In situ ptychography during the annealing treatment of heterogeneous nanoporous gold catalysts

Baier, S.; Benzi, F.; Rochet, A.; Scholz, M.; Hoppe, R.; Shi, J.; Wittstock, A.; Bäumer, M.; Damsgaard, Christian Danvad; Schroer, C.G.; Grunwaldt, J.-D.

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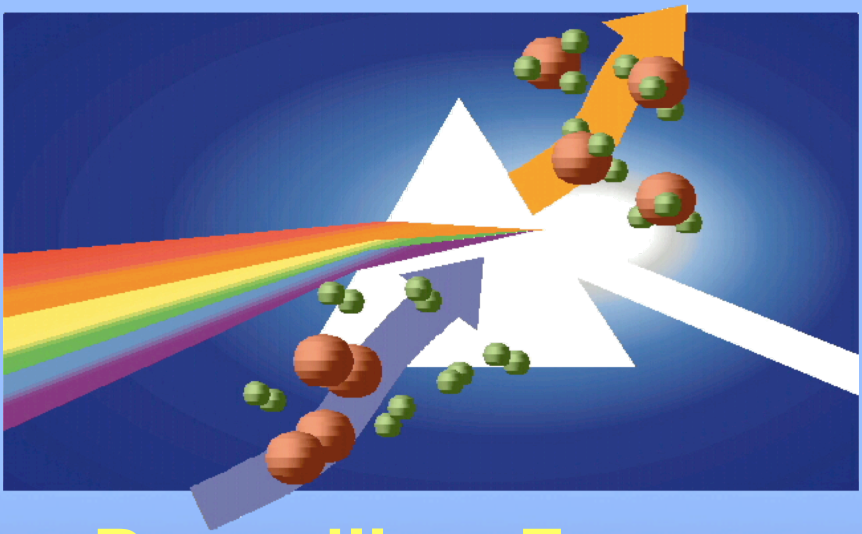
OPERANDO V

5th International Congress on Operando Spectroscopy



Deauville – France

May 17-21 2015

BOOK OF ABSTRACTS

PLENARY LECTURES

PL - 1

Catalytic Mechanisms by Time-Resolved FT-IR Monitoring under Reaction Conditions

Heinz Frei

Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Temporally resolved detection of transient surface intermediates of heterogeneous catalysis by a structure sensitive spectroscopy such as FT-IR, or of homogeneous catalysis under reaction conditions on time scales from seconds to nanoseconds provides detailed insights into factors that limit rates or determine product selectivity. Infrared spectra afford structural characterization of short lived species, and temporal resolution reveals the kinetic relevancy and the role of the observed intermediate in the catalytic cycle. While time-resolved FT-IR spectroscopy is a well-established method for photocatalytic systems (step-scan and rapid-scan techniques), the challenge for application to heterogeneous and homogeneous thermal catalysis is the triggering of the reaction with a short reactant pulse.

For catalysis at the gas-solid interface, gas pulses as short as a fraction of a millisecond that merge with a continuous gas flow of a co-reactant in the immediate vicinity of the catalyst surface allow for the detection and temporal resolution of all sequential steps even for complex reactions such as hydroformylation of ethylene to propionaldehyde over supported Rh nanoparticles.[1] Heterogeneous multi-electron catalysis of importance for solar fuel generation such as oxygen evolution from water can readily be triggered by light pulses but faces the challenge of sensitive infrared detection at the aqueous-solid interface. Here, the attenuated total reflection method allowed recently the detection of two surface intermediates in the case of Co oxide (Co_3O_4) catalyst, namely a Co(IV)=O and a superoxide species.[2] Concurrent operando XPS or X-ray absorption measurements, which have been demonstrated for water oxidation at Ir oxide catalyst surfaces in aqueous solution offer determination of the oxidation state of the metal along with the molecular structure of a surface hydroperoxide monitored by FT-IR, thus providing complete characterization of the intermediate.[3-5] Recent mechanistic studies of homogeneous catalysis in liquid solution utilize pulsed activation of a visible light sensitizer[6] or of the catalyst,[7,8] which in the latter case enabled the observation and detailed structural characterization by rapid-scan infrared spectroscopy of a gold catalyzed arylative ring expansion in organic solvent. Insights gained from transient FT-IR studies will be discussed in the context of complementary information available from other structure specific operando methods.

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PL - 2

Probing Catalysts and Identifying Catalytic Reaction Mechanisms under Industrially Relevant Conditions

Institute of Chemical Research of Catalonia (ICIQ)
Av. Paϊsos Catalans 16, 43007 Tarragona, Spain; Email: aurakawa@iciq.es

Atsushi Urakawa

The importance of studying catalytic reactions under working and industrially relevant conditions has been the key motivation for the creation of *operando* spectroscopic approach in R&D of catalyst materials and catalytic processes. This *operando* approach using technologically relevant catalysts avoids widely debated materials and pressure gaps which often cause discrepancies between the results from catalytic testing and the insights gained by spectroscopic investigations of model systems and model reaction conditions. Nowadays, the importance of *operando* approach is unquestionable; however, challenges remain in the mode of operation for such spectroscopic measurements especially under technically demanding extreme reaction conditions or when sophisticated operations such as unsteady-state operation are required.

In this contribution, selected state-of-the-art examples mimicking the operation condition of laboratory catalytic reactors for *operando* spectroscopy are described. Particular emphasis will be given on the investigations of reactions such as CO_2 conversion and automotive catalysis under different modes of operation (batch, flow, steady-state, unsteady-state) and under extreme conditions (e.g. high pressure) using IR, Raman, XRD, and XAFS. The design aspects of *operando* spectroscopic cells and probe installation are discussed in detail.

Furthermore, the general problem of *operando* measurements lies in the interpretation of complex spectra due to increased spectral complexity arising from the use of realistic materials and reaction conditions. The practical power of multivariate analysis on the elucidation of key chemical elements from complex *operando* spectroscopic data sets will be shown and discussed.

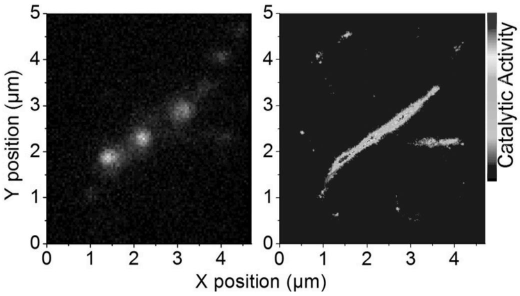
PL - 3

ADVANCED OPTICAL MICROSCOPY FOR RESOLVING CATALYSIS AT THE SINGLE PARTICLE AND SINGLE TURNOVER LEVEL

Maarten Roeffaers[1], Johan Hofkens[2]
[1]Center for Surface Chemistry and Catalysis, KU Leuven, Belgium
[2]Department of Chemistry, KU Leuven, Belgium
E-mail: maarten.roeffaers@biw.kuleuven.be , Johan.hofkens@chem.kuleuven.be

Fluorescence microscopy is a recent addition to the toolbox for *in situ* study of solid catalytic materials. It combines ease of use with non-invasiveness, high sensitivity and temporal resolution.[1,2] However, due to the diffraction of light, an optical microscope has a limited spatial resolution, which is insufficient to distinguish the nano-sized domains in catalytic solids. One of the commonly followed routes in biology to overcome the diffraction-limited resolution is the localization of individual molecules.

Here we show how mapping of single catalytic turnovers yields diffraction unlimited activity images of working zeolite catalysts.[3,4] Whereas (biological) single molecules fluorescence studies so far rely on large polycyclic substrates which cannot enter the zeolite micropores,[1,2] the widespread application in catalysis research critically depends on identifying relevant reagent molecules that are converted into a strongly fluorescent reaction product that is detectable with single molecule sensitivity. Surprisingly, furfuryl alcohol but also several styrene derivatives can be used for such studies (Figure *left*; every white dot is one single fluorescent reaction product). By recording the fluorescence signal generated by every single catalytic conversions and by accurate image reconstruction, a nanoscale activity map can be generated (Figure *right*).



Next to direct observation of catalytic conversions, detailed understanding of catalytic site distribution and accessibility is critical. Rather than looking at the inorganic compositions, as in electron and X-ray microscopy, we use advanced non-linear optical microscopy and organic probes molecules similar to those used in infrared spectroscopy. Stimulated Raman scattering microscopy enables visualizing the 3D acid site distribution in acid zeolite catalysts,[4] and unlike the more commonly used coherent anti-Stokes Raman scattering (CARS), the SRS signal is free from non-resonant background, which allows straightforward quantitative and qualitative analyses. The highly sensitive chemical imaging with sub-micrometer spatial resolution make SRS microscopy a promising tool to investigate catalytic materials.

In this Plenary talk we will show that combining different types of optical microscopy allows the detailed characterization of working zeolite catalysts at the single particle level and ultimately with single molecule sensitivity; as example we will mainly focus on acid mordenites. The presented approach enables unraveling the complex interplay between diffusion, catalytic site distribution and reactions at the single particle level. Furthermore, next to significant intraparticle heterogeneities, the data also reveal important interparticle heterogeneities which have often been overlooked so far.

ACKNOWLEDGEMENT Financial support from European Research Council for financial support (ERC Starting Grant 307523) is gratefully acknowledged.

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PL - 4

Nanocatalysis: Size- and Shape-dependent Catalytic Reactivity

Beatriz Roldan Cuenya

Department of Physics, Ruhr-University Bochum, Bochum 44780, Germany

In order to comprehend the properties affecting the catalytic performance of metal nanoparticles (NPs), their dynamic nature and response to the environment must be taken into consideration. The working state of a NP catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This work provides examples of recent advances in the preparation and characterization of NP catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, and Cu catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), and *in situ* and in *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas-phase oxidation of alcohols (methanol, propanol), the oxidation and reduction of NO, the electrochemical oxidation of propanol and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the NP size, shape and chemical state in the activity and selectivity of the former reactions.

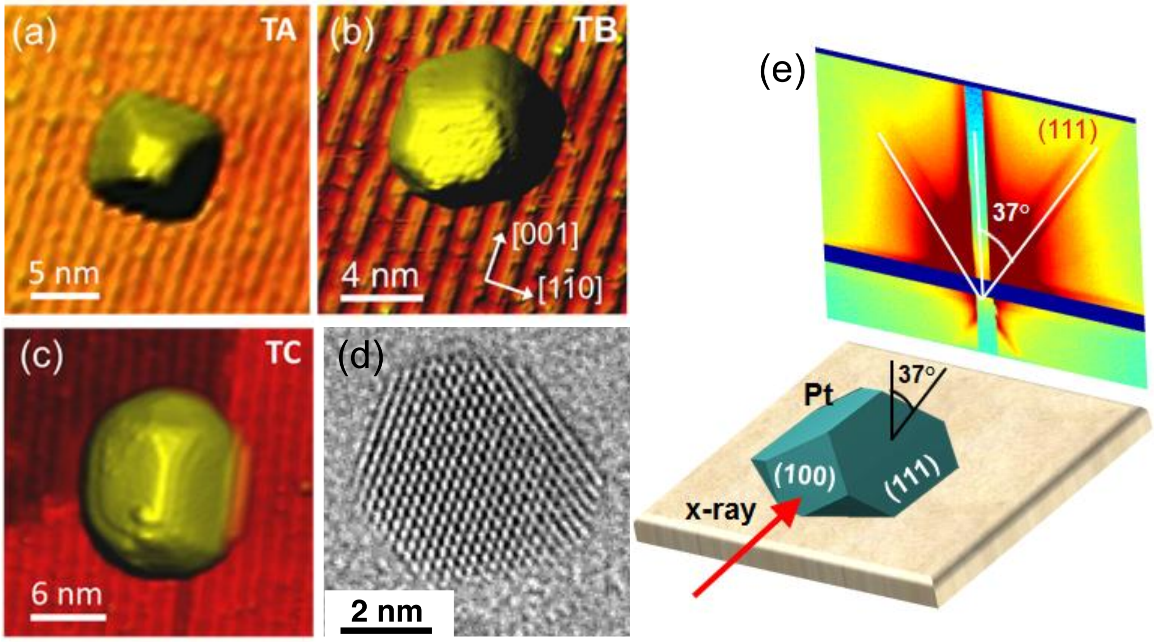


Fig. 1. (a-c) STM images of micellar Pt NPs on $TiO_2(110)$ acquired at RT after annealing in UHV at 1000°C. (d) High resolution TEM image of a Pt NP deposited on SiO_2/Si obtained at RT after annealing at 800°C in H_2. (e) GISAXS data from shape-selected Pt NPs on $SrTiO_3(110)$ acquired in H_2 at 700°C.

