

Swiss Federal Institute of Technology Zürich (ETHZ)

Chimia 50 (1996) 65–73
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009-4293

Heterogeneous Catalysis: From Fundamentals to Reaction Engineering

Alfons Baiker*

Abstract. The development of new catalytic processes making efficient use of energy and raw materials with minimal impact on the environment is an extremely challenging task. The principal aim of our research is to improve the scientific basis for the advancement of heterogeneous catalytic processes for fine chemical synthesis and the abatement of pollutants that are detrimental to the environment. This aim is pursued with strongly interdisciplinary research embracing fundamental aspects of surface reactions, catalyst design and reaction engineering. Our research strategy and the current projects are briefly discussed.

1. General Aim and Strategy

The research of our group is concerned with heterogeneous catalysis, comprising aspects of surface and solid-state chemistry as well as chemical reaction engineering, which are important for the design of new catalytic processes. A strong interplay between fundamental research and reaction engineering is characteristic for most of our projects. The general aim is to improve the scientific basis for the development of novel efficient catalytic processes which eliminate, or at least minimize the use and possible release of hazardous materials. The main research areas and their interrelation are illustrated in a simplified fashion in the *Scheme*.

Catalyst design, which is most crucial for the development of novel catalytic processes, is an extremely interdisciplinary endeavor. It requires some understanding of the mechanism of the catalytic reaction, and knowledge of the crucial properties which determine the activity, selectivity, and lifetime of the catalyst.

Studies of the interrelationship between structural and chemical properties of solid materials and their catalytic properties (structure-activity relationship) are at the origin of catalyst design. These studies are frequently carried out using specially prepared model catalysts which are amenable to analysis with modern surface analytical methods providing structural and chemical information on molecular scale. Various techniques and concepts of solid-state and surface chemistry are applied for modifying and synthesizing catalyst materials with the required structural and chemical properties (molecular engineering). Another crucial aspect of catalyst design, not explicitly shown in the *Scheme*, is the tailoring of the textural properties, *i.e.* geometrical shape, surface area, and pore structure. This tailoring is important for optimizing the mass transfer of reactants and products in the porous network of the catalyst.

Reaction engineering generally deals with reaction kinetics, the selection of a suitable reactor system and the optimization of heat and mass transfer involved in the catalytic process. At present, our main interests in reaction engineering is to explore the influence of supercritical conditions on chemical reactions. Supercritical fluids are applied in the preparation of novel catalyst materials (aerogels), as reactants and as solvents.

Our group is composed of chemists, chemical engineers, and physicists, this together with several national and international collaborations with researchers at universities and in industry provides the multidisciplinary expertise necessary for extending the frontiers of catalytic science.

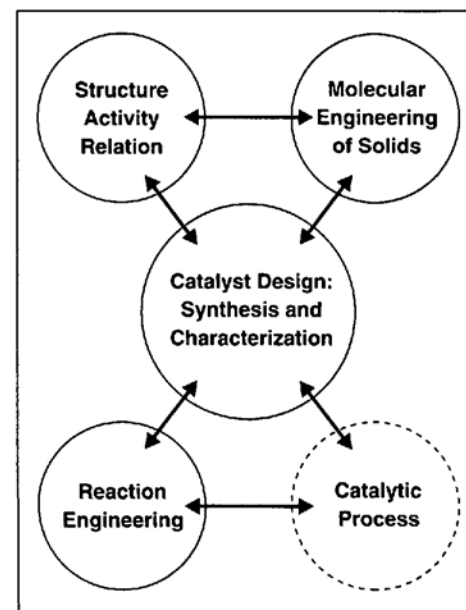
2. Current Research Projects

Our group is organized in four sections which focus on environmental catalysis, catalysis in fine chemicals synthesis, catalyst materials, and model systems. The topics studied in these fields are schematically summarized in *Fig. 1* and will be briefly presented next. For more detailed information on the projects and for gaining some knowledge on the world-wide state of research in the covered fields the reader is referred to the pertinent recent publications and references therein.

2.1. Environmental Catalysis

Reactions relevant to environmental control and energy technology are in the main focus. The principle aim is to provide a basis for the advancement of processes that make efficient use of energy and raw materials with minimal impact on the environment. In addition, catalytic solutions are developed for the abatement of pollutants that are detrimental to the environment.

Scheme



*Correspondence: Prof. Dr. A. Baiker
Department of Industrial and Engineering
Chemistry
ETH-Zentrum
CH-8092 Zürich

2.1.1. Reduction of NO_x by hydrocarbons

Recent research on the catalytic reduction of NO_x emissions from Diesel and lean-burn engines, operating under net oxidizing conditions, has been focused on a new process utilizing hydrocarbons as reducing agent. Our aim is to improve the efficiency of the selective catalytic reduction of NO by hydrocarbons. A prerequisite to reach this goal is the understanding of the complex mechanism of this reaction, including the identification of surface and gas-phase species [1–4]. Kinetic measurements on promising catalysts are performed in a microreactor system linked to an FT-IR spectrometer with heatable gas cell for gas analysis [5].

2.1.2. Dynamic Behavior of Three-Way Automotive-Exhaust Catalysts

One method of controlling automotive emissions is cleaning the exhaust gas by means of three-way catalytic converters, which simultaneously convert hydrocarbons, CO, and NO_x into H_2O , CO_2 , and N_2 . The behavior of catalytic converters under continuous operation of combustion engines has been extensively studied. The objective of our work is to study the dynamic behavior [6][7] and suitability of three-way catalytic converters for use with an intermittently operated engine in a hybrid system with flywheel. For this purpose a special apparatus has been constructed allowing the simulation of the dynamic changes of the exhaust gas to

which a catalytic converter is exposed in a hybrid system. FT-IR spectroscopy and mass spectrometry are used to monitor the gas composition at the converter inlet and outlet, respectively. Newly developed converters with Pd as noble metal are tested and compared with conventional catalytic converters. Fig. 2 demonstrates the beneficial effect of forced λ -cycling (cycling between lean and fat air/fuel mixtures) on the conversion of the primary target species CO, hydrocarbons, and NO in a three-way Pt-Rh/ CeO_2 - Al_2O_3 catalytic converter. The research carried out so far indicates that the effectiveness of three-way catalytic converters can be improved by λ -cycling and that exhausts of hybrid systems can be efficiently cleaned, if the frequency and amplitude of the cycling is properly adjusted.

2.1.3. Selective Catalytic Reduction (SCR) of NO_x by NH_3

The selective catalytic reduction (SCR) of NO_x by NH_3 is an effective method for treating flue gases from stationary combustion sources. Our research concentrates on the development of novel efficient catalysts. Supported by studies on the reaction mechanism, a series of new catalysts based on vanadium oxide [8–11], chromium oxide [12–14] and tungsten oxide [15] have been developed. Special attention is given to the influence of oxygen, H_2O , and SO_2 on the behavior of these catalysts. Another focal point is the design of cata-

lysts which are efficient for converting NH_3 slipping from the De NO_x unit to nitrogen by selective oxidation. Kinetic models [16] are developed with the aim to simulate the dynamic behavior of SCR catalysts and to aid in the scale up of the microreactor experiments to technical honeycomb structures.

2.1.4. Catalytic Combustion

Catalytic combustion offers an efficient way for complete combustion of fuels over wide air/fuel ratios without significant NO_x or soot formation and permits system designs with improved combustion efficiency and energy recovery. Of special interest are applications with high heat throughput, such as gas turbines and industrial boilers, where requirements of the catalyst systems are severe and high thermal stability is an essential prerequisite. These properties can be found with unsupported [17][18] and supported perovskite-type oxides [19][20]. The main focus of the work includes the development of new materials having high thermal stability and durability, and low light-off temperatures for the 'clean' combustion of hydrocarbons.

