had the smallest amount of TCP into the bioreactor after the dilution). This shows again that having chlorinated aromatics and aliphatics can aid in TCP biodegradation, but by having more of the carbon invested in simpler organics that are easier to degrade, we produce an effluent of overall higher quality. Effluent D showed poor COD removal and biomass accumulation, which was unexpected since a large percentage of the substrate was easy to degrade non-chlorinated aliphatics, and also had the most TCP remaining in the effluent, although it was still a small concentration (near 10 μM TCP). The reason for the poor performance is that the absence of TCP-like compounds to help the TCP degrading community resulted in poor TCP removal and more importantly, less resistance to TCP and TCP-like compound inhibition. Community analysis is still underway.

The final set of experiments used model compounds to simulate the photocatalytic effluents. We used single carbon sources so that we could more directly understand how substrate composition affects bioreactor performance and community diversity. We used 4-chlorocatechol (4CC) to simulate a "lightly" photodegraded effluent, 2-chloromuconic acid (2CMA) to simulate a moderately degraded effluent, and acetate to simulate a general heavily degraded effluent. As expected, both COD removal and biomass accumulation increased as we went from 4CC to 2CMA to acetate, simpler organics yield more energy per unit substrate and are easier to mineralize in the same amount of time. Upon reaching steady-state we perturbed each of these reactors with a 100 μM spike of TCP. Perturbation analysis is used to gauge the stability, resistance, and resilience of different communities. We found that the perturbation significantly impaired the acetate community whereas it did not impair the 4CC community, as we would expect. However, we also found that the 2CMA community reacted positively to the perturbation, confirming what we found from the previous experiments, that by supplying these intermediate compounds we can sustain a community that accumulates more biomass and removes more COD, but that we can also still maintain a degree of resistance to the inhibitory effects of the complex organics without having to solely supply those complex organics alone, which would lead to poor biomass accumulation and COD removal. Analysis of the community diversity is still underway.

CRG: The Natural Environment

The natural environment collaborative research group is focused on elucidating and understanding the mechanisms of microbial resistance to metal stress. Results were obtained in three highly inter-related sub-areas:

1. Metal speciation and bioavailability

2. Mechanisms of microbial metals resistance

3. Formation, structure, and reactivity of biologically produced manganese oxides.

Project: Metal Speciation and Bioavailability

Biogeochemical Modeling:

We carried out extensive modeling exercises to help us understand the conditions under which bioprotection ought to work. For these exercises, we chose a microbial community comprised of fermenting bacteria and sulfate-reducing bacteria. The fermenting bacteria convert complex organic compounds to acetate, which is then oxidized by the sulfate reducers. The sulfate reducers produce sulfide, which serves an as anion to precipitate the metal species (Zn^{2+} in our exercises) and as a ligand to form the metal-sulfide complexes. In principle, the sulfate reducers should be able to generate sulfide that protects both types of bacteria.

The modeling exercises support our hypothesis that the sulfate reducers can bioprotect both species. Furthermore, the results indicate that complexation is the dominant protection process when the Zn loading is low, but precipitation becomes dominant when the Zn loading is high. The results also demonstrate the mutualistic relationship between the fermenters and the sulfate reducers: The fermenters provide substrate to the sulfate reducers, while the sulfate reducers generate sulfide to protect both species. Two-dimensional modeling underscored the need to have both reactions occurring together to have the most complete bioprotection.

After extensive investigation of alternatives for a model microbial ecosystem to test our bioprotection concepts, we selected *Acetobacteruim woodii* and *Desulfobacter postgatei* as model fermenter and sulfate reducer, respectively. *A. woodii* ferments lactate or glucose to acetate, which is the sole electron donor of *D. postgatei.* Their growth conditions are compatible. Therefore, they form a well-understood ecosystem in which mutualistic bioprotection can work. We also determined that Zn and Cu are interesting metals that exhibit relevant toxicity responses for our model system.

Metal Biofilm Interactions:

No noticeable changes in uronic acid content were observed in both EPS with and without Cu exposure, showing that the EPS from PDO300 biofilms was mainly composed of uronic acid (≥ 95 %) independent of Cu stress. Although chemical composition did not change in the EPS from mucoid strains of *P. aeruginosa* in response to Cu stress, it still remains unknown whether or not there will be quantitative or qualitative changes in the chemical composition of the EPS from wilde-type or other variants of *P. aeruginosa* due to the physiological response of heavy metal stresses. Related to this, further experiments will include wilde-type and other variants of *P. aeruginosa* to determine changes in chemical composition of the EPS in response to Cu and Zn stresses.

Conventional wet chemical assays were simple and rapid to determine the chemical composition of the EPS, but they implied analyzing each chemical component separately and specifically. In addition, they provided only bulk content measurements of polysaccharides in the EPS. Furthermore, there were difficulties in the standardization of the method for the quantification of polysaccharides because various types of polysaccharides such as acidic, neutral, anionic polysaccharides responded differently to these methods.

On the contrary, the TMS derivatization technique followed by GC-Mass analysis was found to be useful in determining the chemical composition of the EPS. It allows the simultaneous identification and quantification of neutral sugars, acidic sugars, and amino sugars as well as lipids and amino acids. Further study on the chemical composition of the EPS, therefore, will focus on quantitative analysis of chemical components of the EPS from different *P. aeruginosa* biofilms by the TMS derivatization-GC-Mass analysis along with Pyrolysis-GC-Mass spectrometry.

In addition, a recent study suggested that extracellular DNA could be an important component of the EPS because of its importance in the initial stage of biofilm formation by *P. aeruginosa*. We observed furfuryl alcohol peaks from both pyrolysates of the EPS from PAO1 and PDO300 biofilms, which might be the chemical marker of DNA. DNA analysis will be performed to determine whether the chemical signature of DNA can be identified, and if DNA is an important component of the EPS from *P. aeruginosa* biofilms.

Project: Mechanisms of Microbial Metal Resistance

Role of Biofilms in metal stress:

We found that biofilm *P. aeruginosa* is more resistant to the heavy metals zinc, copper, and lead relative to free-swimming *P. aeruginosa*. Biofilm cells were viable at concentrations varying from 2 to 20 fold the minimum inhibitory concentrations of the free-swimming cells. For example, biofilm *P. aeruginosa* was viable up to 0.8 mM total added Pb, while free-swimming *P. aeruginosa* ceased to be viable at 0.3 mM added Pb. The viability testing of biofilms and free-swimming *P. aeruginosa* was originally performed in a minimal media that was found to complex and precipitate a majority of the heavy metals. To minimize these effects, the work was repeated in a buffered saline solution where complexation and precipitation reactions with metals were negligible. We verified this using a copper ion selective electrode. Using the buffered saline solution we found a similar trend: biofilm *P. aeruginosa* was more resistant to heavy metal stress than free-swimming *P. aeruginosa*.

The resistance of *Paracoccus denitrificans* to heavy metal stress was also examined to verify that biofilm protection is consistent across different bacterial species. *P. denitrificans* is an environmental bacterium capable of denitrification. We found that biofilm *P. denitrificans* was more resistant to a lead stress than free-swimming *P. denitrificans*. Based on these two observations, we can suggest that, in general, biofilms are more resistant to metal stress than free-swimming bacteria.

We also examined whether the role of the metal in biofilm formation in the case of *P. aeruginosa.* For instance, would *P. aeruginosa* preferably form biofilms in response to metal stress because it is in a more resistant state or would the biofilm formation be hindered by the presence of the metal at a certain concentration? We found that the percent of bacteria attaching to a surface over two hours decreased in the presence of lead ($p < 0.01$). Attachment was also found to decrease in the presence of calcium, which is not toxic to *P. aeruginosa* at the added amount. It is unclear at this time why the addition of lead or calcium would cause a decrease in attachment to surfaces. One explanation could be that the addition of cations result in their adsorption at the surface sites where the biofilm attaches, preventing therefore the attachment of the bacteria. We are examining the role of other cations to verify that this observation can be explained using surface chemistry.

We have initially compared the heavy metal resistance of isogenic non-mucoid and mucoid (EPS overproducer) strains. Initial investigations indicate that there is little difference between the two strains in terms of heavy metal resistance.

Project: Formation, Structure, and Reactivity of Biologically produced Manganese oxides.

The oxidation of Mn(II) occurs because of the presence of a bacterial protein/enzyme compound that is embedded into the sheaths formed by *Leptothrix Discophora* SP6 - the organism that we use for precipitating biological MnO_x.

We have tried using a variety of extraction and separation methods to isolate the compound responsible for the oxidation of Mn(II) without success. However, we have learned some information about this protein and, in particular, why we now know that its characterization and its separation will be challenging. Most of the separation methods that we have tried and that are traditionally used in biochemistry to separate protein have failed because we think that the protein is folded inside the sheath in a specific configuration that confers its reactivity. We can separate fractions of the sheaths with the protein embedded into it mechanically, but then we loose the activity with time as the sheath fragments disaggregate, releasing the protein.