PL - 5

Ligand design in homogeneous catalysis: rational design, catalyst decomposition and mechanistic studies

Paul C. J. Kamer
University of St Andrews

The reactivity of organotransition metal complexes is dependent on the ligand environment of the metal. Ligand development has led to a tremendous growth of transition metal catalysis in organic synthesis owing to the obtained high reactivity under mild conditions and the large functional group compatibility. The major activity of our group is in the field of ligand synthesis based on phosphorus donor atoms by rational design assisted by molecular modelling. Ligand design is supported by thorough mechanistic (in-situ) studies of catalytic reactions to acquire insight in structure-activity relations. Ligands like phosphines, phosphoramidites and phosphites have a large effect on rate and selectivity of several transition metal catalysed carbon-carbon bond formations. We have been exploring several approaches to develop new selective catalysts. Besides the study of well-known steric and electronic ligand effects the influence of ligand geometries around the metal centre is a key issue in this research. In addition ligand effects on catalyst decomposition are being explored. These concepts are explored in import C-C and C-X coupling reaction as well as in carbonylation chemistry.

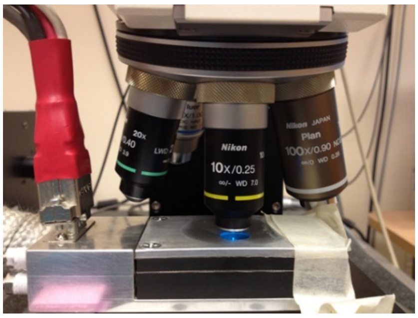
PL - 6

Operando Spectroscopy of Ionomer Metal Interfaces

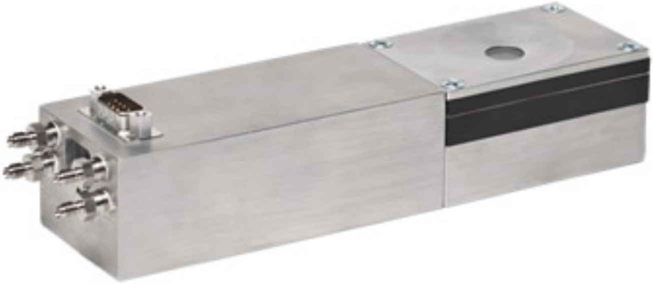
Eugene S. Smotkin
Department of Chemistry and Chemical Biology, Northeastern University, Boston MA 02115

Abstract

The membrane electrode assembly is a polymer electrolyte membrane sandwiched between anode and cathode catalytic layers. The electrocatalytic layers are contacted to porous carbon paper or cloth that serve both as current collectors and reactant diffusion layers. Membrane electrode assemblies have applications in organic synthesis, environmental remediation energy conversion and storage devices. Each application requires an ionomer-catalyst interface that is optimized for the required chemical reaction. Optimization requires methods for characterization under *relevant* conditions. Because the active state of the ionomer-catalyst interface exists only during electrocatalysis,[1] characterization is best done at normal operating temperatures with typical reactant stream flow (*i.e.*, Operando). Operando methods preclude the use of supplemental electrolytes (e.g., H_2SO_4 or $HClO_4$) that contribute mobile anion adsorbates and dehydrate at the high end of relevant temperatures. The presentation will discuss operando IR spectroscopy, X-ray absorption spectroscopy and finally Raman Spectroscopy of polymer electrolyte membrane electrode assemblies. Highly detailed descriptions of our current structure of the operando cells will be provided along with discussion of acquired potential dependent spectra. New developments in infrared band assignments of Nafion that are relevant to analysis of operando spectra will also be presented.



Operando Raman Cell



Operando IR-XAS Cell

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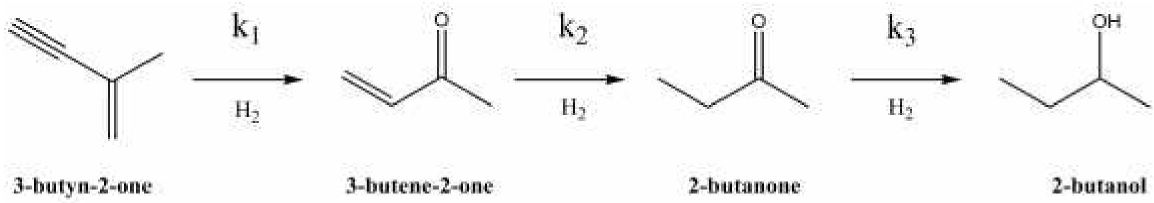
KEYNOTE LECTURES

KN - 1

The use of infrared spectroscopy to probe consecutive gas phase hydrogenation reactions over supported metal catalysts

David Lennon, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK.

A major goal in contemporary heterogeneous catalysis is to define structure/activity relationships for specified reactions. Supported palladium catalysts have wide application in selective hydrogenation reactions, therefore it is highly desirable to correlate product yields with certain catalyst specifications, so that optimum catalyst formulations maximize the atom economies of particular unit operations. A previous study from this group examined crotonaldehyde hydrogenation over supported Pd catalysts [1]; the present work extends concepts explored in that earlier work by investigating the gas phase hydrogenation of an α,β-unsaturated ketone (3-butyne-2-one, $CH{\equiv}C(C{=}O)CH_3$) over alumina-supported Pd catalysts – Scheme 1.



Given the variety of functional transformations evident within Scheme 1, infrared analysis of the reaction mixture within a batch reactor is selected to examine the reaction chemistry [2]. Periodic scanning of the gas phase enables the change in the gas composition present over the catalyst to be determined as a function of time, Figure 2. The study highlights the benefits and disadvantages of the use of infrared spectroscopy within a catalytic batch reactor.

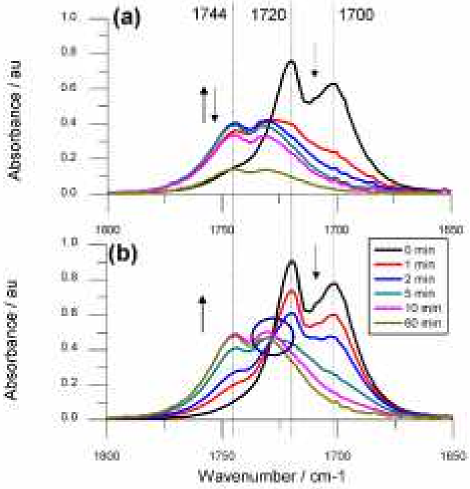


Figure 1 The infrared spectrum (1800-1650 cm^{-1}) for the hydrogenation of 3-butyne-2-one as a function of time (0-60 minutes) over (a) 5% $Pd(NO_3)_2/Al_2O_3$ and (b) 1% $PdCl_2/Al_2O_3$. The circle in (b) signifies an isosbestic point at 1730 cm^{-1}.

The work shows that the structure/activity relationship originally proposed for the hydrogenation of an alkene aldehyde [1] is equally applicable to an alkynic ketone; implying that the original site-selective model is generic for the hydrogenation of α,β-unsaturated carbonyls over supported Pd catalysts. The presentation will further illustrate how certain catalyst preparative procedures can perturb active site distributions, which may then influence resulting product distributions and reaction profiles.

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KN - 2

Dynamic behavior and chemical functionality of SO_2 oxidation catalysts studied by *operando* Raman spectroscopy and electron microscopy

Filippo Cavalca, Stig Helveg, Jens Hyldtoft, Kurt Christensen and Pablo Beato
Haldor Topsoe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark
e-mail address:fcav@topsoe.dk

Abstract

Sulfur oxide belongs to the more troublesome pollutants having a damaging effect on human health and ecosystems. Reduction of SO_2 emissions is favorably done by oxidation followed by condensation into sulfuric acid. The industrial catalyst for SO_2 oxidation consists of vanadium oxides mixed with alkali metal pyrosulfates supported on a porous silica carrier. The supported phase is dispersed in the form of a liquid film when the catalyst is in operation [1], and vanadia dissolved in the molten pyrosulfate catalyzes the oxidation in homogeneous fashion. As the liquid state is only present during catalysis and the reaction conditions are harsh, it has so far been challenging to obtain relevant information about the catalytic active species and their dynamic behavior during SO_2 oxidation. In this work, *operando* Raman spectroscopy and electron microscopy [2] was combined to assess the physical and chemical state of the catalyst under realistic working conditions. By means of *operando* Raman spectroscopy [2], the effect of temperature, gas composition and catalyst composition were investigated by a new experimental *operando* set-up, which allows mimicking the environment in an industrial catalytic converter (see Figure 1).

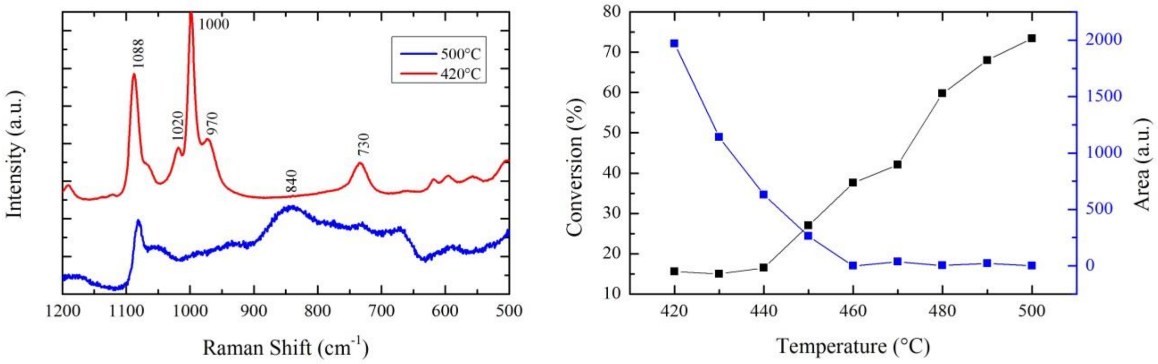

Figure 1. Left: *operando* spectra of SO_2 oxidation model catalyst in reaction atmosphere at different temperatures. Right: Correspondent peak fitting of the 1000cm^{-1} peak (blue squares) and measured catalyst activity as a function of temperature (black dots).

Furthermore, by means of transmission electron microscopy (TEM), the first ever observations of the liquid film upon catalyst activation are obtained enabling a dynamic description of the dispersion of the vanadia phase into the silica pore system. The complementary information provides unprecedented insight into the dynamic behavior and chemical functionality of the active state of SO_2 oxidation catalysts.

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KN - 3

A Decade of *Operando* Spectroscopy in Catalysis

Israel E. Wachs*, Anisha Chakrabarti, Michael Ford, Daniel Gregory, RongRong Hu, Christopher Keturakis, Soe Lwin, Yadan Tang, Zhou Yang, and Minghui Zhu
Operando Molecular Spectroscopy & Catalysis Laboratory,
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015 USA
*iew0@lehigh.edu

This presentation will focus on critically reviewing the impact of applying the *operando* spectroscopy methodology to the study of catalysts over the past decade. It will review the new fundamental catalyst structure-activity insights that have been obtained by application of the *operando* spectroscopy methodology approach to catalysis research and novel instrument developments. It is important to assess the impact that the *operando* spectroscopy methodology approach has had on catalysis science in the past decade and to discuss future directions.

Operando spectroscopy catalytic studies over the past decade have spanned multiple catalyst types with major activity in the areas of supported and bulk metal oxides. Oxidation reactions have been quite commonly studied, particularly the methanol oxidation reaction by both unsupported and supported metals as well as supported metal oxides using methods such as *operando* NAP-XPS, FTIR, EPR and Raman spectroscopy. The oxidative dehydrogenation of propane by supported metal oxides has also been studied by many groups, employing methods like *operando* Raman, UV-vis and EPR spectroscopy. The *operando* spectroscopy methodology has not received as much attention for catalysis by metal sulfides and polyoxometalates (POMs), with the harsh experimental conditions of catalysis by sulfides being a significant hurdle. Emphasis will be placed on the new catalysis science fundamental insights that have been attained for each class of catalysts by application of the *operando* spectroscopy methodology.

The *operando* spectroscopy methodology was first adopted by optical characterization methods and followed by magnetic and X-ray methods, with the latter receiving much attention in recent years. *Operando* Neutron Scattering has been used to simultaneously probe the crystal structure and state of charge of Li-ion batteries and fuel cells under different relevant conditions. Near ambient pressure XPS and near ambient pressure electron microscopy were also developed in this period. Some spectroscopic techniques, such as IR spectroscopy (Attenuated Total Reflection-IR for liquids) are even capable of simultaneously tracking both the catalyst surface and reaction products in the same spectrum. *Operando* spectroscopy studies have been reported in recent years for gas-solid (fixed-bed and fluid bed modes), liquid-solid and liquid phases. Future *operando* spectroscopy instrument needs and developments will also be proposed.

KN - 4

Ultrafast Spectroscopy Reveals Photo-excited Charge Transfer Pathway of a Photocatalytic Metal-Organic Framework.