2.1.5. Low-Temperature CO Oxidation

CO oxidation catalysts with high activity are not only interesting for environmental applications, but also find important use in orbiting CO_2 lasers and CO detectors. Studies in our group have shown

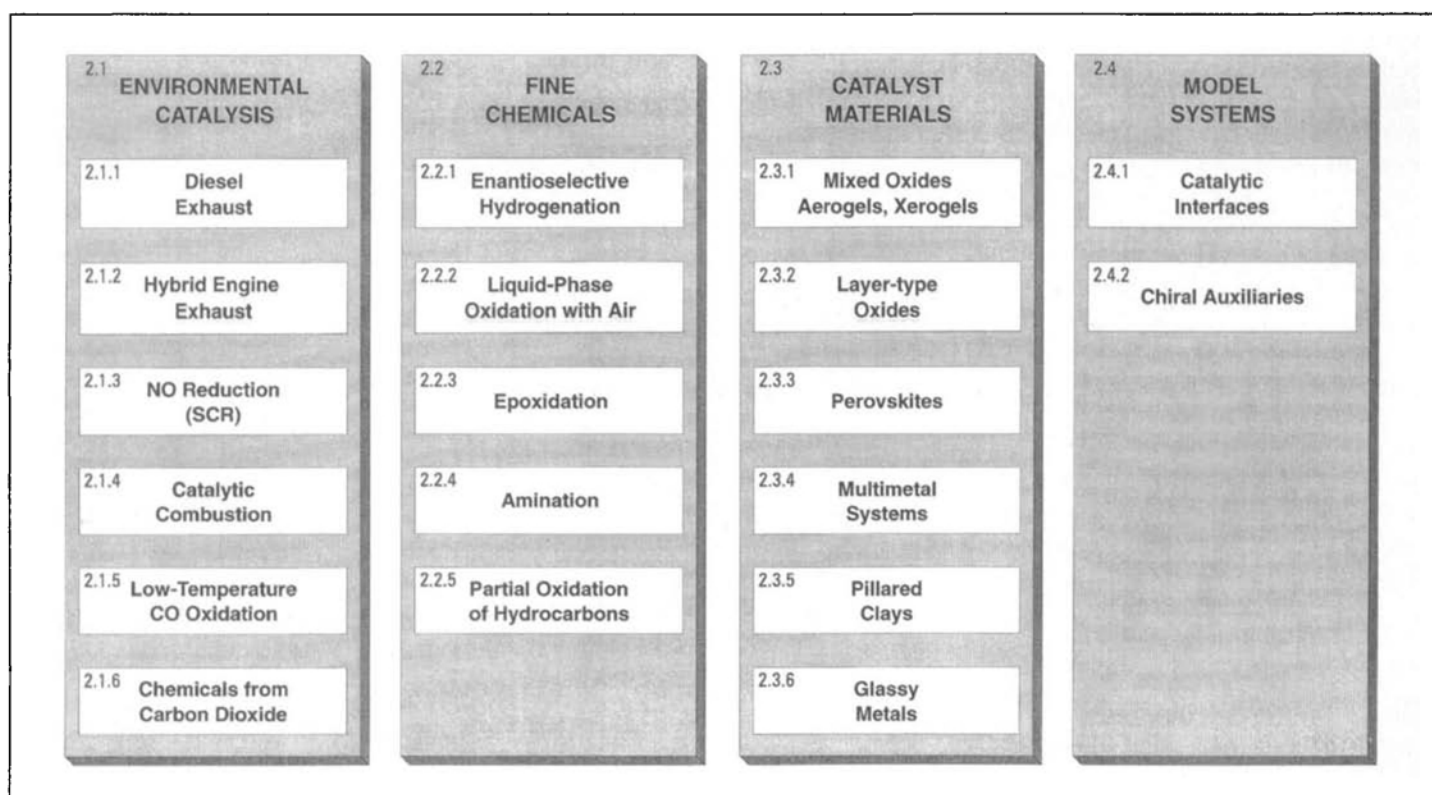


Fig. 1. Survey of present research projects. Numbers indicate corresponding paragraphs in text.

that highly active CO oxidation catalysts for low-temperature applications can be prepared from Zr-based amorphous Au and Pd alloys as catalyst precursors [21–24]. Pd/ZrO₂ prepared from oxidation of glassy Pd-Zr alloys was also found to be extremely active for the disproportionation of CO which is followed by incorporation of carbon into the Pd lattice [23]. Further efforts towards designing efficient low-temperature CO oxidation catalysts with improved long-term behavior are presently undertaken.

2.1.6. Chemicals from CO₂

Based on its large-scale availability, CO₂ represents a suitable starting material for the manufacture of valuable chemicals and fuels. The objective of the work is the development of heterogeneous catalytic processes, starting from CO₂ as the source of carbon, to produce various chemicals such as alcohols, amines, and formamides. Recently we demonstrated that organonitrogen compounds such as methylamines can be produced in a one-step reaction over Cu/Al₂O₃ catalysts starting from CO₂, H₂, and NH₃ [25]. Further research comprises the heterogeneous catalytic production of *N,N*-dimethylformamide (DMF) from CO₂, hydrogen, and dimethylamine under supercritical conditions. Besides conventional transition-metal-based catalysts, new catalytic sol-gel-hybrid systems are prepared.

2.2. Catalysis in Fine and Pharmaceutical Chemistry

Research in this field is driven by the effort of the fine chemical and pharmaceutical industries to replace wasteful non-catalytic processes by economical and clean catalytic routes. Heterogeneous catalysis is gaining increasing importance in the production of fine chemicals and pharmaceuticals due to its definite technical advantages. The aim of our research is to provide the fundamental catalytic and reaction engineering elements which industry needs for designing new environmentally friendly and economic catalytic processes. Generally, this comprises reaction mechanism, catalyst design, solvent-reactant interaction, mass transfer, and reactor design. Understanding of the interplay of these elements is crucial for successful development of novel catalytic processes.

2.2.1. Enantioselective Hydrogenation on Chirally Modified Pt Metals

The enantioselective hydrogenation of various organic compounds possessing C=O, C=N, or C=C functional groups is investigated in three-phase reactors [26–