We have tried to characterize the coordinative environment of Mn when it is bound to that protein by EPR. These experiments were performed in collaboration with Prof. B. Hoffman's group in the Department of Chemistry at Northwestern University. For this purpose we used freshly extracted active sheath material. But we were only able to obtain EPR spectra that showed aqueous Mn(II), even in excess of the active sheath extracts. After exposure of the solutions to oxygen, we could see that the EPR signal decreases with time indicating that the reaction was taking place. However we were not able to obtain any spectral signature of the ligation of Mn(II) by the active site of the protein. This indicates that the complexation of Mn(II) is either relatively weak or result in the formation of an outer-sphere complex, or that only a very small fraction of Mn(II) is ligated. Yet it is quite efficient in carrying the oxidation of Mn(II).

Our attempts to use Energy Filtered Transmission Electron Microscopy (EF-TEM) to characterize and map the oxidation state of Mn in the thin sections that we used for our previous TEM work showed us the limitation of the technique when we are in the presence of a large matrix of either organic compounds, like an embedding resin, or water. To distinguish between Mn(III) and Mn(IV) using L edges, as it has been previously performed by Prof. Dravid's group on manganese oxides inorganic materials, is limited in our case by the large signal in PEELS (Electron Energy Loss Spectrometry) that comes from the matrix – from the elements C and O. This technique works well with whole mounts materials placed on TEM grids, but in our case since we need to retain the aqueous nature of the MnOx specimens – else as we have monitored by XAS the structure and the average oxidation state of Mn evolves rapidly – the specimen preparation leads to poor signal to noise/background ratios.

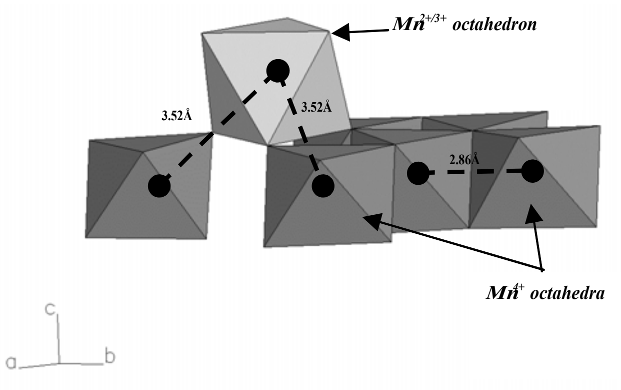


Figure 4 Polyhedral model of the Mn coordination to the layered vacancies. The extra-layer Mn^{2+} or

In the domain of the detailed analyses of the XAS data that we have gathered on the various MnO_x samples that were produced, we made some progress in elucidating the structure of the precipitates. Our previous results, both in XAS and UV-Raman spectroscopy lead to 2 possible structures for the MnO_x formed by *Leptothrix Discophora* SP6: either a tunnel structure comparable to Todorokite or a layered structure similar to Chalcophanite. *Ab initio* calculations performed with FEFF8.1 and parameterization of transferable functions between the various MnO_2 polymorphs used as standards lead to the conclusion that the Mn oxides formed were layered structures (Fig. 4). This appeared first to be in disagreement with the previous UV-Raman results, but new data obtained on colloidal MnO_x precipitates formed using an abiotic precipitation reaction lead to a similar peak that was first only attributed to the Todorokite structure.

To summarize our major research findings for the past year are:

1. The protein/enzyme that is responsible of the oxidation of Mn(II) to MnO_x binds a small fraction of the Mn(II).

2. The catalytic activity of this compound is very dependent on its folding in the sheath.

3. The MnO_x produced has a layered structure.

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University of California-Santa Cruz

University of California-Santa Barbara

University of California-San Diego Scripps Inst of Oceanography

Woods Hole Oceanographic Institution

Bates College

Wheaton College

University of British Columbia

Montclair State University

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Center for Environmental BioInorganic Chemistry (CEBIC) Fifth Year Conference June 8-11, 2003. The following list of people attended the CEBIC Summer Conference and are not CEBIC participants.

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Activities and Findings

Research and Education Activities:

Research and Education Activities:

The Center for Environmental BioInorganic Chemistry, CEBIC, is an Environmental Molecular Science Institute (CHE-9810248, $1.5M/year; 10/1/1998 û 9/30/2003). After receiving a one year no cost extension during 2003/2004, the original project is now completed. It is, however, being continued by CHE û0221178 which is now in its third year of operation, the first year of the new project having overlapped with the 5th year of the first one.

On the research front, CEBIC has achieved new and productive collaborations among its investigators resulting in both ground-breaking work and a high level of productivity. This is demonstrated by a larger number of CEBIC publications: nearly one hundred, including a significant proportion in high visibility journals such as Science, Nature,JACS and PNAS - see Bibliography. The central theme of CEBICs research has been the elucidation of the nature and function of metalloenzymesand metal binding compounds that control key processes in the chemical cycles of carbon and nitrogen in the environment and, as a result, link the biogeochemical cycles of major elements with those of trace metals. The three major research foci of CEBIC have been on 1) Iron Chemistry and Biology in Seawater,

2) Inorganic Carbon Acquisition (and Carbonic Anhydrases) in Marine Phytoplankton, and 3)
Hydrocarbon Metabolism in Bacteria. In addition a number of CEBIC projects have focused on various processes that influence the nitrogen
cycle and oceanic primary production.

Each year several CEBIC projects have been in the forms of seed projects designed to allow investigators (chiefly young investigators) to implement new ideas. As described below, during the last year of operation, seed projects included investigations of Silicic Acid Transport in Diatoms, Programmed Cell Death in Marine Phytoplankton, Spectroscopic Characterization of Atmospheric Iron, Speciation, Bioavailability of Molybdenum in Soils, and Microbial Arsenate Reduction. Several new researchers thus became involved in CEBIC: Mark Hildebrand at Scripps, Kay Biddle at Rutgers, Anne Kraepiel at Princeton, Yuan Gao at Montclair State, Mak Saito at Woods Hole Oceanographic Institution, and Maria Maldonado at British Columbia. (The last three of these had previously worked on CEBIC projects as postdocs in one of the CEBIC PI's groups.)

Aside from progress in specific research areas, which are described under 'Findings', CEBIC has been successful in other dimensions that are no less important. In particular it has attracted as researchers some of the most promising young scientists and given them a chance to work with several CEBIC research groups. This in turn has fostered productive collaborations among participating laboratories, such as those between Princeton, Rutgers and ExxonMobil to work on hydrocarbon degradation, among the three University of California campuses, WHOI and Rutgers to work on iron and Trichodesmium, between McGill and Princeton to work on the isolation of metalloenzymes from marine diatoms,etc. In addition, the opportunities offered by some CEBIC groups to use particular facilities (e.g., the access and expertise provided by ExxonMobil to perform X-ray spectroscopy at the Stanford Synchrotron) or to participate in oceanographic cruises (particularly those organized by the University of California at Santa Cruz in the California Upwelling and off the Peru Coast) have proved extremely valuable. It is clear that CEBIC has markedly enhanced the career prospects for the young scientists involved in it and several of them are now embarking on successful academic careers of their own.

CEBIC has provided a particularly good environment for nurturing the careers of young scientists, including a high proportion of women and
a few ethnic minorities. A large number of young CEBIC researchers are women (perhaps as a result of the involvement of four distinguished
senior women scientists as PI's) and several are under-represented minorities.

CEBIC has been particularly active in the development of outreach activities both through the direct involvement of its researchers and by being the principal force behind the organization of the outreach programs of the Princeton Environmental Institute (PEI) and Princeton
University. Our outreach activities have been focused in the high poverty districts of Central New Jersey and included direct involvement in the classroom as well as the professional development of teachers. Our teacher training and curriculum support activities have been particularly extensive and largely directed at the elementary and middle schools. Each year, CEBIC researchers have in various ways helped further the education of 150 to 200 school teachers. We have also put much effort in improving the efficiency and increasing the scope of all outreach activities on campus. As a result, Princeton has established a Princeton University Science Education Consortium which will provide coordination for all outreach efforts on campus, give them heightened visibility in the community, and provide them with resources and long term stability.

In addition to its specific scientific, educational and outreach goals, CEBIC was founded with the explicit ambition to help 'change the existing culture in both the field of environmental sciences, by making it more mechanistic and molecular, and the field of chemistry by making it more environmental.' To this end we have strived to keep CEBIC intellectually open. For example, we have invited prominent bioinorganic chemists and environmental scientists, not directly involved in the Center, to participate in our yearly conferences and provided seed funding to several research groups which were not part of the original proposal but keen to collaborate on projects of mutual interest. We have also developed new curriculum material for introductory chemistry courses that uses biogeochemical cycles to illustrate chemical concepts. While it is of course difficult to gauge the fulfillment of this 'cultural goal,' a measure of success is provided by the fact that several research projects that were initiated in CEBIC have now received independent funding from NSF and by the success of the new Gordon Research Conference on Environmental BioInorganic Chemistry, which was launched in 2002 and met again in June 2004.