M. A. van der Veen,[1] J. Garcia-Santaclara,[1] K. Mazur,[3] M. Nasalevich,[1] J. Gascon,[1] F. Kapteijn,[1] A. 1 Houtepen,[2] F. Grozema,[2] M. Bonn,[3] J. Hunger[3]
1 Catalysis Engineering, Delft University of Technology, Delft, the Netherlands
2 Opto-electronic materials, Delft University of Technology, Delft, the Netherlands
3 Max-Planck Institue for Polymer Research, Mainz, Germany
m.a.vanderveen@tudelft.nl

Photocatalysis can be used to harvest solar energy and to enable visible-light driven organic synthesis. The use of metal-organic frameworks for this purpose is receiving more and more attention.[1] Artificial photosynthesis by metal-organic frameworks is a budding field in which the possibilities are endless due to variation of organic ligands and inorganic nodes in the frameworks, and the inclusion of additional catalytic sites by embedding nanoparticles or homogeneous catalysts.[2] A fundamental understanding of the photocatalytic process by these systems has the potential to move this field forward greatly. The photocatalytic process starts by photoexcitation of the metal-organic framework. The photoexcited electrons and holes need to subsequently be transferred to occluded species in the pores. These species can directly be reactants, or well-defined included catalytic centres that improve the efficiency of the overall reaction.[3] For the photocatalytic reaction to be efficient, this charge transfer needs to occur faster than charge recombination. As such charge transfer is at the core of photocatalytic conversions. Our aim is to elucidate the pathway and life times of the photo-excited electron and hole to formulate strategies for improved MOF-based photocatalysts.

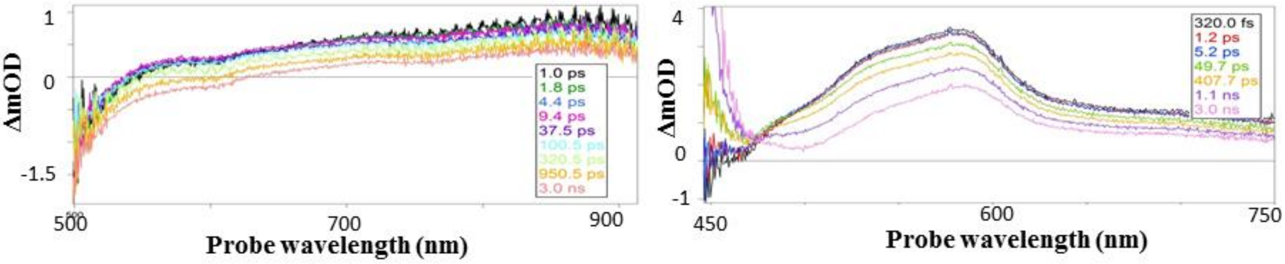

Figure 1. Probe spectra of the change in optical density at different times after photo-excitation of left) NH2-MIL-125 and right) NH2-MIL-125 with included phenolic hole shuttle, both in DMF.

We measured the photo-excited state and charge transfer of a metal-organic framework, namely the photocatalytically active NH$_2$-MIL-125, with femtosecond pump-probe spectroscopy. This metal-organic framework built up from Ti$_8$OH$_4$O$_4$ clusters linked into a porous 3-D framework by aminoterephtalates has already been shown to photocatalytically reduce CO$_2$.[4] We obtain transmission UV-Vis (fig. 1) and mid-IR probe spectra after photo-excitation with subpicosecond time resolution. We find that the photo-excited hole resides on the amino group of NH$_2$-MIL-125. To efficiently utilize these holes in a photocatalytic reaction, they need to be transferred efficiently to species inside the pore cages. We included a molecule that mimics the tyrosine-histidine pair that shuttles holes to the oxygen evolution centre in natural photosynthesis inside the pores.[5] We observed that the charge transfer to this phenolic molecule is much faster (< 200 fs) than charge recombination (see fig. 1). This shows that fast and efficient charge transfer from metal-organic frameworks to adsorbed species is possible. The next step is to include an oxidative catalytic site, and to optimize hole transfer from the phenolic shuttle towards the catalytic centre.

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KN - 5

Monitoring of catalytic processes in liquid phase by combined *in situ* ATR-IR, UV-vis, and Raman spectroscopy - benefit and challenges

Ursula Bentrup
Leibniz-Institut für Katalyse e. V. an der Universität Rostock (LIKAT), Germany
ursula.bentrup@catalysis.de

Introduction

In situ spectroscopy is the only approach to derive reliable information on the mode of catalyst action and reaction mechanisms as well as on structure-reactivity relationships in catalysis [1]. Especially in heterogeneous catalysis, the application of a variety of *in situ* methods has gained a lively development during the last two decades. But also in homogeneous catalysis, *in situ* characterization methods are increasingly applied [2]. Referring to the use of vibrational and optical spectroscopic methods it can be stated that each method provides specific information and has its distinct advantages and disadvantages. Therefore, the coupling of spectroscopic methods offers a new perspective for getting a more complete picture due to the increased amount of incoming information and, thus, enables deeper insights into the relevant reaction, knowledge concerning the specific catalyst mode of action and impact of possible solvent interactions. In this respect, it is the primary objective of this contribution to demonstrate the variability of *in situ* spectroscopic methods regarding investigation of mechanistic aspects in homogeneously catalyzed reactions.

Results and discussion

The application of *in situ* spectroscopic methods (ATR-IR, Raman, and UV-vis) as well as the benefit of their coupling for the real-time monitoring of homogeneously catalyzed reactions is exemplarily demonstrated by means of four selected examples of use. Thus, the different mode of catalyst action is demonstrated on two exemplary reactions in which imides and amides are selectively reduced by phenylsilanes. It could be proved by combined *in situ* ATR-IR and UV-vis spectroscopy that in one reaction the silane and in the other reaction the carbonyl group of the amide is activated by the respective catalyst.

The benefit of method coupling is also demonstrated with the example of the Fe-catalyzed formic acid decomposition. Based on the specific information provided by each method, the catalytically active intermediate iron complex could be identified and the influence of chloride admixture on this complex formation and catalyst deactivation could be elucidated. Furthermore, it has been shown that the solvent is involved in complex formation and interacts with the reactant.

By means of Lewis acid mediated cyclization reactions it is demonstrated that the reactant activation proceeds in a different way with $AlCl_3$ on the one hand and $TiCl_4$ on the other. Additionally, it could be shown that crystallized and structurally characterized potential intermediates are not ever the real intermediates existing in solution under reaction conditions which nicely demonstrates the benefit of *in situ* spectroscopic studies enabling the real-time detection of intermediates.

In the photochemical rhodium catalyzed octane dehydrogenation *in situ* ATR-IR and UV-vis spectroscopy were successfully applied to elucidate the early stages of active catalyst formation. Thus, different intermediate complexes were detected and characterized supported by accompanied DFT calculations.

In summary, it is demonstrated that *in situ* vibrational and optical spectroscopy offers a great potential for the real-time monitoring of various types of reactions in liquid phase, for mechanistic studies as well as process control and kinetics which is a precondition for the development of tailored catalysts and optimized reaction conditions. Specific problems arising from method coupling will also be addressed.

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KN - 6

In situ MAS NMR technique for the unravel mechanisms of hydrothermal synthesis of solids

Yu. G. Kolyagin, I.A. Kasyanov, I.I. Ivanova

Chemistry Department, Lomonosov Moscow State University, Moscow, Russia, iiivanova@phys.chem.msu.ru

Hydrothermal synthesis is the main synthetic route leading to wide variety of materials such as zeolites, zeotypes, mesoporous and micro-mesoporous materials, hybrid inorganic-organic frameworks and other types of solids used for adsorption, catalysis, separation and etc. The improvement of existing materials and rational design of novel ones require the profound understanding of the mechanism of their synthesis. This information can be best obtained by *in situ* techniques, among which MAS NMR technique is one of the most informative, since it can follow the fate of various nuclei both in solution and in solid state. However, the direct application of MAS NMR, requiring fast sample spinning, for the investigation of hydrothermal synthesis *in situ* is strongly impeded by the conditions of this procedure: aggressive media, high pressure and temperature, and therefore is limited to either *ex situ* investigations of interrupted synthesis or *in situ* investigations at atmospheric pressure. Here we report on the development of specially constructed autoclave-type MAS NMR cell, which can be used in standard MAS NMR set-up for the investigation of hydrothermal synthesis *in situ* in the range of pH from 1 to 14, under elevated pressures up to 15 bars and temperatures up to 473 K.

The capabilities of the techniques have been verified on the hydrothermal synthesis of zeolites and aluminophospahates. The synthesis of BEA zeolite was studied at 140 °C using ^{1}H, ^{27}Al and ^{29}Si MAS NMR; the duration of experiments was 60-80 hours; spectra were recorded every 4 hours. In the case of VPI-5/AlPO-11 materials, the synthesis was followed at 100 – 190 °C for 60 hours using ^{1}H, ^{27}Al and ^{31}P MAS NMR, spectra being recorded every 10 – 60 minutes. The results obtained showed that the application of *in situ* MAS NMR approach provides unique information on the dynamics of various nuclei in reagents, intermediates and final products directly during the hydrothermal synthesis. It was found out that the spectral data for ^{1}H nuclei allow to follow the changes in pH and to study the kinetics of organic templates' transformations. At the same time, ^{27}Al, ^{29}Si and ^{31}P MAS NMR permits detecting various mobile and rigid inorganic species, gives insight into the formation of intermediate unstable phases, including protozeolitic phases, and allows to follow their transformation into solid zeolitic structures. It has been demonstrated that the spectral data give insight into the mechanism of the main steps of synthesis, including, gel formation, gel aging, crystal nucleation, growth and recrystallation; provide information on the kinetics of each reaction step; enable detection intermediate species stable only under hydrothermal conditions. The technique can be used without interrupting the synthesis and perturbing the crystallization process, it reduces the time and minimizes the amount of sample required for mechanistic studies by several orders of magnitude and allows for isotopic labeling of specific nuclei.

The comparison of the results of *in situ* MAS NMR experiments with *ex situ* studies performed using XRD, SEM, TEM, IR and adsorption techniques outlined that the kinetic parameters obtained using both approaches are in good agreement and pointed to full identity in structure and morphology of final products. The main benefit of the *ex situ* approach is the possibility to apply the whole complex of modern physicochemical techniques, which allows to obtain comprehensive information on the structure and properties of stable intermediate products. The *in situ* MAS NMR approach makes it possible to follow the nuclei dynamics directly during the synthesis and to get additional information about the unstable intermediate products. Combination of these two approaches will lead to fast progress in understanding the mechanisms of synthesis of different solids and therefore will facilitate the development of novel advanced materials.

The authors thank the Russian Science Foundation for the financial support (grant 14-23-00094).

ORAL PRESENTATIONS

O1 - 1

In operando DRIFTS/MS studies on CO_2 reduction over Pd/γ-Al_2O_3 catalysts

Xiang Wang[1], Ja Hun Kwak[2] and János Szanyi[1]*

[1]Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA, USA

[2]Department of Chemical Engineering, UNIST, Ulsan, Korea

*janos.szanyi@pnnl.gov

In order to develop new, highly efficient catalyst for the reduction of CO_2 it is critical to understand the mechanistic details of the reaction. Recently we have shown that transition metals (Pd, Ru) supported on oxide surfaces (γ-Al_2O_3) exhibit high catalytic activities with selectivities strongly depending on the metal dispersion. At very high (atomic) dispersion these metals produce primarily CO, while at low dispersion (large metal clusters) the dominant product is CH_4. We have also shown that efficient CO_2 reduction catalysts need to be bifunctional: it has to bind (activate) both CO_2 and H_2. Here we report on the results of our DRIFTS/MS study on the reduction of CO_2 over 0.5 and 5% Pd/γ-Al_2O_3 catalysts. We investigated the formation and subsequent reactions of carbonates and bicarbonates in their reactions with H_2. We observed the ready formation of bicarbonates (and carbonates) on the alumina support upon exposure of the catalysts to CO_2. Bicarbonates were stable surface species even at elevated temperatures. Switching the gas flow from CO_2 to H_2 resulted in the immediate appearance of Pd-bound, adsorbed CO, and the gradual formation of surface formates, and the concomitant disappearance of bicarbonates. The formation of CO was transient, as it was further converted to CH_4. Exposure of an H_2-reduced Pd/γ-Al_2O_3 catalyst to CO_2+H_2 gas mixture produced surface bicarbonates very fast, while formates developed gradually (Fig. 1). With the appearance of bicarbonates+formates, adsorbed CO was observed, and CH_4 was detected in the mass spectrum. Switching the gas flow back to H_2/He resulted in the fast disappearance of bicarbonates, and the slow decrease in intensity of the formate IR bands. The results of these studies suggest that over these catalysts, and under the conditions applied here, both bicarbonates and formates play critical roles in the CO_2 reduction mechanisms. Further details of the reaction mechanism will be obtained in our ongoing SSITKA experiments, and will be discussed in the presentation.