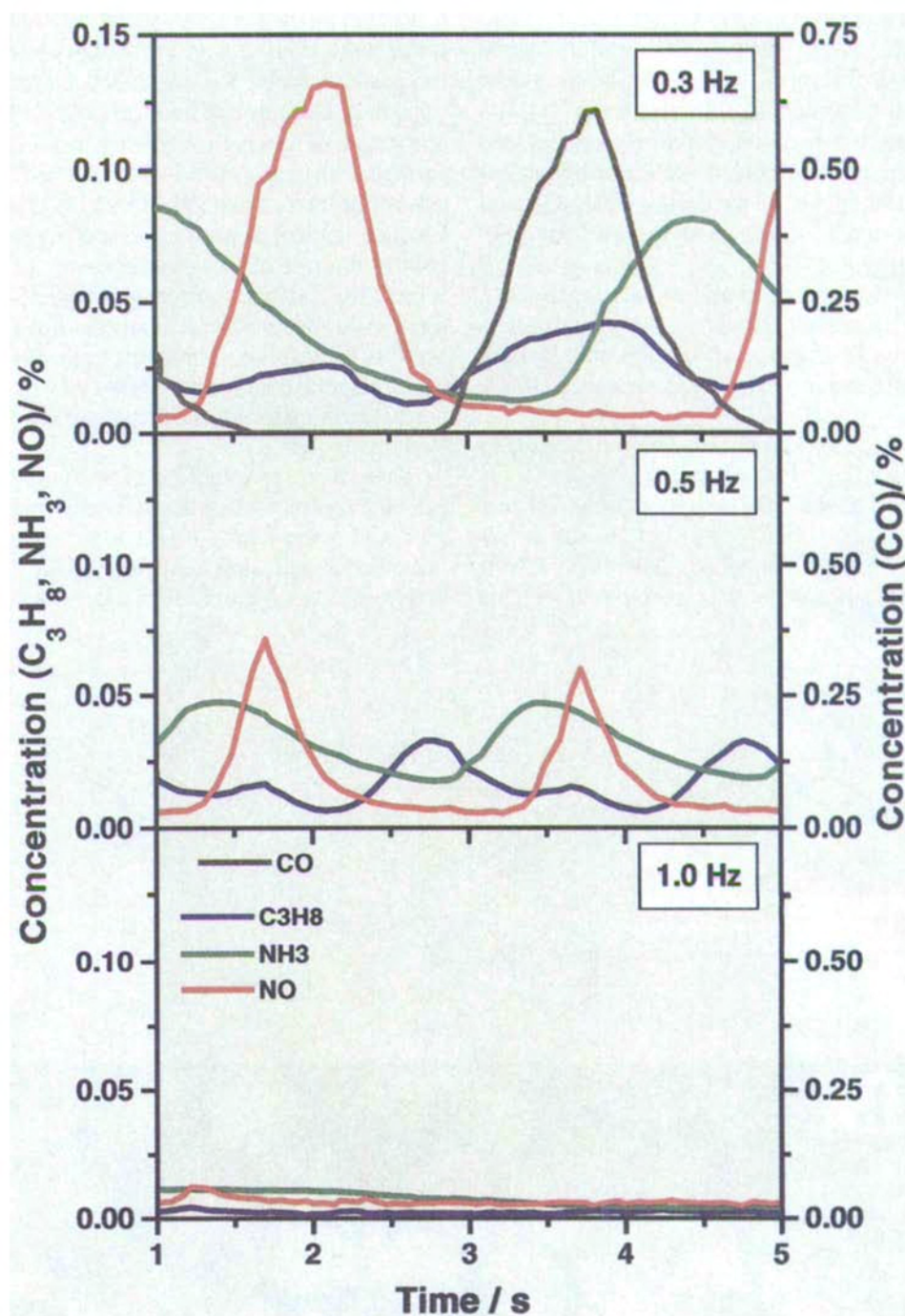


Fig. 2. Time-dependence of concentrations of harmful products measured at the outlet of a three-way Pt-Rh/CeO₂-Al₂O₃ catalytic converter during λ -cycling with different frequencies (0.3, 0.5, 1 Hz). Concentrations were measured by combined use of FT-IR spectroscopy and mass spectrometry. The simulated exhaust gas contained a mixture of CO and H₂ (3:1), O₂, NO (2000 ppm), C₃H₈ (500 ppm), C₃H₆ (500 ppm), CO₂ (12%), H₂O (10%), and N₂ (balance). The λ -value, defined as the normalized molar air/fuel ratio, was changed in the range $\lambda = 1.05$ (lean mixture) and $\lambda = 0.95$ (fat mixture) by altering the flows of O₂ and CO/H₂, respectively. Note the extreme effect of the λ -cycling frequency on the concentrations of the harmful gases, indicating that forced cycling between lean and fat air/fuel ratio can be a powerful tool for improving the efficiency of catalytic converters. Measurements were performed at 583 K and with a gas hourly space velocity (GHSV) of 100'000 h⁻¹.

30]. The chiral information is transferred by a chiral auxiliary (modifier) which is adsorbed on the surface of supported Pt or Pd catalysts. Besides, chiral materials of natural origin, such as cinchona alkaloids, several chiral N-compounds have been synthesized and tested in these reactions. Our aim is to gain information about the crucial factors determining the behavior

of these complex catalytic systems. Based on this knowledge, new efficient catalytic systems are designed.

Substantial effort has been made to reveal the nature of reactant-modifier and solvent-modifier interactions and the mechanism of enantiodifferentiation, using molecular mechanics and *ab initio* calculations [31–33], X-ray crystal-struct-

ture analysis and 2D-NMR. As an example, Fig. 3 depicts the structure of the complex formed upon interaction between co-adsorbed (*R*)-2-(pyrrolidin-1-yl)-1-(naphth-1-yl)ethanol (chiral auxiliary) and reactant in the enantioselective hydrogenation of methyl pyruvate over Al₂O₃-supported Pt, as predicted by molecular modeling.

Regarding novel engineering aspects, we have recently shown that enantioselective hydrogenation can be successfully carried out in supercritical solvents [34].

2.2.2. Aerobic Oxidation on Pt Metals in the Liquid Phase

The selective transformation of primary and secondary alcohols to the corresponding carbonyl compounds or carboxylic acids is the only example in which a

truly heterogeneous catalyst can be used under mild conditions and with molecular oxygen as oxidant. Striking enhancement in activity and selectivity of supported Pt and Pd can be achieved by modifying their surface with heavy-metal atoms, or with organic N-bases and phosphines [35–39]. Electrochemical methods are applied to control the rate of oxygen transport, the selectivity, and the nature of catalyst deactivation during reaction. The structure and stability of Pt-based bimetallic catalysts under reaction conditions are studied with *in situ* scanning tunneling microscopy and cyclic voltammetry.

Several water-soluble and -insoluble primary and secondary alcohols are used as model compounds. A recent example is the direct, one-step oxidation of L-sorbose to 2-keto-L-gulonic acid, a key inter-

mediate in the synthesis of vitamin C [38] [39].

2.2.3. Epoxidation of Olefins

New highly active and selective heterogeneous epoxidation catalysts (aerogels) are developed using the solution-sol-gel method combined with ensuing supercritical drying [40–44]. The structure of the mixed oxide TiO₂/SiO₂ is tuned to the requirements of the epoxidation of bulky cyclic olefins, which are of great practical importance in the fine chemical and pharmaceutical industry. Both the relative proportion of Si–O–Ti structural units, estimated by FT-IR analysis [41], and the pore size were found to be crucial design parameters. Fig. 4 shows the dependence of the relative proportion of Si–O–Ti connectivities and pore size on the TiO₂ con-