Findings:

Findings:

1) Iron Chemistry and Biology in Seawater
The largest research effort of CEBIC has been focused on the question of iron in the oceans. As a result of this work, we are beginning to understand
what controls the chelation of iron in seawater, its uptake by the plankton and its effect on primary production.

1.1) Siderophores. The pioneering work of the Butler group on identifying siderophores in marine bacteria has met with great success.
The structures of two new suites of siderophores from a marine alpha-proteobacterium and a synechococcus species have now been determined.
These siderophores each contain a Fe(III)-binding portion that coordinates Fe(III) by two hydroxamate groups and an alpha carboxylate group.
The fatty acids range from one or two C8 to C12 appendages. The amphiphilic properties as well as the photoreactivity are under
investigation. Grovesã group has worked on the synthesis, structure and molecular dynamics of Fe and Ga complexes of schizokinen and the
amphiphilic siderophore acinetoferrin. A large conformational change in acinetoferrin upon binding iron suggests a functional role for the
observed changes in lipophilicity. These studies are central to understanding what roles the lipophilic side chains of the amphiphilic marine siderophores play in iron acquisition.

1.2 Fe Uptake by Phytoplankton. Most of the Fe in seawater is present in oxyhydroxide colloids or bound to strong chelators. Previous
CEBIC work has established that a reductive mechanism is involved in Fe uptake by eukaryotic phytoplankton. The Morel group has
demonstrated that marine diatoms produce superoxide (O2-) enzymatically in their external medium and that Fe(III) reduction is at least partly
effected by reaction with O2-. The production of O2- by diatoms is important both for the redox cycling of Fe in surface seawater and
potentially as a defense against bacterial colonization. Both Maldonadoãs and Priceãs groups have documented the importance of Cu nutrition in the uptake of Fe by diatoms. These results confirm that, as in yeasts, Fe transport in diatoms involves a multicopper oxidase and point at an important interaction between Fe and Cu in the nutrition of marine phytoplankton. In addition, measurements by the Maldonado group of Fe and Cu quotas in diatoms cultures suggest that the two metals may substitute for each other in some pathways in open ocean species.

1.3) Fe Nutrition and Storage in Cyanobacteria. Using genomic information we have undertaken to identify Fe storage proteins in the dominant families of marine cyanobacteria trichodesmium and Prochlorococcus . The Morelãs and Stiefelãs group have focussed on the DNA-binding protein (Dps) from Trichodesmium. This protein has been cloned and overexpressed and is now being characterized. A putative bacterioferritin gene has also been identified in the trichodesmium genome. These two proteins act as iron storage proteins and in addition Dps has been shown to protect organisms from oxidative stress. In February 2004, we took advantage of a cruise organized by Ken Bruland to conduct field experiments in the Pacific Ocean and collect samples to analyze for the presence of both bacterioferritin and Dps. We are in the process of analyzing the samples by quantitative PCR. Saitoãs group has begun a project to characterizie the effect of iron limitation on marine cyanobacterial strains using proteomic methods. Methodologies for protein extraction and 2D gel analysis have been developed in recent months, and preliminary 2D gels of Prochlorococcus and Crocosphaera have been obtained.

2) Inorganic Carbon Acquisition (and Carbonic Anhydrases) in Marine Phytoplankton. From previous CEBIC work, it has become apparent that the acquisition of inorganic carbon is a key to the relative success of various species of phytoplankton in the sea and that carbonic anhydrases (CA) with unusual metal centers play a critical role in this process.

2.1) C4 Photosynthetic Pathway in Diatoms. Morelãs and Reinfelderãs groups have continued their collaboration to elucidate the mechanisms of inorganic carbon acquisition in marine diatoms. Specific inhibition of the C4 carboxylase PEPCase resulted in a dramatic decrease in photosynthesis in several species of marine diatoms but not in the C3 marine Chlorophyte Chlamydomonas sp. Elevated CO2 or low O2 restored photosynthesis to the control rate. Short-term carbon uptake and release experiments that employed a protein denaturing cell extraction solution revealed that much of the carbon transported by diatoms during photosynthesis is stored as organic carbon before being fixed in the Calvin cycle. Together these results demonstrate that the C4 pathway is important in carbon accumulation and photosynthetic carbon fixation in diatoms at low (atmospheric) CO2.

2.2) Cadmium Carbonic Anhydrases. Morelãs group is continuing its study of the novel cytoplasmic and periplasmic CA which are integral to the inorganic carbon acquisition system of diatoms. One isoform of an internal CA (TWCA1, the first of the delta class of CA) can use indifferently Zn or Co as its metal center in vivo. Another isoform (CDCA the first of a zeta class of CA) uses Cd as its metal center. This enzyme has been sequenced and over-expressed in E. coli and we have now studied its regulation as a function of the CO2, zinc and cadmium concentrations in the medium. Most dramatic is the demonstration by quantitative reverse transcriptase PCR of a rapid increase in CDCA transcription upon addition of Cd to the medium, demonstrating that the regulation of this enzyme is controlled by the availability of cadmium in seawater. We have begun a new collaboration with the group of Christianson at the University of Pennsylvania to characterize the protein and are planning field experiments to test its presence in seawater.

2.3) Other Cd Enzymes. The discovery of CDCA as the first native Cd enzyme brings up the question of what other Cd enzymes may exist. High levels of Cd in the cosmopolitan coccolithophore Emiliana huxleyi makes it likely that this organism also uses Cd in a biochemical function. Since CAs are apparently not important in this organism, we have begun a systematic investigation of the biochemical role of Cd in E. huxleyi, beginning with the hypothesis that Cd may serve as a metal center in alkaline phosphatase.

3) Hydrocarbon Metabolism in Bacteria.
Our work on hydrocarbon metabolism in bacteria, which is carried out as four-way collaboration between the research groups of Groves (Princeton), Zylstra and Young (Rutgers) and Narehood-Austin (Bates), aims to identify the principal alkane degrading organisms in the environment, characterize the relevant family of genes/proteins, develop appropriate probes and investigate the mechanisms of hydrocarbon oxidation.

3.1) Anaerobic Oxidation. Our studies of the anaerobic mechanisms of hydrocarbon degradation are focused on the sulfate reducing strain AK01 and on strains of the denitrifier Azoarcus isolated from natural consortia. We have determined that AK01 initiates activation of hexadecane by a subterminal fumarate addition. Using a hexadecane synthesized with a deuterated chiral carbon in the subterminal position as substrate, we shall test if the fumarate addition is through a radical mechanism. A denitrifying consortium which degrades hexadecane is being evaluated for its similarities or differences in activation mechanism from the known sulfate reducing strains. Both 16S rDNA and nosZ PCR products were obtained indicating the presence of the genus Azoarcus which is known to include strains that attack toluene by a fumarate addition mechanism. Another Azoarcus strain (identified by 16S rDNA) has been isolated which degrades naphthalene under denitrifying conditions. GC-MS analyses indicate the presence of the metabolites 2-naphthoic acid and hexahydro-2-naphthoic acid, which are those reported for sulfate reducers. Hence, it suggests that a similar exogenous carboxylation takes place to activate the naphthalene molecule in denitrifying organisms. We have also taken a proteomics approach to identify genes for the anaerobic degradation of alkanes. Two dimensional gel electrophoresis identified several proteins that are synthesized during growth on alkanes which are not synthesized during growth on other substrates. Efforts are now being made to obtain enough of these proteins for N-terminal sequencing so that the corresponding gene(s) can be cloned.

3.2) Aerobic oxidation. We have continued to investigate the mechanism by which the metalloenzyme AlkB hydroxylates alkanes. It appears that the mechanism by which AlkB hydroxylates alkanes is sensitive to the concentration of hydrocarbon substrate in the medium. The less substrate is in the medium, the longer the radical persists in the enzymeãs active site. So far, AlkB is the only enzyme where we see this result. Interestingly, we see it with both the wild type organism and an E. coli clone that contains AlkB..

We have studied two new organisms, R. erthyropolis and B. cepacia, that are thought to contain enzymes that are structurally similar to AlkB. We have shown that both of these organisms metabolize norcarane, and do so with substrate-based radical lifetimes that are between 1-3 nanoseconds [1] a result that is very similar to the result we see with AlkB. These results are consistent with the hypothesis that similar enzymes will show similar behavior in our whole cell screens. In contrast, molecular probe studies of an unusual hydroxylase from a new species have shown an unusually large degree of radical rearrangement product. The enzyme responsible for the reaction appears not to be of the AlkB family and we suspect it may be the first member of a new family of hydroxylases.

3.3) We continue our collaborative studies on cytochrome P450 (with Paul Ortiz de Montellano at UCSF) and toluene monooxygenase (with Brian Fox at the University of Wisconsin).

4) Nitrogen Cycling.

Over the past year our investigations of the trace metal requirements for the principal microbial transformations of nitrogen in seawater and have been focused on field studies of denitrification and nitrous oxide production.