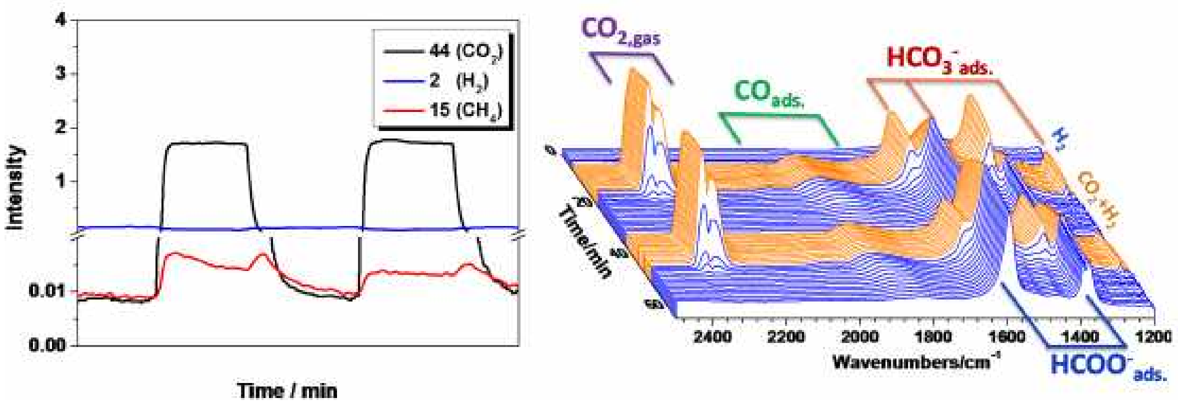


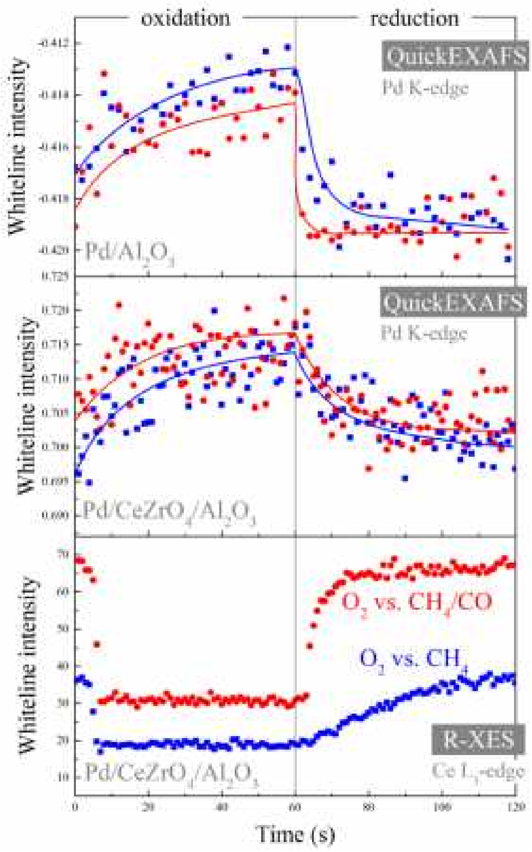
Figure 1. Intensities of selected mass fragments as a function of time-on-stream (left panel) during gas switching (shown in the IR spectra; right panel) over a 0.5% Pd/γ-Al_2O_3 catalyst at 425 K.

O1 - 2

Influence of CO on methane oxidation of TWC by combined spectroscopic and modulation approach

V. Marchionni (valentina.marchionni@psi.ch), O. V. Safonova, M. Nachtegaal, O. Kröcher, D. Ferri
Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Natural gas, which is mostly composed of methane (CH_4), is an abundant resource, with largest world-wide reserves than crude oil. Together with the increasing production of biogas, it is receiving renewed interest as clean alternative fuel to gasoline and diesel. However, CH_4 is a potent greenhouse gas; therefore, catalytic after-treatment of the exhaust gases is necessary to reduce the emission of unburned CH_4. Typically, palladium based three-way catalysts (TWC) are employed but only few studies have addressed the mechanistic details of CH_4 abatement of TWC, which is CH_4 oxidation in the presence of other pollutants such as CO and NO_x.



The aim of this study is to describe the influence of CO on CH_4 oxidation under pulsed reaction conditions simulating the operation of a TWC. For this purpose different spectroscopic methods are combined; in order to better compare the results a single cell, specifically conceived for operando experiments[1], and a single set up have been designed. Modulation excitation spectroscopy (MES) and phase sensitive detection (PSD) are also exploited to enhance the sensitivity towards structural changes. Modulation experiments were performed on 1.6 wt.% Pd/Al_2O_3 and 1.6 wt.% Pd/CeO_2-ZrO_2/Al_2O_3 at 320ºC while synchronously collecting time-resolved spectra. The Pd K-edge Quick-EXAFS results show that the catalyst exhibits mainly variations of the oxidation state around the reduced state, since prior to the modulation experiments the samples are subjected to in situ degreening in stoichiometric conditions. Pd is partially re-oxidized during the O_2 pulse, and completely reduced in the subsequent rich pulse; on Pd/Al_2O_3 the reduction of the noble metal is faster than its re-oxidation. The effect of ceria is to delay Pd reduction and to decrease its extent thus improving the catalytic activity. Resonant X-ray emission spectroscopy (R-XES) at the Ce L_{III}-edge was used to explicitly follow the oxidation state of the O_2 storage component. R-XES data reveal that the ceria is slowly reduced and immediately re-oxidized when changing reaction atmosphere in agreement with its storage function. The gaseous products analyzed by online mass spectrometry provided the information on the catalytic activity. In the presence of oxidized noble metal CH_4 oxidation was observed; under rich condition CH_4 decomposition or reforming takes place producing H_2. CO inhibits Pd re-oxidation and decreases methane conversion; as a result, the water gas shift reaction plays an important role under rich conditions. Ceria is greatly reduced in presence of CO and mitigates the reduction of Pd due to CO. The present study should contribute shading light on the elementary steps of the complex reaction network involved in the three-way catalysis of CH_4 abatement in order to support ongoing catalyst development.

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O1 - 3

Probing Reactive Platinum Sites in UiO-67 Zirconium Metal-organic Frameworks with in situ and operando Pt L3-edge XAFS

Sigurd Øien,[1] Giovanni Agostini,[2,3] Stian Svelle,[1] Elisa Borfecchia,[2] Kirill A. Lomachenko,[2,4] Lorenzo Mino,[2]Erik Gallo,[2,3]Silvia Bordiga,[2] Unni Olsbye,[1] Karl Petter Lillerud,[1] Carlo Lamberti[4,5,*]

[1] inGAP Centre for Research Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway.
[2] Department of Chemistry, NIS and INSTM Reference Centers, University of Torino, Via Quarello 15, I-10135, Torino, Italy.
[3] European Synchrotron Radiation Facility (ESRF), 6 Rue Jules Horowitz, BP 220 38043, Grenoble Cedex 9, France.
[4] Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia.
[5] Department of Chemistry, CrisDi Centre for crystallography, University of Torino, Via Giuria 7, I-10125 Torino, Italy.

carlo.lamberti@unito.it

The structure of the families of isostructural UiO-66, 67 and 68 MOFs was solved combining XRPD data and Zr K-edge data collected at the ESRF [1-3]. In this work we present functionalization of UiO-67 MOFs with bpydcPt^{II}Cl$_2$ and bpydcPt^{IV}Cl$_4$ coordination complexes acting as linkers in the MOF framework. XRPD and Pt L$_3$-EXAFS (I811, MAX-II, Lund) studies prove that we obtained the target structure on both long-range (ordered MOF framework) and short-range (local environment of Pt sites) scales. Pt L$_3$ valence-to-core RIXS (ID26, ESRF) support previous findings. UiO-67-Pt MOFs show a high accessibility and reactivity to molecules of small- (H$_2$), medium- (Br$_2$) and large-size (thiol). H$_2$-TPR treatments have been followed under *operando* condition by EXAFS, showing that Cl ligands can be selectively removed as HCl molecules in the 600-700 K temperature range, resulting in bpydcPt^{0}complexes linked to the MOF framework. This result has been obtained after sophisticated parametric refinement, where all EXAFS spectra collected in the 300-750 K range have been refined together adopting the Einstein model for the Pt–N and Pt–Cl Debye-Waller factors. The large pore size of UiO-67 allows for Cl to S ligand exchange reactions with bulky ligands such as toluene-3,4-dithiol. Framework bpydcPt^{II}Cl$_2$ complexes can also be oxidized at room temperature to bpydcPt^{IV}Br$_4$ with strong oxidation agents such as Br$_2$ from the liquid phase (oxidation path in). XANES spectroscopy was used to monitor the changes in the Pt oxidation state along the observed reactions, while EXAFS monitored the ligand exchange in the first coordination shell of Pt. Platinum bipyridine functionalized UiO-67 displays the same exceptional stability as the parent material, as testified on both long and local range by in situ XRPD and Pt L$_3$-edge EXAFS data collections.

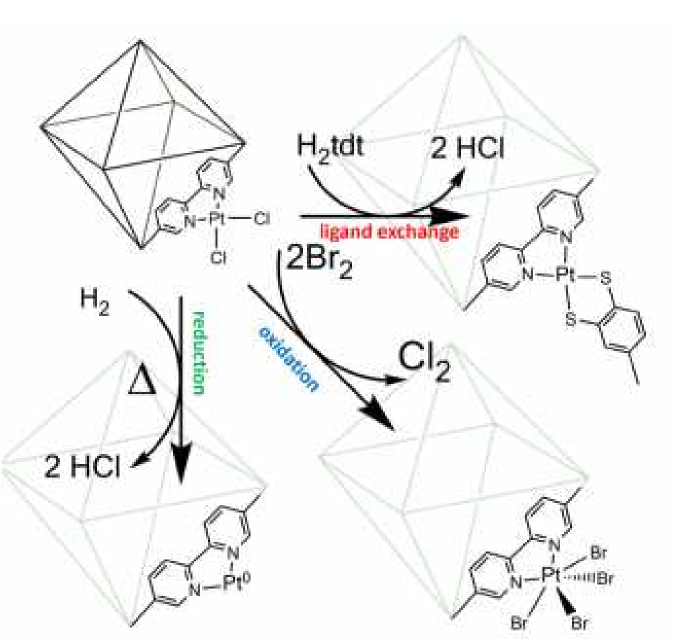

Figure 1: Schematic representation of the reactivity of Pt^{II} species in functionalized UiO-67-Pt MOFs highlighted in the EXAFS and XANES study reported in this work. The sketched square bi-pyramid represents the octahedral large cavity of UiO-67 (~ 16 Å in diagonal).

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O1 - 4

Combined IR spectroscopy and kinetic modeling of NO_x storage and NO oxidation on Fe-BEA SCR catalyst

Stavros Skarlis[1,2], David Berthout[1], André Nicolle[1], Christophe Dujardin[2], Pascal Granger[2]
[1] IFP Energies Nouvelles, 1 et 4 avenue de Bois-Préau 92852 Rueil-Malmaison Cedex, France
[2] UCCS, Université Lille1 Sciences et Technologies, ENSCL, 65 avenue Paul Langevin, 59650 Villeneuve d'Ascq, France
* christophe.dujardin@ensc-lille.fr

Introduction and Objectives

The selective catalytic reduction of nitrogen oxides (NO_x) through urea or ammonia is currently recognized as the predominant technology for NO_x emissions control of mobile diesel engines [1]. Iron exchanged BEA zeolites are promising candidates for SCR applications under lean conditions. The reduction of NO_x over Fe-zeolites is performed through a complex reactions network, which involves disproportionation of NO_2 towards nitrite/nitrate adspecies and subsequent interactions of the latter with chemisorbed ammonia, yielding N_2 and H_2O. A multi-site kinetic model for NO_x adsorption /desorption and NO oxidation on Fe-BEA was developed based on in-situ IR spectroscopic measurements [2].

Materials and Methods

A 1.75 wt.% Fe-BEA catalyst was synthesized from H-BEA zeolite (Si/Al = 11.8), applying wet ion exchange. Fe-BEA sample was calcined in air at 500°C. Self-supported wafers of 2 cm^2 (10 mg) was placed in a single wafer reactor. NO_x surface species were in-situ characterized by using a Thermo 6700 and a Thermo 380 FTIR spectrometer for the analysis of adsorbed species and gas phase respectively. Zero-dimensional models of a single wafer considered as a single continuous stirred tank was developed and implemented into the simulation environment LMS.Imagine.Lab AMESim [3].

Results and Discussion

NO and NO_2 adsorption, along with NO/O_2 co-adsorption were investigated on H- and Fe-BEA samples, in order to elucidate the contribution of acidic and iron sites. Simultaneously an in-situ IR spectroscopic study allowed to characterize a variety of NO_x adspecies, including iron nitrosyls, nitrosium anions, nitrites as well as aluminum and iron based nitrates.