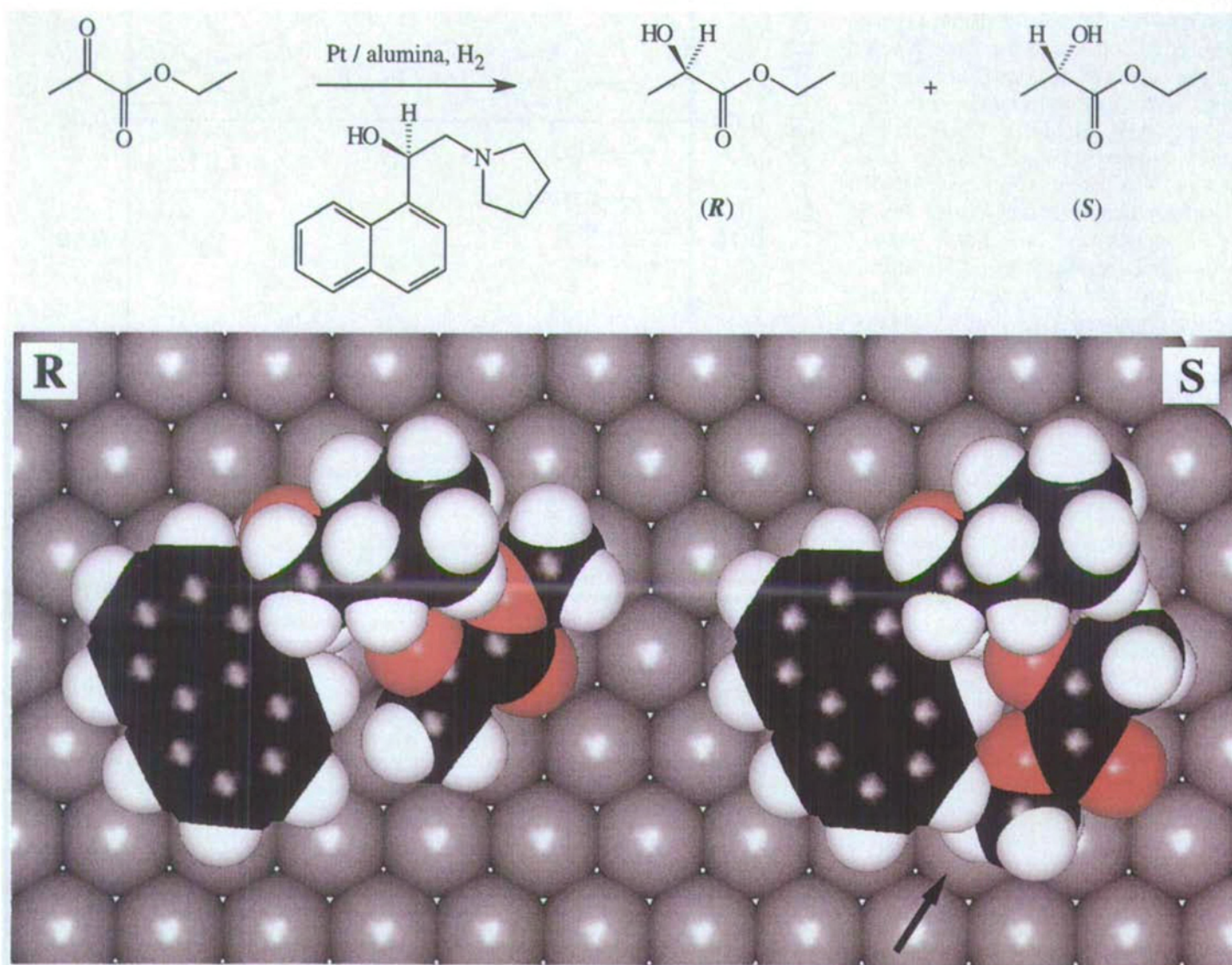


Fig. 3. Molecular modeling of complexes formed between co-adsorbed protonated (*R*)-2-(pyrrolidin-1-yl)-1-(naphth-1-yl)ethanol (modifier) and methyl pyruvate (reactant) which yield (*R*)-methyl lactate or (*S*)-methyl lactate upon hydrogenation [32]. The auxiliary is assumed to be adsorbed via π -bonding of the naphthyl ring on the Pt surface. A Pt (111) surface is used for illustration. Note the strong steric hindrance (marked by arrow) in the complex leading to (*S*)-methyl lactate, which results in a lower stability of this complex favoring the formation of (*R*)-methyl lactate. Similar behavior has also been found in the calculation of the structure of the interaction complex between protonated cinchonidine and methyl pyruvate [31]. O is red, C is black, H is white, and Pt is gray. The N-atom of auxiliary is covered and not seen in the top view.

tent of the aerogels. Most interesting is the finding that the activity of the aerogels for epoxidation of cyclohexene, represented by the initial rate, shows a similar dependence as the relative proportion of Si–O–Ti connectivities, indicating that these structural units can be associated with the active centers. In contrast to the rate, the selectivity to the epoxide (*ca.* 100%) does not depend on the Ti content in the concentration range shown. Similar behavior was observed for the epoxidation of several other olefins, including cyclododecene, norbornene, limonene, and α -isophorone [41–44]. At present, we focus on the selective epoxidation of olefins possessing more complex structure and on fine tuning the acidic properties of the aerogel catalysts.

2.2.4. Amination of Alcohols

The solid-catalyzed amination of alcohols is an economically important route for the synthesis of aliphatic amines, aminoalcohols, and cyclic amines [45][46]. Our experience earlier gained in the amination of long-chain aliphatic alcohols [45] is extended to diols and polyols. The aim is to synthesize polyamines with high yield and suppress the cyclization, dimerization and other side reactions. Supported metal as well as acidic catalysts are tested in the amination of symmetric and non-symmetric triols. The main focus is on the catalyst design and reaction mechanism. The experiments are performed in batch and continuous reactors suitable for the use of supercritical NH_3 .

2.2.5. Partial Oxidation of Hydrocarbons

The aim of this work is to find selective catalysts for the transformation of alkylaromatic compounds and small-chain hydrocarbons to valuable intermediates. The reactions are performed in continuous flow microreactors equipped for *in situ* studies (TPR, TPO) of the redox behavior of the catalysts. Sol-gel-derived oxides and mixed oxides, and zeolite-type catalysts are currently being tested and evaluated. Recent examples are the partial oxidation of *o*-xylene over non-promoted [47] and promoted vanadia-titania catalysts [48] [49], and the oxidative dehydrogenation of 10,11-dihydro-5H-dibenz[*b,f*]azepine to 5H-dibenz[*b,f*]azepine over Na-promoted iron-, manganese-, and cobalt-oxide catalysts [50–52].

2.3. Catalyst Materials

The synthesis of novel chemically and structurally tailored catalytic materials represents one of the most rewarding challenges in catalysis research. The activities in this section greatly influence those in

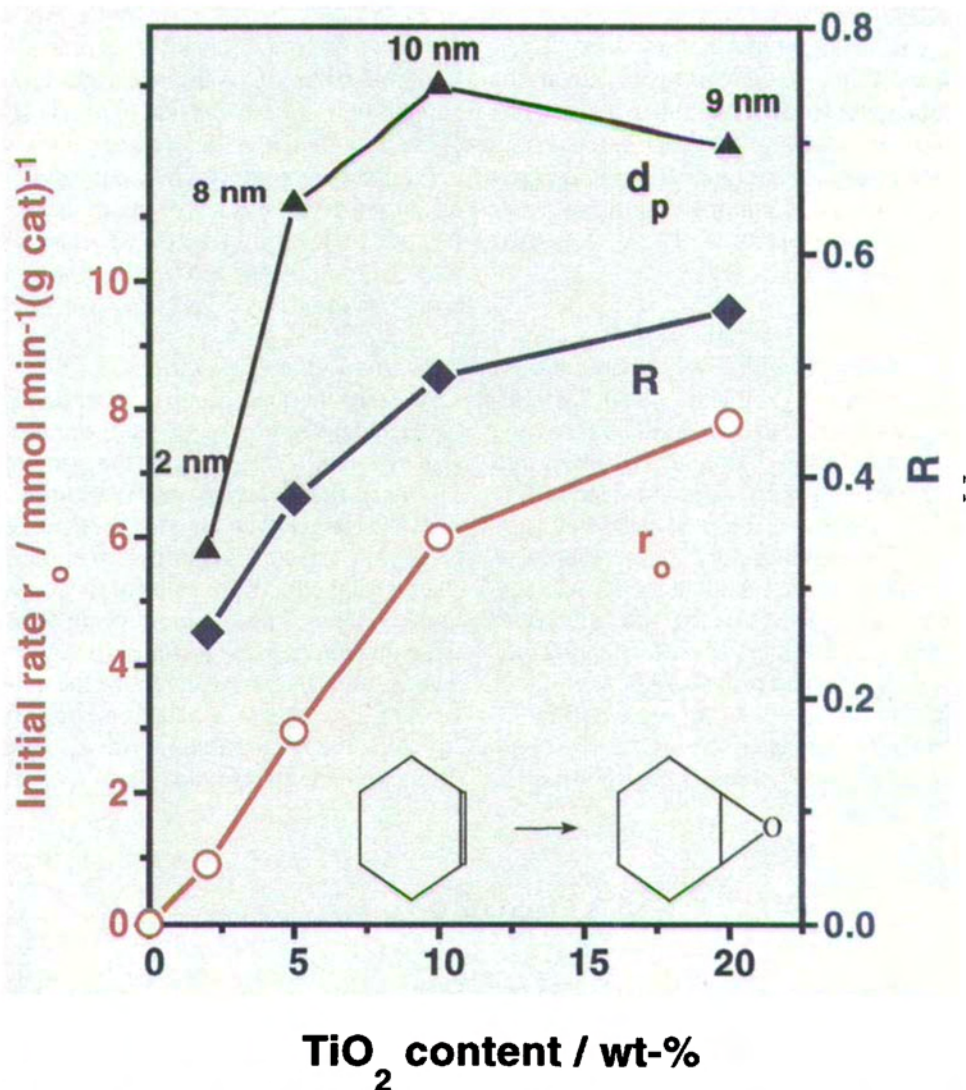


Fig. 4. Influence of TiO_2 content of TiO_2 - SiO_2 aerogels on relative proportion of Si–O–Ti connectivities $R = [\text{Si–O–Ti}]/[\text{Si–O–Si}]$, mean pore diameter (d_p), and initial rate (r_o) of cyclohexene epoxidation with tert-butyl hydroperoxide at 60°C. Note the striking similarity in the dependencies of r_o and R on the TiO_2 content. Data taken from [40].

the other three sections (environmental catalysis, fine chemicals synthesis, and model systems). The aim is to develop strategies for tailoring the structural and chemical properties of solid catalysts and to explore the potential of new catalytic materials. Various techniques of solid-state chemistry, particularly the application of molecular design concepts are used to tailor materials according to the structural and chemical requirements imposed by their application in environmental and fine chemical catalysis.