In the fall of 2003, we participated in a research cruise to the oxygen minimum zone of the Eastern Tropical North Pacific. We sampled at two stations, one near the coast and one offshore, at depths extending through the oxygen minimum zone. Incubation experiments to test the effect of various treatments on denitrification were performed. Treatments included additions of copper, iron and organic matter. Only the organic additions affected the accumulation rates of nitrite and nitrous oxide in the bags. In addition, many samples for nitrous oxide and oxygen concentration and bacterial abundance by various flow cytometric measures were made in the incubations and at additional stations. Samples for analysis of nitrite reductase gene abundance and activity were also collected. Experiments are underway to investigate the synergistic effects of copper, iron and silver on denitrification in cultured bacteria. Methods for fluorescent detection of denitrification activity based on detection of NO using flow cytometry were initially attempted on the cruise and are under investigation on cultures as well.

5) Seed Projects.

Seed projects (typically funding a young investigator for one year at a modest level) have been a source of innovation in CEBIC. Some of these projects may ¶graduateã to become full-fledged CEBIC projects. Two seed projects (by Saito and by Maldonado) are closely tied to ongoing projects on Fe nutrition of marine phytoplankton and have been reported above. The following four other seed projects are presently under way.

5.1) Silicic Acid Transport in Diatoms (Mark Hildebrand; Scripps Institution of Oceanography, UCSD). This projects aims at identifying silicic acid transporters (SITs) in diatoms to understand the mechanism of silicic acid uptake and its control. To date we have sequences from 20 different SIT genes, with multiple gene copies represented in all but one species. Amino acid alignment of these newly isolated SITs reveal 18% amino acid identity, narrowing the number of conserved residues possibly essential for function. Detailed comparative sequence analysis is underway to determine whether any amino acids have been positively selected for during evolution.

We have successfully expressed SIT4 from C. fusiformis in the yeast, Saccharomyces cereviseae. Western blots confirmed SIT4 expression and localization in the insoluble fraction suggesting that the protein may be plasma-membrane bound. Experiments to determine if the SIT is functional are underway. Because of the difficulties in purifying the SIT protein from yeast, we are expressing a small portion of the SIT (about 44 amino acids) in E. coli. This has been successful, and we are accumulating enough protein to be used for antibody generation for localization studies within the diatom and to confirm the computer-generated model of SIT topology.

5.2) Spectroscopic Characterization of Atmospheric Iron (Yuan Gao; Montclair State University). This project is driven by the idea of integrating ¶real world÷ research with college education, aiming at the involvement of minority undergraduate students. The teaching objective is to develop the studentsã understanding of conducting research, and the approach is ¶you learn by doing.÷ The scientific objective is to quantify dissolved fraction of atmospheric iron (Fe), which is critical to address the bioavailability of atmospheric Fe to phytoplankton growth.

In February, 2004, two undergraduate students, Beatrice Machoka (minority) majoring in

Biochemistry and Ben Glaz majoring in Chemistry, were selected and started working on the project by reading relevant literatures and participating in group discussions. During the spring break,the students conducted field work at Rutgers Marine Field Station at Tuckerton in southern New Jersey, where they installed a new aerosol sampler (AEROSOL Model 500EL) and an automatic precipitation collector (MIC-1B). Since then, they have been collecting both weekly aerosol samples and event-based precipitation samples at this coastal location. Currently, the students are working on the development of analytical procedures for dissolved Fe measurements using a new Shimadzu UV/VIS spectrophotometer.

5.3) Microbial Arsenate Reduction (Peter Jaffe; Princeton University). The biogeochemical cycle of arsenic strongly depends on microbial transformations comprising oxidation, reduction, and methylation. With the genetic information available in the Genbank database, we developed degenerate primers to the functional genes encoding arsenate reductase in denitrifying isolates and the estuarine sediments from Chesapeake Bay. Novel genotypes of arsenate reductase genes were detected from the denitrifying isolates belonging to Bradyrhizobium and Azoarcus genera, which were able to grow on arsenate as electron acceptors. Diverse arsenate reductase genes were found in the sediments from three different station of Chesapeake Bay. An anaerobic microcosm was established with one of the sediment samples to confirm arsenate reduction activities in the sediment community. Physiological and genetic responses of arsenate reducing communities in the sediment were monitored using anion exchange chromatography and quantitative PCR analysis.

5.4) Speciation and Bioavailability of Molybdenum in Soils (Anne Kraepiel and Satish Myneni; Princeton University). We are currently investigating the nature and strength of Mo interactions with natural organic matter using X-ray spectroscopy. Contrary to our expectations, Mo doesnãt bind to the reduced sulfur groups present in fresh organic matter. Instead, the X-ray spectra of Mo associated with organic matter closely resemble the spectrum of the Mo complex with azotochelin, a (bis)catecholate siderophore naturally produced by some soil bacteria. We are now in the process of further characterizing the Mo ligands in organic matter using a variety of model compounds with catecholate and carboxylate functionalities.

Azotochelin was found to form strong complexes with molybdate, tungstate and vanadate. In diazotrophic cultures of Azotobacter vinelandii growing with trace concentrations of molybdate, the addition of azotochelin failed to inhibit growth, even though the addition of azotochelin should have brought the concentration of unchelated molybdate below the limiting threshold for azotobacter. Azotochelin additions also restored growth rates in cultures of RP70.11, the mutant of A. vinelandii that produces only the vanadate nitrogenase, when they were vanadate limited. On the basis on these results, we hypothesize that azotochelin may be a ¶vanadophore÷, and even possibly a ¶molybdophore÷ for Azotobacter.

5.5) Programmed Cell Death in Marine Phytoplankton. (K. Biddle and P. Falkowski; Rutgers University). The overarching objective of this project is to determine if transition to iron stress activates a programmed cell death (PCD) cascade in, marine phytoplankton. We have observed catastrophic cell death in aging cultures of Trichodesmium sp.and E. huxleyi which included ultrastructural, physiological, and biochemical characteristics similar to those identified with PCD processes in metazoans and higher plants. Caspase activity, which is extremely low in actively growing cells, increased dramatically once cells reached stationary and death phases. We have been successful at demonstrating this phenomenon by specific fluorescence staining of individual Trichodesmium cells. We have also obtained cDNA clones for metacaspase transcripts isolated from expression sequence tag (EST) libraries of E. huxleyi. Based on analysis of full-length cDNA sequences, E. huxleyi contains three highly conserved, but distinct metacaspases, which encode for a ~45 kD protein. So far, we have verified that our clone contains the 5' end of the EST transcript and we have detected it in healthy cells via RT-PCR. We are currently examining whether these genes are up regulated in Fe-stressed cells.

Training and Development:

Training and Development:

The development of educational programs has been a central part of CEBICãs agenda since its inception. CEBIC is administratively imbedded in the Princeton Environmental Institute (PEI) which directs vigorous programs at the undergraduate, graduate and postdoctoral levels.
Because CEBIC PIs are deeply involved in PEIãs teaching program, this existing structure has allowed CEBIC to efficiently involve students in its research and to bring the results of that research into the classroom. Through its Seed Projects, and Summer Undergraduate Research Fellowship Program, CEBIC has involved students at other, primarily undergraduate institutions and community colleges (see Outreach). These activities has been strengthened and widened with the participation of young professors at Montclair State University and at Bates and Wheaton colleges. The scientific thrust of the Center, at the cutting edge of both bioinorganic chemistry and environmental science is resulting in the development of new curricula for students at all levels. In this way and through the formation of a new cadre of young professors (many of whom are female and under-represented minorities), CEBIC will have, a wide impact on the future education of chemists and environmental scientists.

UNDERGRADUATE PROGRAM
Chemical Education. CEBIC has stimulated some exciting teaching that we intend to build on and further disseminate over the next few years.
We have found biogeochemical cycles to be a powerful vehicle for teaching basic chemical concepts. At Princeton, Ed Stiefel has developed a course in the residential college that uses biogeochemical cycles to teach students about chemistry in the natural world. At Bates College,Rachel Austin has developed an introductory chemistry course for majors that relies exclusively on biogeochemical cycles to illustrate all of the course concepts. In the accompanying lab, students monitor the chemistry of a marine aquarium and measure the chemicals involved in the nitrogen cycle (Wenzel & Austin, 2001).

Environmental Education. PEI has a long-standing Program in Environmental Studies, which offers an undergraduate certificate to qualified students. The program, which attracts a large number of students from many Princeton departments every year, offers two required courses on Fundamentals of Environmental Studies: 1) Population, Land Use, Water and Energy; 2) Climate, Toxics, Air Pollution and Biodiversity.
These courses, which are taught in large part by CEBIC co-PIs, examine the causes and consequences of global or regional environmental change, and analyze strategies for mitigating these perturbations and managing global resources. The research activities of CEBIC provide excellent material for case studies in these courses.

Teaching Through Research. The keystones of a Princeton education are the junior project and the senior thesis that are required of all
undergraduate students. CEBIC provides opportunities for juniors and seniors to work on a variety of thesis projects. The Center has
established a competitive undergraduate research fellowship program that allows students from any of the universities associated with CEBIC,including those involved through seed projects, to pursue research at any of the participating laboratories. Partly because of the opportunities to work at ExxonMobil or to be involved in our oceanographic cruises, this program has proved attractive for students from a wide range of departments, typically in the summers of their sophomore and junior years. Several students from undergraduate institutions such as Bates and Rowan Colleges have also been involved in our research and they seem to have particularly benefited from this opportunity. We have now expanded this program to the local community colleges (see outreach).