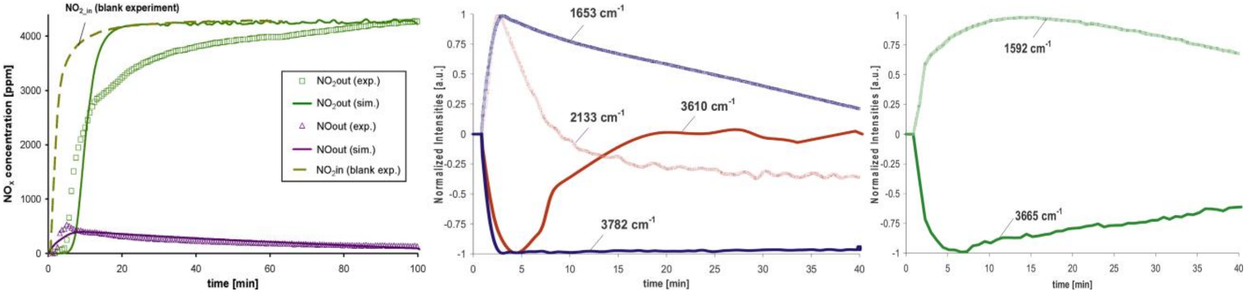

Fig. NO_x concentrations and evolution of adsorbed species during NO_2 storage on Fe-BEA at 30◦C (He+0.45% NO_2+8% O_2)

Surface nitrites, nitrates, as well as gaseous NO evolution were observed upon NO_2 adsorption and disproportionation. The latter reaction occurred on cationic OH^+ and Al and Fe sites located in neighboring positions. Nitrites species were predominant up to 100°C, whereas NO_3 were found to be stable at higher ones. NO_3 formation on metallic sites was modeled by adopting a global Fe site, which was assigned to either a pair of two isolated and/or binuclear Fe^{3+} species or a pair of Fe^{3+}/OH^+. NO oxidation over the Fe-BEA catalyst was studied through a stepwise TPD experiment. Zeolitic aluminum and Fe^{3+}–O were found to be the respective active sites in the case of NO oxidation. The model involving five surface sites can be calibrated in order to correctly simulate experimental data for Fe-zeolites taking into account structural properties of the catalyst.

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O1 - 5

Elucidating structural changes and redox behavior of model molybdate catalysts under ammoxidation conditions: An *operando* Raman spectroscopic study

Jana Engeldinger, Ursula Bentrup, Achim Fischer*, Horst-Werner Zanthoff*
Leibniz-Institut für Katalyse e. V. an der Universität Rostock (LIKAT), Germany
*Evonik Industries AG, Hanau, Germany
jana.engeldinger@catalysis.de

Introduction

Selective catalytic oxidation and ammoxidation of hydrocarbons are important processes in chemical industry. Amongst those the ammoxidation of propene to acrylonitrile has a foremost commercial position. Multicomponent molybdate catalysts are used for this reaction containing mainly bismuth, iron and cobalt molybdate [1]. Although, the function of the different molybdate phases and the reaction mechanism are known in principle, their specific interaction, termed as synergetic effect, is not fully understood. However, *in situ* spectroscopic studies enabling a deeper insight into structure reactivity relationships of such catalyst systems are rare. Because Raman spectroscopy has been proved to be a powerful tool for characterizing molybdate structures [2], it was the aim of this work to study structural changes and redox behavior of the different molybdate phases in model catalyst systems under ammoxidation conditions using *operando* Raman microspectroscopy.

Experimental

For this purpose, a special setup was established enabling Raman spectroscopic investigations under reaction-like conditions with simultaneous product analytics by mass spectrometry (MS). Model molybdate catalysts containing Bi, Fe, and Co were used to study the influence of different reactive gas mixtures (NH_3/He, NH_3/propene/He, O_2/He, NH_3/propene/O_2/He) on catalyst performance and structural changes of the molybdate phases at selected temperatures.

Results and discussion

Changes of single molybdate phases proceeding under different reaction conditions are detectable by shifting of characteristic Raman bands as well as changes of their relative intensity as exemplarily shown in Figure 1 for different binary and ternary molybdate systems. During exposure of Fe/Co and Fe/Bi molybdate to NH_3/propene/O_2/He feed the characteristic band of $Fe_2Mo_3O_{12}$ (776 cm^{-1}) vanishes, and a band related to $FeMoO_4$ (920 cm^{-1}) appears. This effect is much lower pronounced in the Fe/Bi/Co molybdate. Simultaneous product analysis shows, that the Fe/Bi/Co molybdate system works more selectively than the binary systems as indicated by a distinct lower CO_2 formation. Furthermore, it could be evidenced that different compositions of the ternary systems influences the redox behavior as well as the acrylonitrile formation.

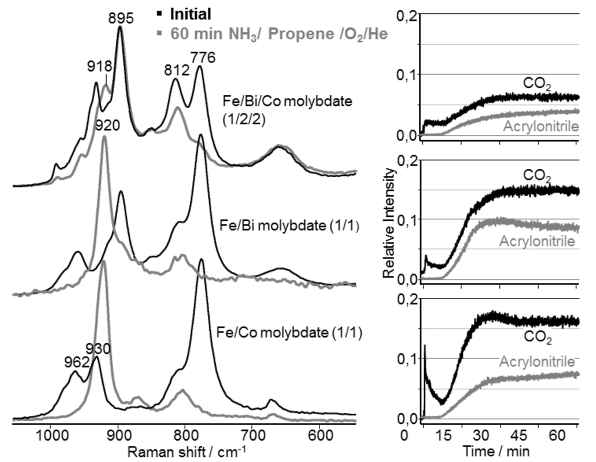

Figure 1. Raman spectra of Fe/Co, Fe/Bi and Fe/Bi/Co molybdate systems obtained after 60 min exposure to NH_3/Propene/O_2/He at 424°C and corresponding MS profiles from acrylonitrile and CO_2.

The redox behavior was studied by performing cycles of reduction (NH_3/propene/He) and reoxidation (O_2/He). Thus, it was found that only in the presence of Bi molybdate a nearly complete reoxidation takes place, whereas $CoMoO_4$ inhibits the reoxidation of Fe(II) by stabilization the latter in a $Fe_xCo_{1-x}MoO_4$ phase. Obviously, $CoMoO_4$ and $Bi_2Mo_3O_{12}$ influence the redox behavior of $Fe_2Mo_3O_{12}$ in a different manner, whereas the presence of $Bi_2Mo_3O_{12}$ seems to be important for optimizing the Fe(II)/Fe(III) redox cycle.

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O1 - 6

Operando spatially- and time-resolved XAS and valence-to-core XES to study the mechanism of the NH_3-SCR over Fe- and Cu-zeolites

D.E. Doronkin, T. Günter, H.W.P. Carvalho, A. Boubnov, M. Casapu, J-.D. Grunwaldt*
Karlsruhe Institute of Technology, Kaiserstr. 12, 76131 Karlsruhe, Germany
presenting author: dmitry.doronkin@kit.edu
* grunwaldt@kit.edu

In the last years, Fe- and Cu-exchanged zeolites have received significant attention due to their superior performance and thermal stability as compared to the widely used and studied V_2O_5-WO_3/TiO_2 for selective catalytic reduction (SCR) of NOx with NH_3 [1]. A detailed understanding of the structural parameters is still essential for future high performance and enhanced durability. This will allow further tuning of the preparation methods and rational design of improved catalysts.

Among the different characterization methods, X-ray absorption spectroscopy (XAS) is one of the few techniques which can be applied under realistic reaction conditions without altering the process dynamics. Important information such as oxidation state, coordination geometry, type and number of nearest neighbors or structural changes due to interaction with reactants, can be derived by monitoring the changes occurring in the pre-edge, edge and extended X-ray absorption fine structure (EXAFS) of an XAS spectrum [2]. Complementary to looking at the metal site with XAS, interactions with reactants can be monitored with valence-to-core (V2C) XES, allowing also to distinguish between atoms with close atomic numbers, like O and N [2, 3].

Here we report results of a spatially- and time-resolved operando XAS study on various Fe- and Cu-zeolite catalysts and XES studies of Fe-ZSM-5 and Cu-SSZ-13 catalysts during SCR of NOx with NH_3 [3,4]. For this purpose, well defined Fe- and Cu-zeolites with high metal dispersion were prepared and compared to commercial samples. The catalysts were pre-characterized by XRD, BET surface area, AAS and UV-Vis spectroscopy. For the operando XAS/XES studies, a quartz capillary microreactor which allows on-line recording of the catalytic performance was used; the catalytic performance was compared to lab reactors. The catalyst bed was heated by a hot gas blower between 185 – 550 °C while dosing a gas stream containing 0 – 1000 ppm NO, 0-1000 NO_2, 0 – 1200 ppm NH_3, 5% O_2, ~1.5% H_2O in He. The spatially- and time-resolved XAS measurements were carried at the SuperXAS beamline (SLS, Swiss Light Source) and the XES data were acquired at the High-Brilliance X-ray Spectroscopy beamline ID26 (ESRF, European Synchrotron Radiation Facility). Simulated XES-spectra were calculated by DFT for comparison with the obtained data.

Strong gradients of Fe and Cu oxidation state and a decrease of coordination number of the studied metal atom have been observed along the catalyst bed for processes involving NOx and NH_3. This indicates a reaction of NOx and NH_3 adsorbed on Fe^{3+} ($Cu^{2+)}$ leaving Fe^{2+} (Cu^{+}) with a lower coordination number [4]. Reoxidation of metal sites by oxygen is suggested to be the rate-limiting step of the NH_3-SCR which is strongly inhibited by NH_3 at lower temperatures for Fe-zeolites (in contrast to Cu-zeolites). Concurrently, it was observed that water inhibits the SCR reaction by coordination to the Fe-active center. This is further supported by application of V2C-XES. This method provided evidences of the adsorption of NH_3 and NO in the presence of water and in combination with DFT-calculations allowed the identification of potential reaction intermediates for the SCR process on Fe-ZSM-5 zeolite [3]. V2C-XES of the Cu-SSZ-13 zeolite revealed a mechanism with different adsorbed intermediate species as they were found for Fe-ZSM-5. The data significantly extend the understanding of SCR-catalysts and demonstrates the potential of new operando photon-in/photon-out techniques.

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O1 - 7

Probing active sites in supported Ni catalysts during butene oligomerization by operando EPR and XAS spectroscopy under elevated pressure

J. Rabeah[1], J. Radnik[1], V. Briois[2], D. Maschmeyer[3] and A. Brückner[1]

[1]Leibniz Institute for Catalysis, Albert-Einstein-Str. 29a, 18059 Rostock (Germany), [2]Ligne SAMBA, Synchrotron SOLEIL, L'Orme des Merisiers, BP48, Saint-Aubin 91192 Gif-sur Yvette (France), [3]Evonik Industries AG, Paul-Baumann-Str. 1, 45772 Marl (Germany)

Industrially important linear C_8-C_{12} olefins are produced by oligomerization of butenes (raffinate III) in the OCTOL^{TM} process at 25-35 bar using supported Ni/SiO_2-Al_2O_3 even with very low Ni contents (< 1 %). This suggested that active sites are single Ni^{n+} species. Indeed we have detected single Ni^+ in used highly active Ni/SiO_2-Al_2O_3 catalysts by EPR at 77 K after removal from the reactor.[1] However, a doubtless relation to reactivity could not be established at that time due to the limited reproducibility of this transfer procedure. Moreover, the possible presence of single Ni^{2+} species, being EPR silent at 77 K, could not be confirmed. Therefore, we have developed an advanced operando EPR setup (Fig. 1) that allows detection of Ni^+ in dependence on the performance of the catalyst without removing it from the reactor by temporarily quenching the system to 100 K. Moreover, in situ XANES and EXAFS measurements were performed under flowing raffinate III at ≈12 bar. To the best of our knowledge, these are currently the only examples of operando EPR and XAS under elevated pressure in catalytic liquid/solid systems.

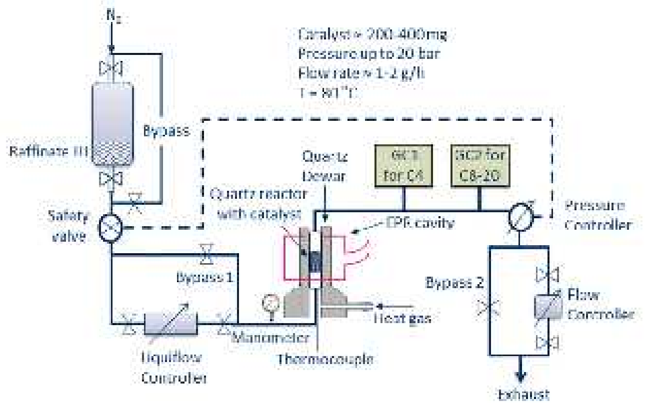

Fig. 1. Operando-EPR setup

Operando EPR revealed different single Ni^+ species stabilized by Brønsted sites the vicinity of Si and Al in fresh 0.4-0.6 % Ni/SiO_2-Al_2O_3 which add butene during reaction, giving rise to an EPR signal characteristic for Ni^+-(butene)$_n$ complexes. This signal decreased strongly during reaction without loss of catalytic activity, suggesting that the active site may contain EPR-silent Ni species.