2.3.1. Mixed Oxides, Aerogels, and Xerogels

Mixing metal oxides on a molecular scale provides interesting opportunities for tailoring acidic and redox properties. A versatile method for achieving intimate mixing is the solution-sol-gel method (SSG) [53] which represents a highly controllable preparation route with inherent advantages, such as molecular scale mix-

ing of the constituents, purity of the precursors, homogeneity of the sol-gel product (isotropy), and the use of different wet-chemical preparation tailoring tools. The SSG method is used combined with either evaporative drying (xerogels) or supercritical drying (aerogels) for preparing single and mixed oxides with unique structural and chemical properties [9][10][40–44][53–57]. The knowledge gained concerning the influence of the SSG and drying conditions on structural and chemical properties of the oxides forms the basis for the development of new xero- and aerogel catalysts, including also sol-gel-derived metal/metal oxide systems [58–61]. One of the critical steps in the preparation of SSG-derived mixed oxides is the drying, *i.e.* the removal of the solvent entrapped in the open gel network. Removal of the solvent by evaporative drying creates differential capillary stress in the gel network which generally results in its structural collapse. This collapse can be avoided by

supercritical drying, which eliminates any liquid-vapor interface inside the gel network during solvent removal. Supercritical drying is achieved either by transferring the solvent into its supercritical state (high-temperature method) or by extracting the solvent entrapped in the gel network using supercritical CO₂ (low-temperature method).

2.3.2. Layer-Type Oxides

Mono- and multilayers of various metal oxides (VO_x [11], MoO_x, CrO_x [13][14], [62–64], WO_x [15]) are built up on oxidic supports (Al₂O₃, TiO₂, ZrO₂, SiO₂, and mixed oxides) by selective reaction of suitable metal-oxide precursors with surface functional groups. These supported oxide layers are excellent model systems, well-suited to study the interactions at oxide-oxide interfaces. The molecular build-up method provides a powerful tool for the development of supported oxide catalysts with controlled surface properties. An example illustrating the opportu-

nities of these layer-type oxide catalysts is presented in Fig. 5, which depicts the immobilization of a VO_x layer on a TiO₂ support by selective reaction of a vanadyl alkoxide with the acidic hydroxy groups of the titania support. This molecular build-up of the active phase has been successfully applied to optimize the structure of VO_x/TiO₂ catalysts used for the selective reduction of NO by NH₃ [11].

2.3.3. Perovskite-Type Oxides

Perovskites are a group of compounds with similar crystal structure as the mineral perovskite, CaTiO₃, with the general formula ABO₃, where A and B are cations and A is larger than B. The ideal cubic perovskite structure is built up of corner-shared octahedra, BO₆, with the B cations in their center. The A cations occupy the large interstices between the anions originating from the arrangement of the corner-shared octahedra. In a stable perovskite structure, the B cations build stable, polar octahedral-site blocks, and the A cations

have the appropriate size to fill the hole between the octahedra. The aim of our work is to study systematically the structure-activity relation of perovskites in oxidation reactions. The research carried out so far on ACoO₃ [17], AMnO_{3+x} and AFeO_{3+x} [18], where A = La, Pr, Nd, and Gd, has clearly demonstrated that thermal stability and the catalytic behavior of perovskite-type oxides can be greatly influenced by the type of A-site cation.

2.3.4. Multimetal Systems

The catalytic behavior of supported metal catalysts can be enhanced by modifying their surface with foreign metal atoms. Two principally different methods are applied for the preparation of supported multimetal catalysts, underpotential deposition of foreign metals onto the catalytically active metal [65][66], and the immobilization of heterometallic clusters. The two methods are used for tailoring the structural and chemical properties of multimetal catalysts used in various reactions.

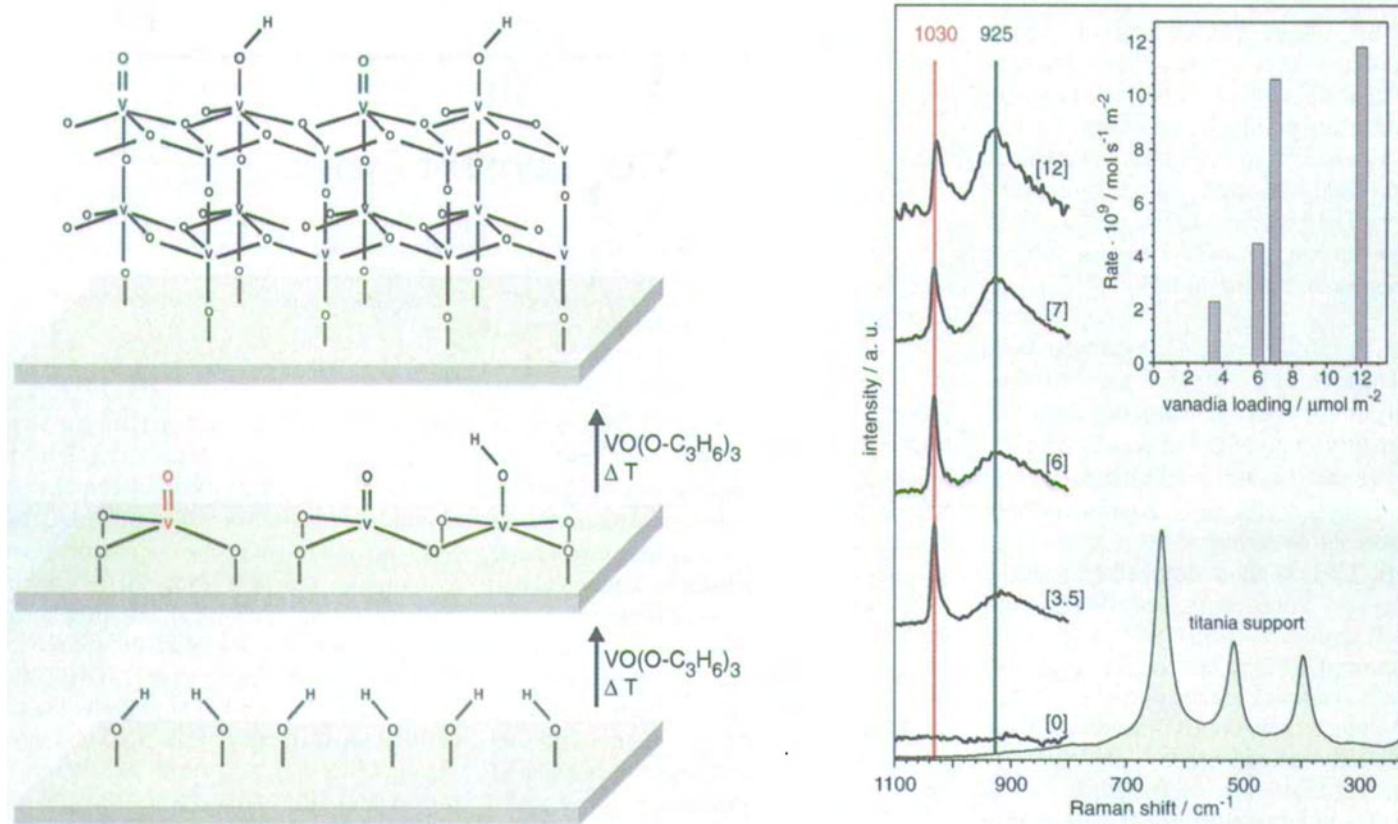


Fig. 5. Schematic illustration of molecular build-up of vanadium-oxide layer on titania support by selective reaction of a vanadyl alkoxide with the surface hydroxy groups of titania and subsequent heat treatment. The structural changes of the vanadium-oxide layer are characterized by FT-Raman spectroscopy. The numbers at the right-hand side of the Raman spectra indicate the corresponding vanadia loading [$\mu\text{mol m}^{-2}$]. At low vanadia loadings, the Raman spectrum shows a sharp prominent band at ca. 1030 cm^{-1} , which is assigned to distorted tetrahedrally coordinated vanadium ions present either as monomeric vanadyls or chain-like species, and a broad band centered around 925 cm^{-1} , indicative for polymeric metavanadate-like species. With higher vanadia loading the band around 925 cm^{-1} increases relative to that at 1030 cm^{-1} , indicating that metavanadate-like species become prevalent. The inset on the top right illustrates how this structural change influences the specific reaction rate for the selective reduction (SCR) of NO by NH₃ at 473 K. Note the strong increase of the rate with higher vanadia loading, which indicates that the isolated monomeric tetrahedral vanadia species are only poorly active in SCR. The activity develops strongly when oligomeric and polymeric species are formed, which is in line with the suggestion that SCR of NO requires two adjacent vanadium centers, as it has been recently proved by *in situ* FT-IR spectroscopy [8].