GRADUATE AND POSTDOCTORAL PROGRAM

It is the explicit ambition of CEBIC to promote interdisciplinary science founded on disciplinary strength. In addition to the difficulty of mastering more than one set of facts and principles, a major obstacle to the establishment of new interdisciplinary fields is the absence of appreciation that the practitioners of one discipline have for another and the suspicion that befalls those who transgress through disciplinary barriers. To help resolve these two difficulties, CEBIC PIs are not only learning about each otherãs disciplines and encouraging their students and postdocs to do the same, they are also providing a diverse and supportive intellectual community for young researchers to help them mature as scientists and develop their careers in an interdisciplinary field. In all the activities that allow graduate students and postdocs to explore various aspects of Environmental Bioinorganic Chemistry ¹formal courses in other departments, collaborative work across disciplines and
institutions, seminar series, summer conferences¨ we have strived to make them feel part of a peer group that is larger than their own research group and part of a scientific community that goes beyond that of their nominal disciplinary field. The Gordon Research Conference in
Environmental Bioinorganic Chemistry (2002, 2004) is the logical culmination of this effort. Indeed such conferences are conceived not only to exchange and challenge ideas at the forefront of a field, but also to create a community of scholars and bring new young practitioners into it.

To address directly the scientific underpinning of Environmental Bioinorganic Chemistry, Professors Groves and Stiefel have developed a new graduate course related to their CEBIC research, 'Metals in Biology,' which was offered in the spring term of 2003. The course is a survey of the 25 elements whose bioinorganic chemistry is relevant to the environment (biochemical cycles), agriculture, and health. The course includesin-depth coverage of key metal ions, including manganese, iron, copper and molybdenum. It focuses on redox roles in anaerobic and aerobic systems and on metalloenzymes that activate small molecules and ions, including hydrogen, nitrogen, nitrate, nitric oxide, oxygen, superoxide and hydrogen peroxide.

DIVERSITY

CEBIC is deeply committed to help increase the participation of women and under-represented minorities in science. Our record on the
participation of women is, we believe, excellent. The participation of four senior women PIãs has certainly helped CEBIC attract young women
participants: two of the four new co-PI's are women, several of the seed projects were granted to young women professors, and more than half of the postdocs, graduate students and undergraduates in CEBIC are women. But, as is well known, the numbers in the 'pipeline' can be
misleading. The real challenge is to have women stay in the scientific profession (and of course find in it satisfaction and success). CEBIC

appears to be a particularly propitious environment to help nurture the career of young woman scientists. It turns out that three of these young women are Hispanic Americans: two have graduated and embarked on academic careers of their own; one is completing her PhD.
Unfortunately the involvement of African Americans in CEBIC is only at the Undergraduate level (where it is noticeably high because of our program with the community colleges). All in all, our record of involvement of under-represented minorities in CEBIC is better than the national situation. We consider it an important mission of CEBIC to continue promoting the involvement of women and minorities in the scientific profession and help them develop their careers.

Outreach Activities:

Outreach Activities:

CEBIC investigators have played a significant role in education outreach programs at their home institutions and in the surrounding community. Our efforts include: professional development with school teachers working on school science reform in the region, collaboration with community college faculty and students, public lectures, and undergraduate research fellowships. Our goal is to engage faculty, postdoctoral fellows and university students to enhance scientific and technological understanding. A summary of the CEBIC Outreach program can be found at http://www.princeton.edu/~cebic/outreach.html.

CEBIC Undergraduate Research Fellowships and Community College Program

CEBIC supported four undergraduates during the summer of 2003 through its CEBIC Summer Undergraduate Research Fellowship Program.
The following students pursued research at CEBIC laboratories regarding the role of trace metals in the environment: Joanne S. Chong, with Professor Maria Maldonado at the University of British Columbia; Evan Chyun, with Professor Bess Ward at Princeton University; Amber Paschal, with Professor Lily Young at Rutgers University; Patrick Schlottel, with Professor Edward Stiefel at Princeton University. More information about their research can be found at http://www.princeton.edu/~cebic/CEBICfellows2003.htm

Princeton and Rutgers Universities have developed partnerships with their local county community college faculty and students through the CEBIC Community College Partnership. These partnerships are important outreach efforts as county colleges often do not have the facilities to engage their students in research. Through these partnerships, students and faculty at the junior colleges have been able to learn research techniques and gain experience with equipment not available on their campuses. During the spring term of 2004, CEBIC supported two students from Mercer County Community College: Linda Johnson worked in the lab of Pr. Jay Groves, Chemistry, and Kejekodunmi Kehinde worked in the lab of Pr. Francois Morel, Geosciences. At Rutgers University, Pr. Gerben Zylstra, Biotechnology Center for Agriculture and the Environment, supported two Middlesex County Community College undergraduates, Lena Shablya and Christopher DeSevo. All four county college students will continue their research in the summer of 2004 through our CEBIC Summer Undergraduate Research Fellowship Program (which will be supported by NSF's EdEn initiative for the first time this year). As part of our outreach to the Community Colleges, we have also participated in the Distinguished Lecture Series at Mercer County Community College,

New Jersey. In November 2003, Pr. Bess Ward to
faculty and students and discussed her research in the ice-covered lakes of Antarctica. To
access Ward's presentation, see
http://www.princeton.edu/~cebic/distinguishlecseries.htm

Professional development with teachers and students in grades 6-12.

Thirteen middle school teachers spent a week at the Princeton Environmental Institute CEBIC Summer Institute during July of 2003. The teachers worked with Pr. Fran_ois Morel, CEBIC Director, and Dr. Elizabeth Malcolm, Geosciences CEBIC postdoc, as well as Dr. Eileen Zerba, PEI. Professor Morel discussed nitrogen cycling and how his research is conducted. Malcolm discussed mercury in aquatic systems. The teachers conducted experiments in the laboratory and the field. See http://www.princeton.edu/~cebic/summerinst2003.htm for more information. The CEBIC Summer Institute offered a unique opportunity for teachers in grades 6-8 to enhance their knowledge of science content. The institute also enables teachers to develop the skills they need to apply their science knowledge to the classroom environment. A 'follow-up' program by Pr. Edward Stiefel for twenty middle and elementary school teachers was held in February of 2004. Stiefel spoke to the teachers about environmental cleanup and led the teachers in experiments regarding chemical concentrations.

Thirty elementary and middle school teachers also attended a week-long environmental studies program at the Princeton Environmental Institute in July 2003. CEBIC sponsors this professional development opportunity for teachers in grades 3-8 to learn more about the water cycle and its over-riding importance in our environment. Dr Steven Carson led the teachers in experiments to investigate the effect of chemicals in water and how the Coriolis effect influences deep ocean boundary currents.

Other CEBIC activities in the schools included:

* Pr. Lily Young, Rutgers University, participated in the High School Science Scholars Program, and the Douglas Science Institute for high school girls during July 2003. The intent of these programs is to foster an interest in science among minority high school students. The students spent six weeks in the lab researching the activity and role of anaerobic microorganisms for natural carbon cycling in the environment.

* Pr. Alison Butler, UCSB, has worked with a high school student, Rachel Li for several years. Li is mentored by graduate student Jessica Martin in Butler's laboratory. During the summer of 2003, Butler also hosted students in grades 4-6 from Goleta, California in her laboratory. The students participated in hands-on experimentation and learned about Butler's CEBIC related research.

* Pr. Thomas Spiro, Chemistry, Princeton University, participates in the Partners in Science Program. Spiro worked in the laboratory with Richard Rotter, a high school teacher in Montgomery, New Jersey for 8 weeks in the summer of 2003 and will continue with Rotter during the summer of 2004. Spiro also helped Rotter to create a new 'Advanced Placement' course in Environmental Science based on his CEBIC research for the district's high school students.

* In August of 2003, Pr. Rachel Austin, Chemistry and Environmental Studies, Bates College, led 40 middle school girls in a two-week

summer institute. The program was hosted by Camp Kieve and focused on research and careers in science.

* Pr. Kenneth Bruland, Marine Science, University of California, Santa Cruz participates in the Monterey Bay Science Project. See http://csmp.ucop.edu/csp/monterey/about.php. Bruland led the program on Language Acquisition through Science Education in Rural Schools in 2003.

700 middle school students and teachers participated in the Science and Engineering Expo at Princeton University on March 17, 2004.
Graduate students Junu Shrestha, Civil and Environmental Engineering and David Edwards, Chemistry, led students in experiments which evaluated iron content in water. The students learned about chemical testing and the properties of minerals that can be found in water.