In situ XAS measurements have shown that Ni^+ single sites in the fresh catalyst are oxidized in the presence of 12 bar raffinate III at room temperature to Ni^{2+} single sites. Upon heating to the reaction temperature of 353 K, an average Ni valence state between I and II is observed, suggesting the action of a Ni^{2+}/Ni^+ redox shuttle under reaction conditions, which is accompanied by a change in the Ni coordination number. No Ni-O-Ni or Ni-Ni interactions could be identified by EXAFS, suggesting that the EPR-silent Ni species under reaction conditions might be single Ni^{2+} but not a $Ni^{+}\cdots Ni^{+}$ dimer. It was also found that a sufficiently high raffinate pressure (≈12 bar) is required to prevent clustering of Ni single sites to Ni^0 particles during reaction, which was observed at a pressure of only 2 bar.

Based on combined operando EPR and XAS results, a possible reaction mechanism is proposed. Moreover, this study shows clearly that for deriving reliable results on structure-reactivity relationships, it is absolutely mandatory to perform spectroscopic characterization studies under relevant conditions, i. e. at high raffinate pressure and elevated temperature.

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O1 - 8

Mechanistic Implications for $V_2O_5/WO_3/TiO_2$ based NH_3-SCR catalysts; Redox properties and Lewis-Brønsted acid site interplay

Søren B. Rasmussen[1]*, Susanne Mossin[2], Marie Hvidberg Velk[2], Miguel Bañares[2,3,4], Philippe Bazin[4] and Marco Daturi[4]

1) Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark; 2) CSC, DTU-Chemistry, Technical University of Denmark, Kemitorvet, DK-2800 Kgs. Lyngby, Denmark; 3) ICP-CSIC, Consejo Superior de Investigaciones Cientificas, Calle Marie Curie 2, Cantoblanco, Spain; 4) LCS-ENSICAEN, Caen, France; *sobr@topsoe.dk

The literature within the DeNOx community has virtually exploded in the recent decade due to great progress by the discovery of the Fast SCR reaction and the rise of the iron and copper based zeolites. The mechanism for the conventional vanadium based NH_3-SCR catalyst was studied in detail in the 1985-2000, and great instrumental improvements for operando spectroscopy have been achieved since then. This work focuses on studying the classical system by operando EPR-Chemiluminisence and SSITKA IR-MS in order to relate mechanistic aspects of the vanadia based system to current literature mainly developed for zeolite based catalysts.

SSITKA results show that neither adsorbed ammonia (on Lewis acid sites) nor ammonium (on Brønsted acid sites) pathway for the SCR reaction can be discarded. Either both species are involved in the reaction mechanism or that the interchange between these two species is so fast that discrimination between them is impossible. EPR and Raman spectroscopy provide structural information to support that the redox site goes through V(V) and V(IV) intermediates, the latter being in significant amounts at low temperatures. Furthermore it is evident that the reduced V(IV) maintains its V=O nature and that the V(V) site includes both V=O and V-OH. Furthermore EPR spectroscopic results convincingly show that it is mainly NO, in the presence of NH_3, that reduces the vanadia site.

Acknowledgements: This project was supported by Spanish Ministry project CTQ2011-25517-MAP-IT, this project and MAB were also funded by “Chaire d’excellence” FEDER-Region Basse de Normandie (France). MAB thanks the Otto Mønsted Foundation Visiting Professor (Denmark) award. Carlsbergfondet is acknowledged for supporting the EPR instrument at DTU.

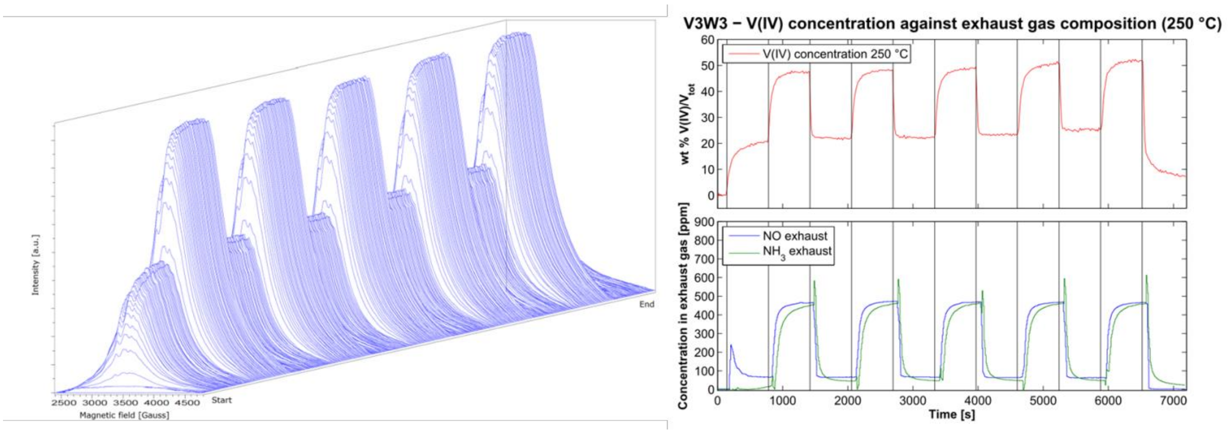

Figure 1. Operando EPR-chemiluminesence profile during SCR gas with and without oxygen (1000 ppm NH_3, NO, 0 or 5% O_2, ~N_2).

O1 - 9

Preferred form of presentation: oral – Scientific session: Reaction mechanisms (1)

$H_3PW_{12}O_{40}$ as catalyst for the gas phase dehydration of methanol: relating changes in the selectivity to dimethylether to the formation of coke thanks to *operando* Raman and UV-Visible characterization

J. Schnee*, E.M. Gaigneaux
Institute of Condensed Matter and Nanosciences (IMCN) – MOlecules Solids and reactiviTy (MOST) – Université catholique de Louvain. Croix du Sud 2, box L7.05.17 1348 Louvain-la-Neuve, Belgium
*josefine.schnee@uclouvain.be

Introduction and Objectives

Heteropolyacids (HPAs) are molecular clusters possessing a very high Brönsted acidity. They are widely used as acid catalysts. For gas phase reactions, the main issue in HPA-based catalysis is the deactivation due to the formation of carbonaceous deposits called "coke" [1]. We currently investigate the catalytic activity of $H_3PW_{12}O_{40}$ (HPW12), the most acidic Keggin-type HPA, in the gas phase dehydration of methanol to dimethylether (DME). DME is nowadays seen as one of the most important and promising renewable fuels for the future [2]. Herein, we demonstrate via *operando* Raman and UV-Visible characterization that changes in the selectivity to DME over $H_3PW_{12}O_{40}$ as catalyst are related to the amount of coke produced and to the latter's degree of disorganization.

Results and Discussion

In the here applied test conditions (800 mg HPW12, 10 vol.% methanol in N_2, 30 ml/min total flow), the conversion of methanol on HPW12 was of 5%, 65% and 90% at respectively 100°C, 150°C and 200°C. It remained then constant up to 350°C. The selectivity to DME was around 90% up to 200°C. From 200°C on, it dropped (85%, 70% and 40% at respectively 250°C, 300°C and 350°C), with methane, ethylene and propylene detected as byproducts. *Operando* UV-Visible spectra reveal an increase of absorption in the visible region as soon as the reaction was started, reflecting the rapid formation of dark-colored coke. Up to 200°C, the UV absorption edge of HPW12 remained visible ($O^{2-} \rightarrow W^{6+}$ charge transfer absorption bands at 250 nm and 350 nm). At 250-300-350°C however, when the selectivity to DME was dropping, the coke's absorption in the visible region reached its maximum and completely masked HPW12's UV absorption edge. On *operando* Raman spectra, the bands of polyaromatic coke became visible at 100°C: a D1 band at 1300-1450 cm^{-1} reflecting disorganized non-graphitic coke and a D2 band at 1600-1650 cm^{-1} reflecting less disorganized coke [3]. Up to 250°C, the D2 band was more intense than the D1 one. At 300°C, the relative intensity of the D1 one started to increase with time on stream. At 350°C, both bands had nearly equal intensities. The increase of relative intensity of the D1 band, reflecting an increase of the structural disorganization of coke, here occurs together with the production of methane which is the byproduct of reactions that increase the aromaticity of coke.

Conclusions

The *operando* Raman and UV-Visible spectra reflect the changes in the selectivity to DME obtained with HPW12. More precisely, a drop of selectivity to DME is associated to an increased production of coke (via UV-Vis) possessing an increased degree of disorganization (via Raman) and higher aromaticity (indicated by the production of methane).

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Monitoring the n-butanol formation from ethanol on hydroxyapatite by *operando* DRIFTS

M. Ben Osman[1], J. M. Krafft[1], T. Yoshioka[2], J. Kubo[2], G. Costentin[1]

[1] Laboratoire Réactivité de Surface UPMC-CNRS, 3 rue Galilée, 94200 Ivry sur Seine (France)
[2]Central Research Center, Sangi Co., Ltd., Fudoinno 2745-1, Kasukabe-shi, Saitama 344-0001, Japan
guylene.costentin@upmc.fr

Context and aim of the work The conversion of ethanol in n-butanol *via* the Guerbet reaction is of particular industrial interest, n-butanol being used as a solvent and as polymer raw materials. Whereas classical basic catalysts (alkaline earth oxide, hydrotalcites…) mainly lead to the formation of acetaldehyde from ethanol, originally, hydroxyapatites (HAp) allow to obtain high selectivities in *n*-butanol or its C≥4 derivatives,[1] probably due to atypical acid-base properties. However, yet, little is known about how HAp proceed at a molecular level.

From the composition ($Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$), PO_4^{3-} and OH^- groups could possibly act as weak basic sites, and Ca^{2+} cations and surface terminated PO-H could act as Lewis and BrØnsted acidic sites, respectively, as confirmed by previous IR studies performed under static conditions combining i) discrimination of bulk and surface signatures of $\nu_{O\text{-}H}$ vibrators by isotopic labelling [2] and adsorption of probe molecules [3]. The aim of the work was to identify i) what is the active acid-base pair responsible for the formation of n-butanol on HAp system, ii) what are the key parameters controlling the conversion and selectivities of the reaction.

Results and discussion Stoichiometric HAp samples (Ca/P=1.67) with different surface Ca^{2+} accessibility (evaluated by CO adsorption at 77K) were prepared by co-precipitation method [4].

The following four successive sequences were followed under *operando* conditions: 1) activation up to 623 K or to 873 K under He flow, 2) reaction 1 step (gas phase reaction at P_{atm} with a reaction temperature of 623 K, W/F=37g.h/$mol_{ethanol}$) was followed for one hour, 3) then the reactant flow was switched to pure He flow maintaining the temperature at 623K, 4) a second reaction step under the same conditions. The IR bands characteristic of the HAp surface can be identified at the end of the activation. During the first reaction sequence, while only a minor amount of acetaldehyde is detected and n-butanol is formed as the main product in the gas phase, the perturbation of both PO-H and O-H surface vibrators is immediately observed. Under He flow, the adsorbed reactant and products are rapidly released in gas phase concomitantly with the partial or complete release of the surface O-H vibrators, depending on the catalysts and on the thermal activation conditions. At reverse, the PO-H vibrators are progressively fully poisoned in relation with the increasing formation of polymeric adsorbates. Switching back to reactant flow (second reaction step) results in the partial or total recovering of the initial conversion level, in relation with the release of the surface OH groups. Regardless of the conversion level, the selectivities are always greatly modified compared to the first reaction sequence: due to the poisoning of surface PO-H, the OH groups that are once more perturbated are not any more sufficient to form *n*-butanol and the acetaldehyde is now obtained as the main product. Moreover, varying the surface Ca^{2+} accessibility, it is shown that surface Ca^{2+} cations are detrimental to the conversion level and favor the acetaldehyde formation. Together with the involvement of basic surface OH groups which amount and availability control the conversion levels, the nature of the acidic sites involved in the active acid-base pair controls the product distribution. Finally, it is concluded that the good performances of the HAp system to form n-butanol can be ascribed to the involvement of an atypical acid-base pair, PO-H-OH.