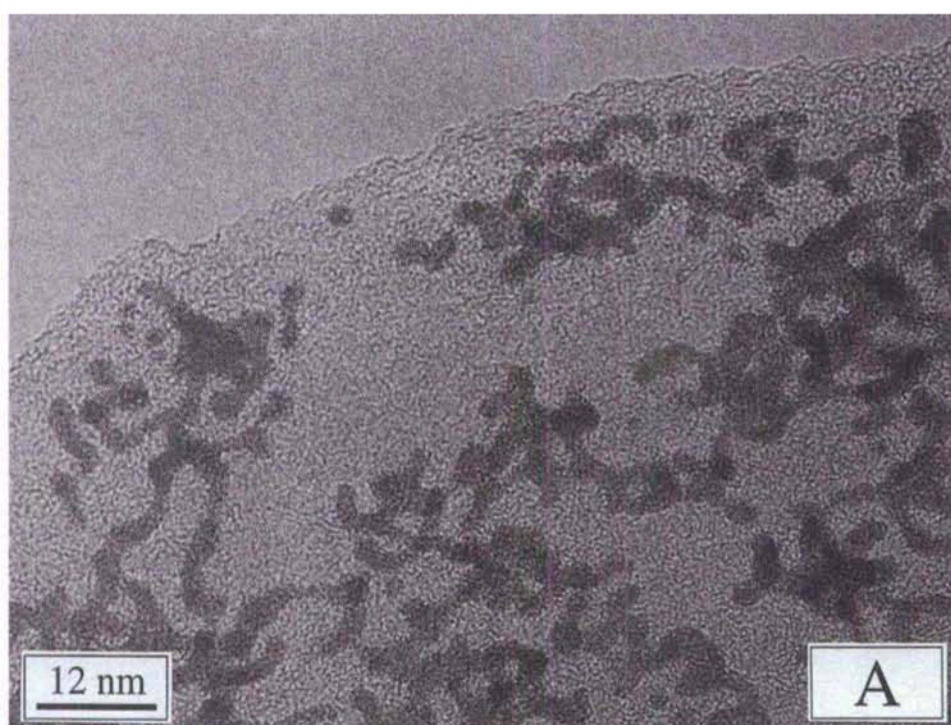
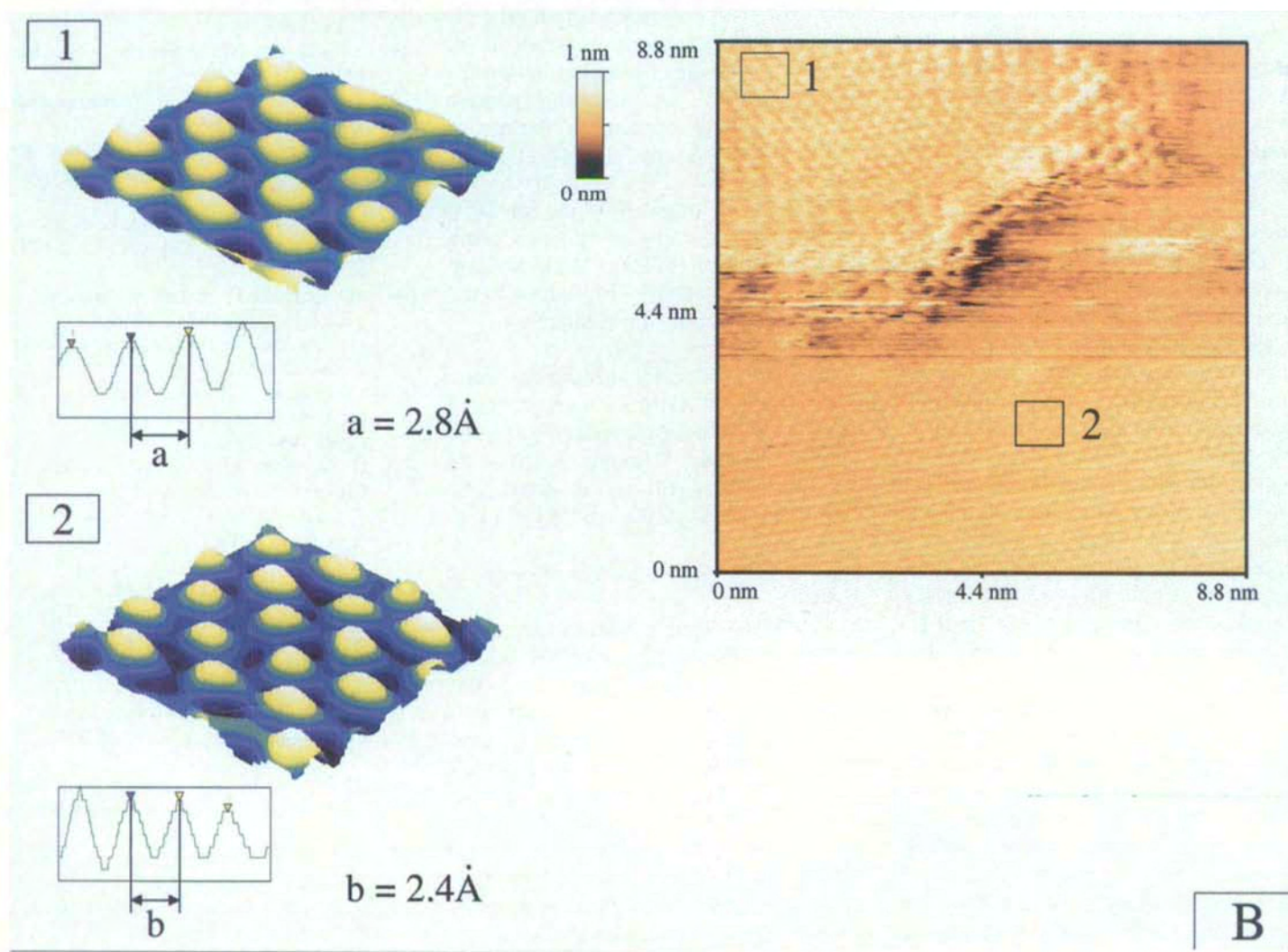


Fig. 6. Structural investigation of platinum/graphite catalyst by high-resolution transmission electron microscopy (A) and scanning tunneling microscopy (B).

A: High-resolution electron micrograph showing the two main forms of platinum aggregates, isolated islands and meander-like structures. The lattice resolution varies due to the different thickness of the aggregates, which has been confirmed by STM [69]. The weakly resolved background fringes originate from the graphite support.

B: STM image on the right side shows a flat monolayer thick platinum particle deposited on the graphite support. High-resolution scans of the areas 1 (platinum) and 2 (graphite) are presented on the left side. The corresponding cross-sections reveal the distances between the Pt and C-atoms, respectively.



2.3.5. Pillared Clays

At present, we focus on hydrotalcite-type compounds. Hydrotalcite (Mg, Al-hydroxycarbonate) belongs to the class of

anionic, basic clays. Its characteristic double-layered structure can be realized with many different cations and offers a pronounced versatility with regard to the ele-

mental composition. These hydrotalcite-like materials are often used as precursors for molecularly mixed hydroxycarbonates, hydroxides, or oxides, which possess ba-

sis and/or redox properties. We study systematically the influence of preparation conditions on the chemical, structural, and catalytic properties of oxyhydroxycarbonates based on Mg, Al, Cu, Fe, and Co [67].