Summer 2004 EdEn Projects

CEBIC received $47,822 in supplemental funds from the EdEn Venture Fund to support two of its main K-12 outreach activities for summer 2004. As a result, we more than tripled the number of undergraduates participating in the CEBIC Summer Undergraduate Research Fellowship Program last summer for a total of 14 students from nine institutions. Five of these students were funded by the EdEn grant, four of whom are from local New Jersey community colleges and one from the University of Puerto Rico.

The other portion of the supplemental funds was used for last year's CEBIC Summer Institute for middle school teachers, which we have committed to tie more closely to CEBIC research. Two week-long units were supported, one on the chemical composition of water and the other on the impact of humans on the environment and the environmental effects on the human body, including the interaction with trace elements. More than 50% of the participants were from high poverty districts in central New Jersey. The EdEn funds also supports the ongoing evaluation of the Summer Institute.

Journal Publications

Auclair, K., Z. Hu, D.M. Little, P.R. Ortiz de Montellano and J.T. Groves, "Revisiting the mechanism of P450 enzymes using the radical clocks Norcarane and Spiro[2,5]octane.", Journal of the American Chemical Society, p. 6020, vol. 124(21), (2002). Published

Austin, R., K. Buzzi, E. Kim, G. J. Zylstra, and J. T. Groves, "Xylene monooxygenase, a membrane-spanning non-heme diiron enzyme that hydroxylates hydrocarbons via a substrate radical intermediate", J. Biological Inorganic Chem, p. 773, vol. 8, (2003). Published

Barbeau, K., E.L. Rue, C.G. Trick, K.W. Bruland and A. Butler, "The photochemical reactivity of siderophores produced by marine heterotrophic bacteria and cyanobacterial, based on characteristic iron (III)-binding groups", Limnology and Oceanography, p. 1069, vol. 48, (2003). Published

Barbeau, K., G. Zhang, D.H. Live and A. Butler, "Petrobactin, a photoreactive siderophore produced by the oil-degrading marine bacterium Marinobacter hydrocarbonoclasticus", Journal American Chemical Society, p. 378, vol. 124, (2002). Published

Butler, A, "Iron acquisition: Straight Up and On the Rocks?", Nature Structural Biology, p. 240, vol. 10(4), (2003). Published

C.E. Mire, J.A. Tourjee, W.F. O'Brien, K.V. Ramanujachary, and G.B. Hecht, "Lead precipitation by Vibrio harveyi: Evidence for novel quorum sensing interactions", Appl. & Environ. Microbiol, p. 855, vol. 70, (2004). Published

Casciotti, K. L., D. M. Sigman and B. B. Ward, "Linking diversity and biogeochemistry in ammonia-oxidizing bacteria", Geomicrobiology, p. 335, vol. 20, (2003). Published

Casciotti, K. L., D. M. Sigman, M. Galanter Hastings, J. K. Bohlke, and A. Hilkert, "Measurement of the Oxygen Isotopic Composition of Nitrate in Marine and Fresh Waters Using the Denitrifier Method", Analytical Chemistry, p. 4905, vol. 74, (2002). Published

Dupont, C. L., L. Wei, T. J. Goepfert, P. Lo and B. A. Ahner, "Diurnal cycling of glutathione and cysteine in marine phytoplankton", Limnology and Oceanography, p. 991, vol. 49(4), (2004). Published

Dupont, C. L., R. K. Nelson, S. Bashir, J. W. Moffett, and B. A. Ahner, "Novel copper-binding and nitrogen-rich thiols produced and exuded by Emiliania huxleyi", Limnology and Oceanography, p. 1754, vol. 49(5), (2004). Published

Fadeev, E.A., M. Luo, and J. T. Groves, "Synthesis, and structures of Iron and Gallium complexes of Schizokinen and the Amphiphilic Siderophore Acinetoferrin", J. Org. Chem, p. 12065, vol. 126, (2004). Published

Fan, C-W., J.R. Reinfelder, "Phenanthrene accumulation kinetics in marine diatoms", Environ. Sci. Technol, p. 3405, vol. 37, (2003). Published

Firme, G.F., K.W. Bruland, E.L. Rue, D.A. Weeks and D.A. Hutchins, "Spatial and temporal variability in phytoplankton iron limitation along the California coast and consequences for Si, N and C biogeochemistry", Global Biogeochemical Cycles, p. 1016, vol. 17(1), (2003). Published

Gao, Y., "Atmospheric nitrogen deposition to Barnegat Bay", Atmospheric Environment, p. 5783, vol. 36(38), (2002). Published

Gao, Y., E. Nelson, M.P. Field, Q. Ding et al, "Characterization of atmospheric trace elements in PM2.5 particulate matter over the New York-New Jersey harbor estuary", Atmospheric Environment, p. 1079, vol. 36(6), (2002). Published

Gao, Y., S-M. Fan, and J.L. Sarmiento, "Aeolian iron input to the ocean through precipitation scavenging: A modeling perspective and its implication for natural iron fertilization in the ocean", J. Geophys. Res, p. 1029, vol. 108(D7), (2003). Published

Granger, J. and B. B. Ward, "Accumulation of nitrogen oxides in copper-limited cultures of denitrifying bacteria", Limnology and Oceanography, p. 313, vol. 48, (2002). Published

Groves, J.T., "The Bioinorganic Chemistry of Iron in Oxygenases and Supramolecular Assemblies", Proc. Nat. Acad. Sci U.S.A., p. 3569, vol. 100, (2003). Published

Ho, T.-Y. A. Quigg, Z.V. Finkel, A.J. Milligan, K.Wyman, P.G. Falkowski, F.M.M.Morel,, "The Elemental composition of some eukaryotic marine phytoplankton", Journal of Phycology, p. 1145, vol. 39, (2003). Published

Hudson, R.J.M., E.L. Rue, and K.W. Bruland, "Modeling complexometric titrations of natural water samples", Environ. Sci. Technol, p. 152, vol. 37, (2003). Published

Hutchins, D.A., C.E. Hare, R.S. Weaver, Y.Zhang, G.F. Firme, G.R. DiTullio, M.B. Alm, S.F. Riseman, J.M. Maucher, M.E. Geesey, C.G. Trick, G.J. Smith, E.L. Rue, J. Conn, and K.W. Bruland., "Phytoplankton Fe limitation in the Humboldt Current and Peru Upwelling system", Limnology and Oceanography, p. 997, vol. 47, (2002). Published

Jayakumar, D. A., C. A. Francis, S. W. A. Naqvi and B. B. Ward., "Diversity of nitrite reductase genes in the denitrifying water column of the coastal Arabian Sea", Aquatic Microbial Ecology, p. 69, vol. 34, (2004). Published

Kim, H-S., P.R. Jaffe, L. L. Young, "Simulating Biodegradation of Toluene in Sand-Column Experiments at the Macorscopic and Pore-level Scale for Aerobic and Denitrifying Conditions", Advances in Water Research, p. 335, vol. 27(4), (2004). Published

Klausmeier, C.A., E. Litchman, S.A. Levin, "Phytoplankton growth and stoichiometry under multiple nutrient Limitation", Limnology and Oceanography, p. 1463, vol. 49(4), (2004). Published

Martinez, J.S. , J.N. Carter-Franklin, E.L. Mann, J.D. Martin, M.G. Haygood, A. Butler, "Structure and dynamics of a new suite of amphiphilic siderophores produced by a marine bacterium", Proc. Natl. Acad. Sci U.S.A., p. 3754, vol. 100, (2003). Published

Milligan, A. J. and F.M.M. Morel, "Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO2.", Limnology and Oceanography, p. 322, vol. 49(2), (2004). Published

Milligan, A.J. and F.M.M. Morel, "A proton buffering role of silica in diatoms", Science, p. 1848, vol. 297, (2002). Published

Morel, F.M.M., and N.M. Price, "The Biogeochemical Cycles of Trace Metals in the Oceans", Science, p. 944, vol. 300, (2003). Published

Morel, F.M.M., E.H. Cox, A.M.L. Kraepiel, T.W. Lane, A.J. Milligan, I. Schaperdoth, J.R. Reinfelder and P.D. Tortell., "Acquisition of inorganic carbon by the marine diatom Thalassiosira weissflogii", Functional Plant Biology, p. 301, vol. 29, (2002). Published

Phelps, D.C. J. Battistelli and L.Y. Young, "Metabolic biomarkers for monitoring anaerobic naphthalene biodegradation in situ", Environ Microbiol, p. 532, vol. 4, (2002). Published

Saito, M. A., D.M. Sigman and F.M.M. Morel, "The Bioinorganic Chemistry of the Ancient Ocean: The Co-Evolution of Cyanobacterial Metal Requirements and Biogeochemical Cycles at the Archean-Proterozoic Boundary", Inorganica Chimica Acta, p. 308, vol. 356, (2003). Published

So, C.M. C.D. Phelps, L.Y. Young, "Anaerobic transformation of alkanes to fatty acids: initial reactions by the sulfate-reducer strain Hxd3 using stable isotope labeled compounds", Appl Environ Microbio, p. 3892, vol. 69, (2003). Published