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O2 - 2

Operando DRIFTS Applied to Fischer-Tropsch Synthesis and CO Methanation Catalysis Systems: An IR/Kinetic Correlation

H. Li[1], **F.Maugé**[1], **F.C. Meunier**[1,2] **A. Travert**[1]
1 Laboratoire de Catalyse et Spectrochimie, CNRS-ENSICAEN, University of Caen, 14050 Caen, France
2 IRCELYON, CNRS - Université Lyon 1, 2 avenue Albert Einstein, F-69626 Villeurbanne, France.

Synthesis gas obtained from biomass gasification (i.e. biosyngas, a mixture of CO, CO_2, H_2 and impurities) is pertaining to the wider societal agendas not only as a sustainable source of fuels and chemicals, but also as a mean for dealing with global warming challenge. A major barrier in the commercialization of biomass gasification is the presence of bio-impurities such as NH_3, HCl, H_2S and tars in the gas products that are detrimental to downstream processes. Two important downstream processes are the conversion of syngas through (i) methanation (MET) for synthetic natural gas production and (ii) Fischer-Tropsch synthesis (FTS) for higher hydrocarbons. The exact role and effects of biomass-derived impurities on the catalysts used for these reactions are poorly known. In this work, the effect of three N-containing compounds (i.e. acetonitrile, ammonia and nitric oxide, introduced at various concentrations 100-30000ppm) on FTS (using a cobalt-based catalyst) and MET (using a nickel-based catalyst) was investigated by operando diffuse reflectance FT-IR spectroscopy (DRIFTS) at atmospheric pressure.

It was found that these compounds all had strong negative effect on the activity, as well as on the alkane/alkene selectivity in FTS. Nevertheless, the deactivation effects were partially irreversible for both MET and FTS, leading to about 20-30% decrease of conversion in FTS. The irreversible part of deactivation was independent to the concentration of introduction of N-compounds. By contrast, the reversible part of deactivation was proportional to the introduction concentration. More importantly, the analysis of catalyst surface by DRIFTS, showed that the deactivation was always accompanied by a significant attenuation of the band characteristic of carbonyl species (2108-1679cm^{-1}), especially for the linear carbonyl (2056cm^{-1}) which also showed an obvious shift to high wavenumber. The experiments carried out at various poison partial pressures allowed us to distinguish the poisoning effect from the natural aging of catalyst and to establish a rate equation accounting for the three deactivation mechanisms evidenced so far (natural ageing, irreversible poisoning and reversible poisoning).

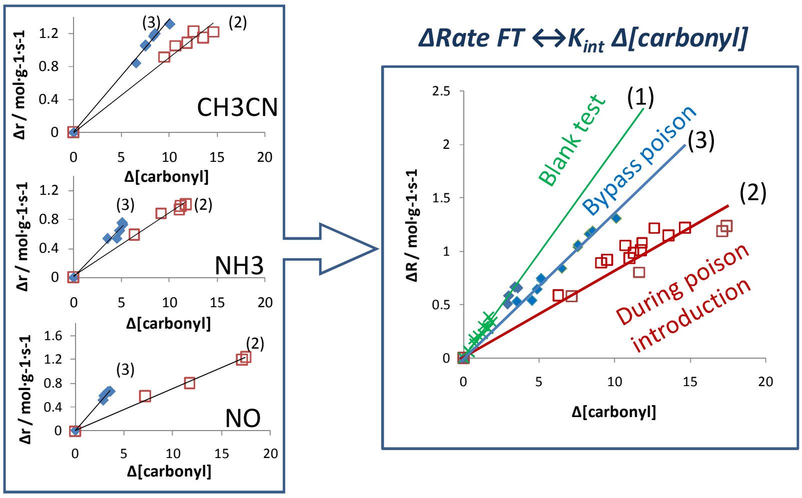

Figure 1: Correlation between extent of poisoning (rate loss) and surface carbonyl perturbation induced by N-compounds.
[X : CO+H_2 (1); ☐ CO+H_2+poison (2); ■ CO+H_2 (poison stop) (3)

Finally a linear correlation between the rate loss (Δr) and the surface carbonyl perturbation (Δ[carbonyl]) was obtained. This proved that under typical FTS or MET conditions, operando DRIFTS met the accuracy requirements for qualitative or quantitative kinetic study.

Acknowledgements: This work was supported by the French National Agency for Research, project BioSyngOp, ANR-11-BS07-026.

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Presenting Author : Haoguang Li – haoguang.li@ensicaen.fr

O2 - 3

Operando IR Study on Surface Reactions during Hydrodeoxygenation of Anisole over Pt/H-BEA

Guo Shiou Foo,[1] Allyson Rogers,[1,2] Matthew M. Yung,[2] Carsten Sievers[1]
[1] Georgia Institute of Technology, School of Chemical & Biomolecular Engineering, Atlanta, GA, USA
[2] National Renewable Energy Laboratory, Golden, CO, USA
carsten.sievers@chbe.gatech.edu

Catalytic upgrading of bio-oils is a key technology for biorefineries. It provides the much needed link between the production of bio-oils by pyrolysis or liquefaction and the synthesis of chemicals and biofuels that can be blended into the existing gasoline pool. Hydrodeoxygenation (HDO) is an attractive approach to achieve this goal by replacing oxygen containing functional groups with hydrogen forming water as the only by-product. The process provides oils with reduced reactivity and corrosiveness and increases the energy density of the product. Nobel metal containing zeolites show considerable HDO activity, but deactivation by coking remains an issue. Further insight into the surface reaction paths for HDO and coke formation is needed optimize the composition of these catalysts as well as the conditions for the HDO process and regeneration procedures. Here, we present the first report on a time-resolved operando IR spectroscopic study on relevant surface species and reaction paths.

The catalysts (H-BEA and 1.3 wt% Pt/H-BEA) were pressed into self-supported wafers that were mounted in a transmission IR cell (Figure 1). The cell was designed for experiments at elevated temperature and atmospheric pressure, and its volume was minimized to provide plug-flow behavior [1]. The feed consisted of a hydrogen flow of 80 sccm·min^{-1} that was passed through an evaporator with anisole. Reactions were performed at 400 °C, and products were analyzed using a GC-FID and a mass spectrometer.

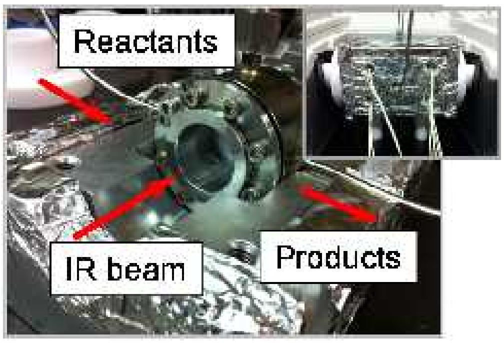

Figure 1: Transmission IR cell.

The initial conversion over both catalysts was 100%, but it started to decrease immediately over H-BEA (Figure 2). In contrast, complete conversion of anisole was observed over Pt/H-BEA for ca. 3 h. Several important changes of surface species on this catalyst were observed, before the conversion started to decreased (Figure 3). In the beginning of the reaction, the band of the semicircle stretching vibrations at 1493 cm^{-1} was significantly more intense than the band of quadrant stretching band at 1593 cm^{-1}. Since the latter is only observed for asymmetrically substituted aromatics, it is concluded that anisole is efficiently deoxygenated over the fresh catalyst. After 52 min on stream the intensity of these bands became almost identical indicating that a larger fraction of the surface species retained oxygen containing functional groups. At the same time the first peak corresponding to ring vibrations of multi-cyclic aromatics was observed at 1528 cm^{-1}. Over the next two hours, this peak grew in intensity and broadened indicating the formation of various multi-cyclic coke species, which cause the catalyst to deactivate. The results suggest that it may be possible to substantially enhance the lifetime of Pt/H-BEA if surface species are removed after 45-60 minutes on stream.

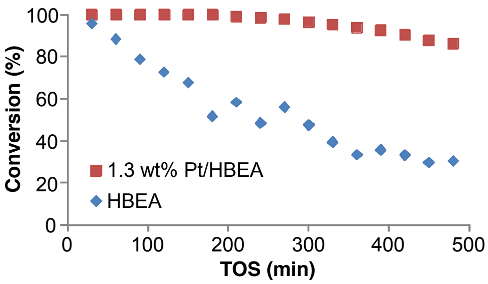

Figure 2: Anisole conversion over H-BEA and Pt/H-BEA.

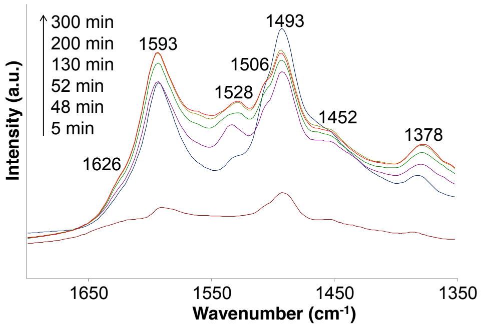

Figure 3: IR spectra of surface species on Pt/H-BEA during HDO of anisole.

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O2 - 4

Operando spectroscopy as a tool for understanding the methanol-to-olefins reaction mechanism and deactivation on chabazite-type catalysts

J. Ruiz-Martinez[1], E. Borodina,[1] Q. Qian[1], C. Vogt[1], F. Meirer,[1] I. Lezcano-González,[1] M. Mokhtar,[2] A.M. Asiri,[2,3] S.A. Al-Thabaiti,[2] S.N. Basahel[2] and B.M. Weckhuysen[1]
[1]Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, Utrecht 3584 CG, The Netherlands
[2]Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[3]Center of Excellence for Advance Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
j.ruizmartinez@uu.nl

Light olefins (ethylene and propylene) are the main building blocks of the chemical industry, being essential for the production of, e.g., plastics and textiles. As the demand of light olefins is continuously increasing, their main fossil feedstock reserves are depleting. The conversion of methanol into olefins (MTO) is an emerging catalytic technology to obtain valuable light olefins from an alternative feedstock, including coal, natural gas and biomass. Zeolite and zeotype materials with Brønsted acidity typically catalyze this process, and high selectivity towards desired light olefins can be achieved with chabazite-framework structure, such as small pore SAPO-34 and SSZ-13 materials. Intensive research have yielded many advances in the understanding of the reaction mechanism, which follows the so-called "hydrocarbon pool mechanism" [1], as well as the deactivation of the material by coke formation. These studies have been mainly performed under ex-situ conditions and theory. The MTO process is very dynamic and, in principle, in-situ spectroscopy will be able to bring new physicochemical insight into the reaction mechanism and deactivation of the catalyst material. This communication reports on our efforts to deeper understand the MTO process with operando UV-Vis and combined UV-Vis/IR spectroscopy on chabazite-type catalysts. More specifically, operando UV-Vis spectroscopy (Fig. 1a) combined with a multivariate analysis of the spectroscopic data revealed that the nature of the active and deactivating species change with the MTO reaction temperature. Operando UV-Vis/IR spectroscopy (Fig. 1b) provided more chemical information on the species inside the catalysts and revealed that the catalyst accessibility is linked with the amount of the methoxy species. Our results provide detailed insights into the active species as well as in the deactivation by coke formation.

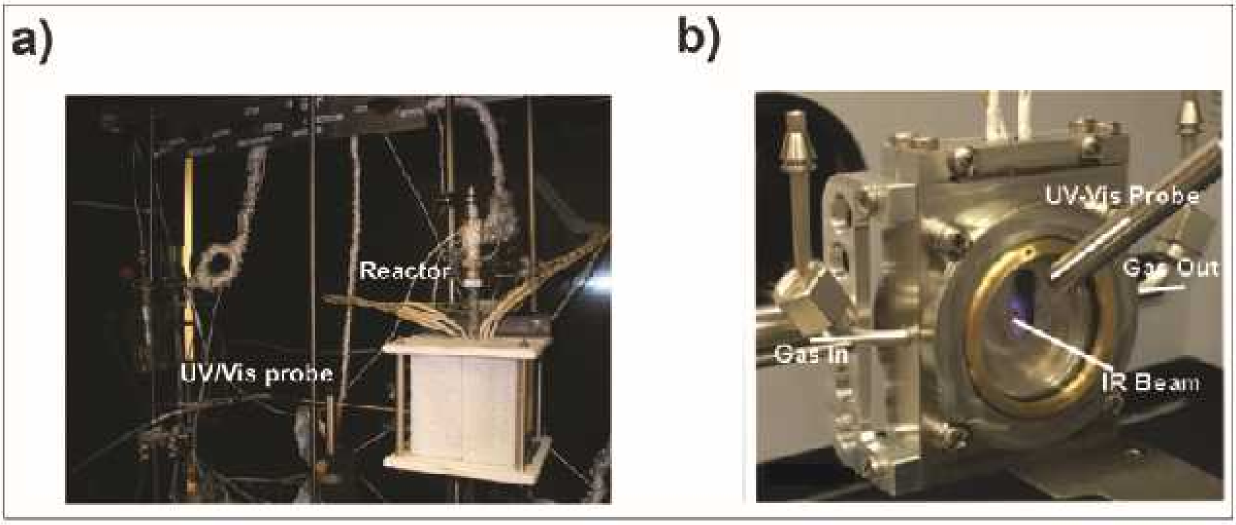

Figure 1. Illustration of the two operando experimental approaches for catalyst investigations. a) Operando UV-Vis spectroscopy setup and b) custom-made reaction cell for the operando UV-Vis/IR measurements.