2.3.6. Glassy Metals

Amorphous metal alloys (glassy metals) have gained considerable interest in catalysis research due to their unique structural and chemical properties [68]. Two principal directions of research are pursued: *i*) studies of the catalytic properties of glassy metals in the as-quenched state; and, *ii*) investigations where the glassy metals are used as precursors to catalytically active materials. The motivation for using the glassy materials in the as-quenched state is based on their unique structural properties, whereas the use of glassy metals as catalyst precursors has opened new routes for the preparation of supported metal catalysts with chemical and structural properties which are hardly achievable with conventional preparation methods. Glassy metals also serve as models for studying several fundamental aspects such as the role of segregation, agglomeration, and disordered structures in multi-metal catalysis.

2.4. Model Systems

There are several reasons for using model catalysts in catalysis research. Technical catalysts are frequently not suitable for fundamental studies due to their highly porous structure and the presence of impurities. Furthermore, most technical catalysts are multiphase systems and the active sites are often located at the interfaces or grain boundaries. In these cases it is difficult to study structure-activity relations, and special model systems have to be prepared [69][70] which are suitable for investigation with powerful surface-analytical tools such as X-ray-, and UV photoelectron spectroscopy (XPS, UPS), ion-scattering spectroscopy (ISS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). The aim is to gain information on the surface properties and on the surface processes on a molecular level. As an example, Fig. 6 illustrates the potential of STM for resolving the surface structure of a platinum on graphite catalyst on atomic scale [69].

Model systems are also prepared for elucidating the structural and chemical properties of novel materials [71][72] or of known materials prepared by new preparation routes [73][74]. Another aim which

is tackled using model surfaces concerns the structure of adsorbed organic auxiliaries as used for the stereochemical control in enantioselective hydrogenation (2.2.1.).

2.4.1. Structural and Chemical Properties of Catalytic Interfaces

Three different classes of interfaces crucial in catalysis are presently focused: metal-metal, metal-oxide, and oxide-oxide.

metal-metal: Pt-metal catalysts promoted by heavy metals show excellent activity and selectivity in the partial oxidation of alcohols to carbonyl compounds. The geometrical and electronic effect of the deposition of Pb and Bi on Pt and Pd is studied with specially prepared bimetallic model systems, using XPS, UPS, LEED, STM, and cyclic voltammetry as analytical tools.

metal-oxide: Structural information concerning metal-oxide interfaces is particularly important for understanding the effects exerted by support materials on the catalytic behavior of metals (metal-support interaction). An interesting example illustrating the importance of the metal-oxide interface in catalysis is CO oxidation on Au-ZrO₂ [21] and Au-TiO₂ [72] catalysts. The crucial role of the Au-ZrO₂ interface is presently investigated using thermal desorption (TDS) of the reactant gases CO, O₂, and CO₂, in addition to the previously mentioned techniques.

oxide-oxide: In many metal-oxide-catalyzed reaction the structural properties of oxide-oxide interfaces are decisive for the catalytic behavior. Presently, we focus on the following oxide-oxide interfaces: TiO₂-SiO₂, V₂O₅-TiO₂, and WO₃-TiO₂.

2.4.2. Chiral Auxiliaries Adsorbed on Metals

Chiral auxiliaries, as used in heterogeneous enantioselective catalysis (Sect. 2.2.1.), are complex organic molecules which are adsorbed on active metal surfaces for stereochemical control. Enantiodifferentiation is induced by interaction of the chiral auxiliary with the reactant molecule. Using STM and suitable model surfaces we try to gain information concerning the structure of the adsorbed organic auxiliaries. The studies are supported by independent quantum-chemical calculations aiming at finding the energetically and sterically most favorable conformation of the adsorbed auxiliaries.

It is my pleasure to thank past and present coworkers for their valuable contributions, their enthusiasm, and perseverance, which have great-

ly stimulated our research. Valuable contributions to our research originating from collaborations with the groups of A. Pfaltz, (MPI für Kohlenforschung, Mülheim an der Ruhr, Germany) in the synthesis of chiral auxiliaries, J. Weber (University of Geneva) in molecular modeling, and A. Wokaun (PSI, Villigen) in spectroscopy, are highly appreciated. Over the years several governmental institutions and private companies have financially supported our research. Supports obtained from the Schweizerischer Nationalfonds, Bundesamt für Energiewirtschaft, Kommission für Technologie und Innovation, Eidgenössische Technische Hochschule, Alusuisse-Lonza, Ciba, DuPont, F. Hoffmann-La Roche, and Sandoz, are gratefully acknowledged.

Received: January 15, 1996

- [1] F. Radtke, R.A. Köppel, A. Baiker, *Appl. Catal. A: General* **1994**, *107*, L125.
- [2] F. Radtke, R.A. Köppel, A. Baiker, *Catal. Lett.* **1994**, *28*, 131.
- [3] F. Radtke, R.A. Köppel, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 427.
- [4] F. Radtke, R.A. Köppel, A. Baiker, *Environ. Sci. Technol.* **1995**, *29*, 2703.
- [5] F. Radtke, R.A. Köppel, A. Baiker, *Catal. Today* **1995**, *26*, 159.
- [6] L. Padeste, A. Baiker, *Ind. Eng. Chem. Res.* **1994**, *33*, 1113.
- [7] S. Tagliaferri, L. Padeste, A. Baiker, *Stud. Surf. Sci. Catal.* **1995**, *96*, 897.
- [8] H. Schneider, S. Tschudin, M. Schneider, A. Wokaun, A. Baiker, *J. Catal.* **1994**, *147*, 5.
- [9] M. Schneider, M. Maciejewski, S. Tschudin, A. Wokaun, A. Baiker, *J. Catal.* **1994**, *149*, 326.
- [10] M. Schneider, U. Scharf, A. Wokaun, A. Baiker, *J. Catal.* **1994**, *150*, 284.
- [11] J. Engweiler, A. Baiker, *Appl. Catal. A: General* **1994**, *120*, 187.
- [12] J. Engweiler, J. Nickl, A. Baiker, K. Köhler, C.W. Schläpfer, A. von Zelewsky, *J. Catal.* **1994**, *145*, 141.
- [13] H. Schneider, U. Scharf, A. Wokaun, A. Baiker, *J. Catal.* **1994**, *147*, 545.
- [14] H. Schneider, M. Maciejewski, K. Köhler, A. Wokaun, A. Baiker, *J. Catal.* **1995**, *157*, 312.
- [15] J. Engweiler, J. Harf, A. Baiker, *J. Catal.*, in press.
- [16] R. Willi, B. Roduit, R. Köppel, A. Wokaun, A. Baiker, *Chem. Eng. Sci.*, in press.
- [17] A. Baiker, P.E. Marti, P. Keusch, E. Fritsch, A. Reller, *J. Catal.* **1994**, *146*, 268.
- [18] P. Marti, A. Baiker, *Catal. Lett.* **1994**, *26*, 71.
- [19] P.E. Marti, M. Maciejewski, A. Baiker, *Appl. Catal. B: Environmental* **1994**, *4*, 225.
- [20] P.E. Marti, M. Maciejewski, A. Baiker, *Stud. Surf. Sci. Catal.* **1995**, *91*, 617.
- [21] A. Baiker, S. Tagliaferri, M. Maciejewski, P. Hug, *J. Catal.* **1995**, *151*, 407.
- [22] S. Gredig, S. Tagliaferri, M. Maciejewski, A. Baiker, *Stud. Surf. Sci. Catal.* **1995**, *96*, 285.
- [23] M. Maciejewski, A. Baiker, *J. Phys. Chem.* **1994**, *98*, 285.
- [24] M. Maciejewski, A. Baiker, *J. Pure Appl. Chem.* **1995**, *67*, 1879.