Tortell, P.D. and F.M.M. Morel, "Sources of inorganic carbon for phytoplankton in the Eastern Subtropical and Equatorial Pacific Ocean", Limnology and Oceanography, p. 1012, vol. 47, (2002). Published

Tortell, P.D., G.R. DiTullio, D.M. Sigman, and F.M.M. Morel, "CO2 effects on taxonomic composition and nutrient utilization in an Equatorial Pacific
phytoplankton assemblage", MEPS, p. 37, vol. 236, (2002). Published

Vela, S. M.M. Haggblom and L.Y. Young, "Biodegradation of aromatic and aliphatic compounds by rhizobial species", Soil Science, p. 802, vol. 167, (2002). Published

Wei, L., J. R. Donat, G. Fones and B. A. Ahner, "Interactions between Cd, and Cu, and Zn influence particulate phytochelatin concentrations in marine phytoplankton: Laboratory results and prelimimary field data
marine phytoplankton: Laboratory results and preliminary field data", Environmental Science and Technology, p. 3609, vol. 37(16), (2003). Published

Xu, G., J. Martinez, J. T. Groves, A. Butler, "Membrane Affinity of the Amphiphilic Marinobactin Siderophores", J. Am. Chem. Soc, p. 13408, vol. 124(45), (2002). Published

Zehr, J. P, and B. B. Ward, "Nitrogen cycling in the ocean: new perspectives on processes and paradigms", Applied and Environmental Microbiology, p. 1015, vol. 68(3), (2002). Published

Bae, M., W. J. Sul, S.-C. Koh, J. H. Lee, G. J. Zylstra, Y. M. Kim, and E. Kim, "Implication of two glutathione S-transferases in the optimal metabolism of m-toluate by Sphingomonas yanoikuyae B1", Antonie van Leeuwenhoek, p. 25, vol. 84, (2003). Published

Chang, H.-K., P. Mohseni, and G. J. Zylstra, "Characterization and regulation of the genes for a novel anthranilate 1,2-dioxygenase from Burkholderia cepacia DBO1", J. Bacteriol, p. 5871, vol. 185, (2002). Published

Quigg, A., Z.V. Finkel, A.J. Irwin, Y. Rosenthal, T.-Y.Ho, J.R. Reinfelder, O. Schofield, F.M.M. Morel, P.G. Falkowski, "The evolutionary inheritance of elemental stoichiometry in marine phytoplankton", Nature, p. 425, vol. 291, (2003). Published

Berman-Frank, I., K.D. Bidle, L. Haramaty and P.G. Falkowski, "The demise of the marine cyanobacterium, Trichodesmium spp., via an autocatalyzed cell death pathway", Limnology and Oceanography, p. 997, vol. 49(4), (2004). Published

Bidle, K. D. and P.G. Falkowski, " Cell death in planktonic, photosynthetic microorganisms", Nature Reviews Microbiology, p. 643, vol. 2, (2004). Published

Klausmeier, C.A., E. Litchman, T. Daufresne, and S.A. Levin, "Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton", Nature, p. 171, vol. 429, (2004). Published

Palleroni, N. J., A. M. Port, H.-K. Chang, and G. J. Zylstra,,, "Hydrocarboniphaga effusa gen. nov., sp. nov., a new member of gamma Proteobacteria active in alkane and aromatic hydrocarbon degradatio", International Journal of Systematic and Evolutionary Microbiology, p. 1207, vol. 54, (2004). Published

Peers, G.S. and N.M. Price, "A role for manganese in superoxide dismutases and growth of iron-deficient diatoms", Limnology and Oceanography, p. 1774, vol. 49(5), (2004). Published

Reinfelder, J.R., A.J. Milligan, F.M.M. Morel,,, "The role of the C4 pathway in carbon accumulation and fixation in a marine diatom"", Plant Physiology, p. 2106, vol. 135(3), (2004). Published

Shaked, Y., A.B. Kustka, F.M.M. Morel and Y. Erel, "Simultaneous determination of iron reduction and uptake by phytoplankton", Limnology and Oceanography: Methods http://www.aslo.org/lomethods/free/2004/0137.pdf, p. 137, vol. 2, (2004). Published

Butler, A., "Acquisition and Utilization of Transition Metal Ions by Marine Organisms", Science, p. 207, vol. 281, (1998). Published

Adams, M.W. W., Stiefel, E.I., "Biological Hydrogen Production: Not So Elementary", Science, p. 1842, vol. 282, (1998). Published

Cullen, J.T., T.W. Lane, F.M.M. Morel, and R.M. Sherrell, "Modulation of cadmium uptake in phytoplankton by seawater CO2 concentration", Nature, p. 165, vol. 402, (1999). Published

Lane, T.W. and F.M.M. Morel, "Regulation of carbonic anhydrase expression by zinc, cobalt, and carbon dioxide in
the marine diatom Thalassiosira weissflogii", Plant Physiology, p. 345, vol. 123, (2000). Published

Lane, T.W. and F.M.M. Morel, "A biological function for cadmium in marine diatoms", PNAS, p. 4627, vol. 97, (2000). Published

Tortell, P.D., G.H. Rau, and F.M.M. Morel, "Inorganic carbon acquisition in coastal Pacific phytoplankton communities", Limnology and Oceanography, p. 1485, vol. 45, (2000). Published

Reinfelder, J.R., A.M.L. Kraepiel and F.M.M. Morel, "Unicellular C4 photosynthesis in a marine diatom", Nature, p. 996, vol. 407, (2000). Published

Cox, E.H., G.L. McLendon, F.M.M. Morel, R.C. Prince, I.J. Pickering and G.N. George, "The active site structure of Thalassiosira weissflogii carbonic anhydrase 1", Biochemistry, p. 12128, vol. 39, (2000). Published

Austin, Rachel N., Hung-Kuang Chang, Gerben Zylstra, John T. Groves, "The Non-Heme Diiron Alkane Monooxygenase of Pseudomonas oleovorans (AlkB)
Hydroxylates via a Substrate Radical Intermediate", J. Am. Chem. Soc, p. 11747, vol. 122, (2000). Published

Beck, N.G., E.L. Rue and K.W. Bruland, "Short-term biogeochemical influence of diatom bloom on the nutrient and trace metal concentrations in a South San Francisco Bay microcosm experiment", Estuaries, p. 1063, vol. 25(6A), (2002). Published

Bruland, K.W., E.L. Rue, J. R. Donat, S. Skrabal, and J. Moffett, "Intercomparison of voltammetric techniques to determine the chemical speciation of
dissolved copper in a coastal seawater sample", Analytica Chimica Acta, p. 99, vol. 405, (2000). Published

Gao, Y., Y.J. Kaufman, D. Tanre, D. Kolber and P.G. Falkowski, "Seasonal distributions of aeolian iron fluxes to the global ocean", Geophysical Research Letters, p. 29, vol. 282, (2001). Published

Casciotti, K. L. and B. B. Ward, "Dissimilatory nitrite reductase genes from autotrophic ammonia-oxidizing bacteria", Applied and Environmental Microbiology, p. 2213, vol. 67, (2001). Published

Lam, P.J., P.D. Tortell and F.M.M. Morel,, "Differential effects of iron additions on organic and inorganic carbon production by phytoplankton", Limnology and Oceanography, p. 1199, vol. 46, (2001). Published

Macrellis, H.M., C.G. Trick, E.L. Rue, G. Smith, K.W. Bruland, "Collection and detection of natural iron-binding ligands from seawater", Marine Chemistry, p. 175, vol. 76, (2001). Published

Maldonado, M.T. and N.M. Price, "Reduction and transport of organically bound iron by Thalassiosira oceanica (Bacillariophyceae)", Journal of Phycology, p. 298, vol. 37, (2001). Published

Martinez, J.S., G.P. Zhang, P.D. Holt, H.-T. Jung, C.J. Carrano, M.G. Haygood and A. Butler, "Self-assembling amphiphilic siderophores from Marine bacteria", Science, p. 1245, vol. 287, (2000). Published

Martinez, J.S., M.G. Haygood and A. Butler, "Identification of a natural desferrioxamine siderophore produced by a marine bacterium", Limnology and Oceanography, p. 420, vol. 46, (2001). Published

Nodwell, L.M. and N.M. Price, "Direct use of inorganic colloidal iron by marine mixotrophic phytoplankton", Limnology and Oceanography, p. 765, vol. 46(4), (2001). Published

Maldonado, M.T. M.P. Hughes, and E.L. Rue, M.L. Wells, "The effect of Fe and Cu on growth and domoic acid production by Pseudo-nitzschia
multiseries and Pseudo-nitzschia australis", Limnology and Oceanography, p. 515, vol. 47(2), (2002). Published

Riebesell, U., I. Zondervan, B. Rost, P.T. Tortell, R.E. Zeebe and F.M.M. Morel, "Reduced calcification in marine plankton in response to increased atmospheric CO2", Nature, p. 364, vol. 407, (2000). Published

Sigman, D.M., K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, M.L. Bender, J.K. Bohlke, "A bacterial method for the nitrogen isotopic analysis of nitrate in marine and freshwaters", Analytical Chemistry, p. 4145, vol. 73(17), (2001). Published