- [25] S.V. Gredig, R.A. Köppel, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 73.
- [26] G. Wang, T. Heinz, A. Pfaltz, B. Minder, T. Mallat, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1994**, 2047.
- [27] B. Minder, T. Mallat, P. Scrabal, A. Baiker, *Catal. Lett.* **1994**, 29, 115.
- [28] B. Minder, M. Schürch, T. Mallat, A. Baiker, *Catal. Lett.* **1995**, 31, 143.
- [29] B. Minder, T. Mallat, A. Baiker, G. Wang, T. Heinz, A. Pfaltz, *J. Catal.* **1995**, 154, 371.
- [30] T. Heinz, G. Wang, A. Pfaltz, B. Minder, M. Schürch, T. Mallat, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 1421.
- [31] O. Schwalm, B. Minder, J. Weber, A. Baiker, *Catal. Lett.* **1994**, 23, 271.
- [32] K.E. Simons, G. Wang, T. Heinz, T. Giger, T. Mallat, A. Pfaltz, A. Baiker, *Tetrahedron: Asymmetry* **1995**, 6, 505.
- [33] A. Baiker, T. Mallat, B. Minder, O. Schwalm, K.E. Simons, J. Weber, in 'Chiral Reactions in Heterogeneous Catalysis', Eds. G. Jannes and V. Dubois, Plenum, New York, 1995, p. 95–104.
- [34] B. Minder, T. Mallat, K.H. Pickel, K. Steiner, A. Baiker, *Catal. Lett.* **1995**, 34, 1.
- [35] T. Mallat, A. Baiker, *Catal. Today* **1994**, 19, 247.
- [36] T. Mallat, Z. Bodnar, P. Hug, A. Baiker, *J. Catal.* **1995**, 153, 131.
- [37] T. Mallat, A. Baiker, *Catal. Today* **1995**, 24, 143.
- [38] C. Brönnimann, Z. Bodnar, P. Hug, T. Mallat, A. Baiker, *J. Catal.* **1994**, 150, 199.
- [39] C. Brönnimann, T. Mallat, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 1377.
- [40] R. Hutter, D.C.M. Dutoit, T. Mallat, M. Schneider, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 163.
- [41] D.C.M. Dutoit, M. Schneider, A. Baiker, *J. Catal.* **1995**, 153, 165.
- [42] R. Hutter, T. Mallat, A. Baiker, *J. Catal.* **1995**, 153, 177.
- [43] R. Hutter, T. Mallat, A. Baiker, *J. Catal.* **1995**, 157, 665.
- [44] R. Hutter, T. Mallat, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 2487.
- [45] A. Baiker, in 'Catalysis of Organic Reactions', Eds. J.R. Kosak, T.A. Johnson, and M. Dekker, New York, 1994, p. 91–102.
- [46] T. Mallat, A. Baiker, in 'Handbook of Heterogeneous Catalysis', Eds. G. Ertl, H. Knözinger, and J. Weitkamp, Verlag Chemie, Weinheim, Part B, Chapt. 4, in press.
- [47] M. Nobbenuis, P. Barnickel, A. Wokaun, A. Baiker, *Chem. Eng. Technol.* **1995**, 18, 17.
- [48] M.G. Nobbenuis, P. Hug, T. Mallat, A. Baiker, *Appl. Catal. A: General* **1994**, 108, 241.
- [49] M.G. Nobbenuis, R. Wessicken, W. Probst, T. Mallat, A. Baiker, *Appl. Surf. Sci.* **1994**, 78, 99.
- [50] A. Knell, D. Monti, A. Baiker, *Appl. Catal. A: General* **1995**, 121, 139.
- [51] A. Knell, D. Monti, M. Maciejewski, A. Baiker, *Appl. Catal. A: General* **1995**, 124, 367.
- [52] A. Knell, D. Monti, A. Baiker, *Catal. Lett.* **1995**, 31, 197.
- [53] M. Schneider, A. Baiker, *Catal. Rev. Sci. Eng.* **1995**, 37, 515.
- [54] M. Schneider, A. Baiker, in 'Encyclopedia of Advanced Materials', Eds. D. Bloor, R.J. Brook, M.C. Flemings, and S. Mahajan, Pergamon, Oxford, 1994, Vol. 1, p. 49–58.
- [55] U. Scharf, M. Schneider, A. Baiker, A. Wokaun, *J. Catal.* **1994**, 149, 344.
- [56] D. Dutoit, M. Schneider, A. Baiker, *J. Porous Mater.* **1995**, 1, 165.
- [57] C. Stöcker, M. Schneider, A. Baiker, *J. Porous Mater.* **1995**, 2, 171.
- [58] M. Schneider, G.D. Duff, T. Mallat, M. Wildberger, A. Baiker, *J. Catal.* **1994**, 147, 500.
- [59] M. Schneider, M. Wildberger, M. Maciejewski, D. Duff, T. Mallat, A. Baiker, *J. Catal.* **1994**, 148, 625.
- [60] M. Schneider, M. Wildberger, D.G. Duff, T. Mallat, M. Maciejewski, A. Baiker, *Stud. Surf. Sci. Catal.* **1995**, 91, 75.
- [61] D.G. Duff, T. Mallat, M. Schneider, A. Baiker, *Appl. Catal. A: General* **1995**, 133, 133.
- [62] U. Scharf, H. Schneider, A. Baiker, A. Wokaun, *J. Catal.* **1994**, 145, 464.
- [63] K. Köhler, J. Engweiler, A. Baiker, *Langmuir* **1995**, 11, 3423.
- [64] K. Köhler, M. Maciejewski, H. Schneider, A. Baiker, *J. Catal.* **1995**, 157, 301.
- [65] Z. Bodnar, T. Mallat, A. Baiker, *Catal. Lett.* **1994**, 26, 61.
- [66] Z. Bodnar, T. Mallat, A. Baiker, in 'Catalysis of Organic Reactions', Eds. J.R. Kosak and T.A. Johnson, Marcel Dekker, New York, 1994, p. 393–402.
- [67] S.M. Auer, M. Schneider, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1995**, 2057.
- [68] A. Baiker, in 'Glassy Metals', Topics in Applied Physics, Vol. 72, Eds. H. Beck and H.J. Güntherodt, Springer Verlag, Berlin, Heidelberg, 1994, p. 121–162.
- [69] F. Atamny, D. Duff, R. Wessicken, A. Baiker, *Catal. Lett.* **1995**, 34, 305.
- [70] Ch. Schild, J. Nickl, A. Baiker, A. Wokaun, *Catal. Lett.* **1994**, 25, 179.
- [71] F. Atamny, A. Baiker, H.J. Muhr, R. Nesper, *Fresenius J. Anal. Chem.* **1995**, 353, 433.
- [73] D. Duff, A. Baiker, *Stud. Surf. Sci. Catal.* **1995**, 91, 505.
- [73] M. Becht, K.H. Dahmen, F. Atamny, A. Baiker, *Fresenius J. Anal. Chem.* **1995**, 353, 718.
- [74] F. Atamny, A. Baiker, *Surf. Sci.* **1995**, 323, L314.

Chimia 50 (1996) 73–78
 © Neue Schweizerische Chemische Gesellschaft
 ISSN 0009–4293

Homogeneous Transition-Metal Catalysis in Asymmetric C–C-Bond Formation. Back to Coordination Polymerization

Giambattista Consiglio*

Abstract. An account is given of the development of the author's research in the field of homogeneous catalysis by transition-metal complexes at the Laboratorium für Technische Chemie of the ETH, Zürich. The main goal is to explore the potentiality of asymmetric transition-metal catalysis for new reactions in which C–C bonds are formed, leading to enantiomerically enriched (pure) products. Increasing attention is given to new carbonylation reactions, in particular to their exploitation for the synthesis of new stereoregular optically active polymers.

Introduction

There is nothing which impresses itself more on the memory than failure! In 1966, I was waiting to be drafted into the Italian army while doing postdoctoral work at the University of Pisa (Italy). I was asked to attempt the preparation of optically active organoaluminium compounds in which the asymmetric C-atom had to be bound to the metal atom. The research was related to the synthesis of optically active

*Correspondence: Prof. Dr. G. Consiglio
 Swiss Federal Institute of Technology
 Department of Industrial and
 Engineering Chemistry
 ETH-Zentrum
 CH–8092 Zürich