Tortell, P.D., "Evolutionary and ecological perspectives on carbon acquisition", Limnology and Oceanography, p. 744, vol. 45, (2000). Published

Webb. E.A., J.W. Moffett and J.B. Waterbury, "Iron stress in open ocean cyanobacteria (Synechococcus, Trichodesmium and Crocosphaera): Identification of the IdiA protein", Applied and Environmental Microbiology, p. 5444, vol. 67(12), (2001). Published

Gao, Y. and J. Anderson, "Characteristics of Chinese aerosols determined by individual-particle analysis", Journal of Geophysical Research, p. 18,037, vol. 106, (2001). Published

Nodwell, L.M. and N.M. Price, "Direct use of inorganic colloidal iron by marine mixotrophic phytoplankton", Limnology and Oceanography, p. 765, vol. 46(4), (2001). Published

Liu A, E. Garcia-Dominguez, ED Rhine & LY Young,, "A novel arsenate respiring isolate that can utilize aromatic substrates", FEMS Microbiol Ecol, p. , vol. , (2004). Accepted

Books or Other One-time Publications

Falkowski, P.G. and Y. Rosenthal, "Biological diversity and resource plunder in the geological record: Casual correlations or causal relationships?", (2001). Proceedings, Published
Bibliography: Proceedings of the National Academy of Science, 98: 4290-4292

Stiefel, E.I. and H.H. Murray, "Molybdenum in the Environment", (2002). Book, Published
Editor(s): B. Sarkar
Collection: Heavy Metals in the Environment
Bibliography: pp. 503-529, Marcel Dekker, New York

Sigman, D.M. and K.L. Casciotti , "Nitrogen isotopes in the ocean.", (2001). Book, Published
Editor(s): Steele, J.H., S.A. Thorpe, and K.K. Turekian
Collection: Encylopedia of Ocean Sciences
Bibliography: pp. 1884-1894, Academic Press, New York

Morel, F.M.M., A.J. Milligan and M.A. Saito, "Marine Bioinorganic Chemistry: The Role of Trace of Metals in the Oceanic Cycles of Major Nutrients", (2003). Book, Published
Editor(s): H.D. Holland, K.K. Turekian, Volume Editor: H. Elderfield
Collection: Treatise on Geochemistry
Bibliography: The Oceans and Marine Geochemistry: Volume 6, pp. 113-143, Elsevier Ltd., Cambridge, UK

Morel, F.M.M. and E. Malcolm, "The Biogeochemistry of Cadmium", (2005). Book Chapter, Accepted
Editor(s): A. Sigel, H. Sigel and R.K.O. Sigel
Collection: Biogeochemical Cycles of Elements
Bibliography: Metal Ions in Biological Systems; Volume 43: pp. 301 Marcel Dekker, New York

Sunda, W., N.M. Price, F.M.M. Morel, "Trace Metal ion buffers and their use in culture studies", (2004). Book, Accepted
Editor(s): R. Anderson
Collection: Algal Culturing Techniques
Bibliography: Academic Press, New York

Groves, J.T, "Models and Mechanisms of Cytochrome P450 Action", (2004). Book, Published
Editor(s): P. Ortiz De Montellano
Collection: Cytochrome P450: Structure, Mechanism, and Biochemistry
Bibliography: 3e, Kluwer Academic / Plenum Publishers, New York, 2004. Pp 1-4

Bruland, K. and M. Lohan, "The Control of Trace Metals in Seawater", (2003). Book, Published
Editor(s): H.D. Holland, K.K. Turekian, Volume Editor: H. Elderfield
Collection: Treatise on Geochemistry
Bibliography: The Oceans and Marine Chemistry: Volume 6, Chapter 2, Elsevier Ltd.

Stiefel E.I, "The Biogeochemistry of Molybdenum and Tungsten", (2002). Book Chapter, Published
Editor(s): A. Sigel and H. Sigel
Collection: Molybdenum and Tungsten: Their Roles in Biological Processes
Bibliography: Metal Ions in Biological Systems, Vol 39, pp. 1-30, Marcel Dekker, New York

2. Stiefel, E.I., "The Biogeochemistry of Molybdenum and Tungsten", in
Metal Ions in Biological Sys

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The CEBIC Web site on the Princeton University server continues to provide information about CEBIC and its activities to scientists and the public. It features a home page with a brief description of the project, investigators and sponsors as well as a side bar with buttons leading to pages for the investigators, projects, publications, proposal, related sites and outreach. The address for the site is www.princeton.edu/~cebic/.

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Investigators - lists all the CEBIC investigators with links to their home web pages. It includes paragraphs on each investigator describing their CEBIC research project. Projects - lists each research project with the names of the investigators working on that project. Publications - lists each book, journal article, or other written material resulting from CEBIC research. Proposal - contains the research project section of the original proposal. Related sites - includes links to other EMSI centers and to web pages developed by individual CEBIC investigators. Outreach- includes a brief description of CEBIC''s outreach program with a link to PEI''s outreach page and links to outreach projects carried out by CEBIC investigators as described above.

http://es.ucsc.edu/~kbruland/
Pr. Bruland recently produced a web page in an initial attempt to make CEBICs field research more accessible to a broader audience: http://es.ucsc.edu/~kbruland/. We hope to expand this website to describe the research cruise activities in a manner that would be of interest to high school and undergraduate classes and students.

Other Specific Products

Contributions

Contributions within Discipline:

Contributions within Discipline:

The Center for Environmental BioInorganic Chemistry brings together scientists working in different disciplines, including in particular pure chemists working in the laboratory on well-defined, simple, small scale model systems and environmental scientists whose work is based partly in the field and addresses complex, dirty, large scale natural processes. (This section thus explains CEBIC's contribution both within its ¶discipline' and outside of it.) The idea behind the Center is that these two types of scientists can contribute to each other's research, that elucidating mechanisms at the molecular level will bring insights into global processes and that the study of natural systems will uncover new, exciting and relevant molecular problems. The young scientists trained in CEBIC will thus constitute a new generation of researchers and teachers, prepared to address a new class of environmental chemical problems and a new kind of molecular environmental science.

Besides the scientific advances resulting from the individual projects (which are, of course, necessary and important in their own right) it is in this wider, quasi philosophical, context that the contributions of the Center should be measured in the long term. While it is obviously too early to attempt such an evaluation, there are already clear signs that CEBIC will be at least partly successful in this wider sense. The relatively large number of high profile publications emanating out of CEBIC is testimony to the fact that exciting and productive science is to be pursued at the intersection of the various disciplines brought together by the Center. Further, the idea that a better understanding of global processes can be gained by elucidating mechanisms at the molecular scale appears to be paying off. For example: i) Our results on the structure of iron siderophores from marine bacteria should bring us one step closer to understanding the biogeochemical cycling of iron in seawater; ii) The discovery of C4 metabolism in diatoms requires a rethinking of the current view of CO2 cycling in seawater; iii) The discovery of Cu limitation of denitrifiers, if confirmed in the field, will lead to a better understanding of the oceanic emission of N2O.

In the case of the Carbonic Anhydrase project, the research path is coming full circle: from the global, to the molecular, to the global again. It is the 'nutrient-like' distribution of Cd in seawater that provided the inspiration to look for a biochemical role for the metal in the first place and led to the discovery of the first Cd enzyme; on the basis of this biochemical role, we now seem to be able to explain the global distribution of Cd in the oceans at new level of detail. The biochemistry of Cd appears to be the key to its geochemistry.

Contributions to Other Disciplines:

SEE ABOVE

Contributions to Human Resource Development:

Contributions to Education and Human Resources:

As detailed under the categories Research Findings and Education and Outreach, CEBIC is making important contributions to the education of undergraduate students, graduate students, middle and high school teachers and the public. Of particular note is the effort of CEBIC, through the support of seed projects and its summer undergraduate felowship program, to foster research training in undergraduate institutions (in addition to its participating research universities): at Middlesex County Community College, Mercer County Community College and Montclair State University in New Jersey; at Wheaton College in Massachusetts; and at Bates College in Maine; and at the University of Puerto Rico. CEBIC is also making it possible for EXXON scientists to teach undergraduate seminars at Princeton thus bringing these experienced industrial scientists in contact with Princeton students.

Contributions to Resources for Research and Education:

Contributions to Education and Human Resources:

As detailed under the categories Research Findings and Education and Outreach, CEBIC is making important contributions to the education of undergraduate students, graduate students, middle and high school teachers and the public. Of particular note is the effort of CEBIC, through the support of seed projects and its summer undergraduate felowship program, to foster research training in undergraduate institutions (in addition to its participating research universities): at Middlesex County Community College, Mercer County Community College and Montclair State University in New Jersey; at Wheaton College in Massachusetts; and at Bates College in Maine; and at the University of Puerto Rico. CEBIC is also making it possible for EXXON scientists to teach undergraduate seminars at Princeton thus bringing these experienced industrial scientists in contact with Princeton students.

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Any Product

Contributions: To Any Beyond Science and Engineering