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O3 - 1

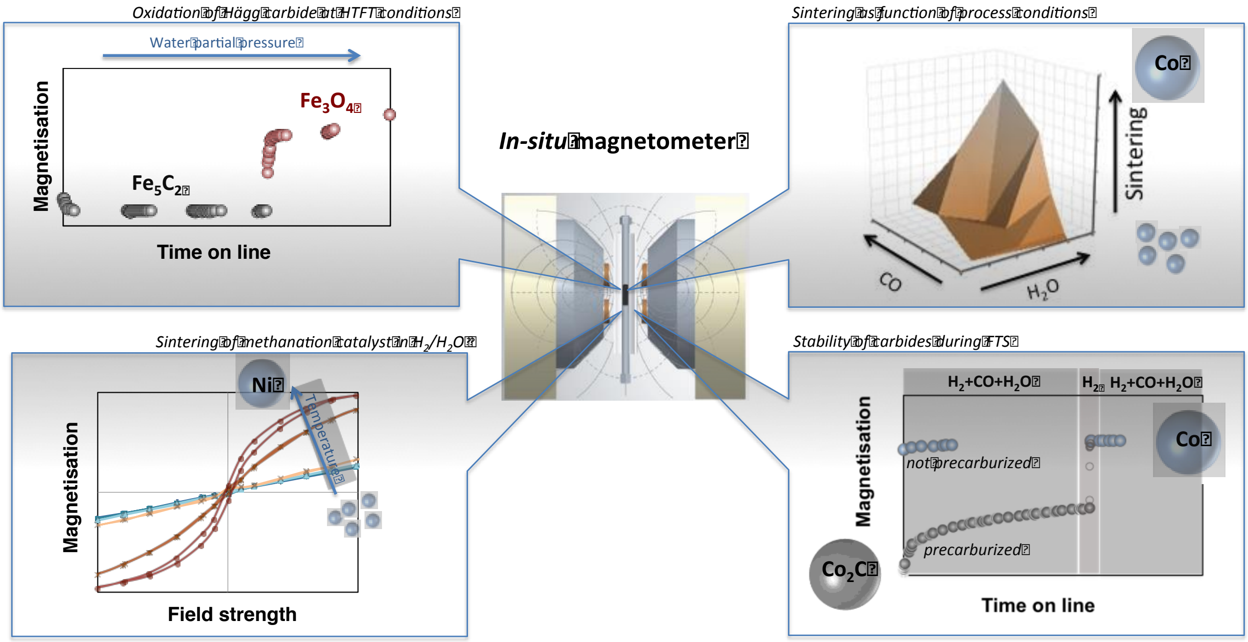
Characterisation of catalysts at working conditions using a novel magnetometer

M. Claeys[1,*], N. Fischer[1], M. Maphutha[1], E. van Steen[1], A. Ferreira[2], D. Moodley[2], A. Saib[2], P. van Berge[2], J. van de Loosdrecht[2], J.L. Visagie[2]

[1] Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa, michael.claeys@uct.ac.za
[2] Sasol Technology R&D, P.O. Box 1, Sasolburg 1947, South Africa

The University of Cape Town, in collaboration with Sasol Technology, has developed an *in-situ* magnetometer, which allows to study ferromagnetic catalysts at industrial conditions of high temperature (>700°C) and high pressure (>50 bar) [1]. This unique set-up can be used to study phase changes (such as reduction, oxidation and carburization) as well as crystallites size changes. In certain cases even crystallite size distributions of the magnetic phase can be obtained. Importantly, while studying these changes, fully relevant kinetic data can be measured on this flow through fixed bed reactor system so that the catalyst performance can be directly linked to its current state. Examples of investigations conducted with the set-up will be given in the paper; these include *inter alia*:

- Sintering of a cobalt Fischer-Tropsch catalyst as function of process conditions [2]
- Role of carbides in cobalt based Fischer-Tropsch synthesis [3]
- Crystallite size dependent oxidation of cobalt Fischer-Tropsch catalysts [4]
- Oxidation of Hägg carbide at High Temperature Fischer-Tropsch synthesis [5]
- Sintering of a nickel methanation catalyst at high temperatures [5]



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[5] in preparation.

O3 - 2

In situ ptychography during the annealing treatment of heterogeneous nanoporous gold catalysts

S. Baier[1], F. Benzi [1], A. Rochet [1], M. Scholz [2], R. Hoppe [3], T. Scherer [4], J. Shi [5], A. Wittstock [5], M. Bäumer [5],
C. D. Damsgaard [6], C. G. Schroer [2, 7] and J.-D. Grunwaldt [1, 8, *]

[1] Institute for Chemical Technology and Polymer Chemistry, KIT, Germany, [2] DESY, Hamburg, Germany, [3] Institute of Structural Physics, Technische Universität Dresden, Germany,[4] Institute of Nanotechnolgy, KIT, Germany,[5] Angewandte und Physikalische Chemie, University of Bremen, Germany,[6] Center for Electron Nanoscopy and Center for Individual Nanoparticle Functionality, DTU, Denmark, [8] Department Physik, Hamburg University, Germany, [8] Institute of Catalysis Research and Technology, KIT, Germany
Presenting author: sina.baier@kit.edu; *corresponding author: grunwaldt@kit.edu

Microscopic studies under controlled environmental conditions (elevated temperature, gas flow, pressure) at different length scales are crucial in order to fully understand structure-activity relationships in catalysts [1]. On the atomic scale, information is normally gained by transmission electron microscopy (TEM), but for the meso scale (50 nm to 1 μm), the short penetration depth of electrons is limiting and X-rays are more suitable [2]. To obtain a high resolution in X-ray microscopy, a highly focused X-ray beam and special techniques like ptychography are required. Moreover, appropriate *in situ* cells need to be developed.

Here we report on a newly developed *in situ* cell, which was used to study nanoporous gold (np-Au). Np-Au with surface areas $> 10\ m^2 / g$ has received strong attention for heterogeneous catalysis and has been modified to be suitable for different reactions such as CO oxidation or water gas shift reaction [3]. Like for traditional catalyst systems, also in these "inverse catalysts", an important issue is the thermal stability. The interface between the oxide nanoparticles and the metal support is crucial for the catalytic activity and prevents coarsening of the gold nanostructure at high temperatures (~500°C). In order to achieve sufficient resolution, ptychography [4], was used to study the coarsening of np-Au at the nm scale, in two different gas environments and at different temperatures of an annealing treatment.

First results on *in situ* ptychography and the corresponding reconstructions of the phase images of a pure np-Au sample will be presented. The setup used for the *in situ* measurements is based on a sample holder composed of a MEMS chip and a cell body with X-ray transparent windows. The sample can be kept under a controlled atmosphere while heating. Figure 1 shows a comparison of a SEM (scanning electron microscopy) image and a ptychogramm, which present the same area of the sample. Complementary to the SEM measurement, the ptychography scans were taken *in situ* under a controlled gas flow at 10^5 Pa and at elevated temperature. Around 500 °C, severe structural changes were visible in the structure of the nanoporous gold: the voids became larger and the density in the ligament structure increased.

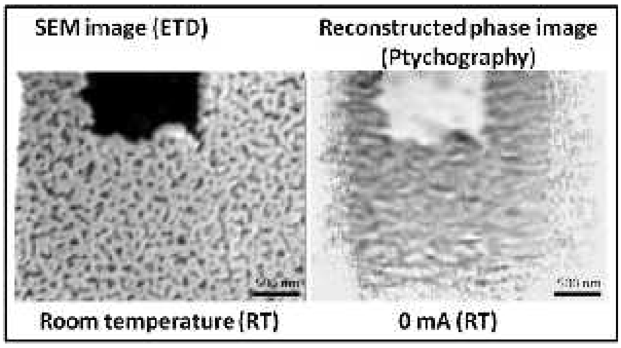

Figure Erreur ! Pas de séquence spécifié.: Comparison of a SEM image and a ptychogram of np-Au in the *in situ* cell before any thermal

The results confirm the possibility of our setup to use the same chip for X-ray imaging and for electron microscopy. Therefore, different length scales (the atomic scale in TEM with restriction to reduced pressure, and the meso scale in X-ray microscopy with the advantages of *in situ* conditions) can be studied at the same area of the sample. This complementary information will help to understand structure-activity relationships and thus help to improve catalyst development.

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O3 - 3

Adding New Tools to the NMR/MRI Toolkit for Innovative Catalytic Research

Igor V. Koptyug
International Tomography Center, SB RAS, Novosibirsk, Russia; koptyug@tomo.nsc.ru

The magnetic resonance imaging (MRI) toolkit can be useful for characterizing the behavior of operating model catalytic reactors. In particular, it allows one to map in situ the distribution of the liquid phase within the catalyst bed, to directly visualize various dynamic processes, and to evaluate local reactant-to-product conversion, as demonstrated using heterogeneous catalytic hydrogenation reactions. In addition, the MRI toolkit can be employed to obtain spatial temperature distributions in the catalyst bed. The viability of the thermometry approach based on the direct imaging of ^{27}Al nuclei of the Pd/Al_2O_3 catalyst bed was demonstrated in the course of hydrogenation of propylene into propane, and later extended toward the two-dimensional temperature mapping of individual catalyst particles during the catalytic oxidation of H_2. MRI could thus become a useful technique for the simultaneous characterization of mass and heat transport in operating catalytic reactors.

The major problem in all such studies is insufficient sensitivity of NMR and MRI. This limitation is particularly severe when one attempts to acquire NMR spectra of short-lived reactive species in mechanistic studies, to detect gases, or to image small objects such as microreactors. An approach uniquely suited for boosting NMR/MRI sensitivity by several orders of magnitude in catalytic context is based on the use of parahydrogen in reactions that involve H_2. Activation of H_2 and hydrogenation of unsaturated substrates catalyzed by transition metal complexes and clusters in solution have been successfully addressed in the past using this approach termed parahydrogen-induced polarization (PHIP). Useful kinetic and mechanistic information was obtained, including the determination of reaction pathways and direct detection of short-lived intermediates not observable with conventional NMR. We have shown that supported metal catalysts are also able to produce pronounced PHIP effects, pointing to the existence of reaction channels that lead to the molecular addition of H_2 to a substrate. This finding is in dissonance with the generally accepted Horiuti-Polanyi mechanism, since dissociative chemisorption of H_2 on metals in combination with rapid surface migration of hydrogens should prevent pairwise H_2 addition to a substrate required for PHIP observation. The unexpected PHIP effects demonstrate structure sensitivity and depend on the nature of metal, support, substrate, etc., paving the way to developing a novel hypersensitive mechanistic tool for heterogeneous catalysis. Recently, PHIP effects were also demonstrated for several metal oxides and bulk unsupported metals used as hydrogenation catalysts. The implications of the results for the mechanisms of heterogeneous hydrogenation processes are discussed.

Further potential extensions of the PHIP technique will be presented, including activation of H_2 by metal-free systems such as frustrated Lewis pairs. Furthermore, efforts to extend the technique toward other types of major industrial catalytic processes are under way. In addition to parahydrogen, they can be based on the use of nuclear spin isomers of other symmetric molecules. Recent progress with the catalytic synthesis and use of nuclear spin isomers of ethylene will be described. In addition to providing useful mechanistic and kinetic information, PHIP is extremely useful for boosting sensitivity in MRI studies of operating reactors. Such applications have been demonstrated recently, including MR imaging of fluid dynamics in microfluidic chips and of a catalytic reaction in an operating model catalytic microreactor.

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O3 - 4

Chemical imaging of single particle catalysis under operating conditions with scanning microfocus XANES-CT, XRF-CT and XRD-CT

Stephen W.T. Price[1*], Andrew M. Beale [2,3], J. Fred W. Mosselmans [1]
[1] *Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0DE, UK*
[2] *UK Catalysis Hub, RCAH, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0FA, UK*
[3] *Department of Chemistry, University College London, 21 Gordon Street, London, WC1H 0AJ, UK*
**corresponding author: stephen.price@diamond.ac.uk*

The highly tuneable, bright X-ray beams provided by synchrotrons are ideal for measuring samples with the low metal concentrations, typical of industrial catalysts, and are extensively used for studying catalytic systems. Recent developments in synchrotron source brightness and detector technology have enabled the development of 'chemical imaging' in which a 2-dimensional or 3-dimensional image of the sample is recorded and where each pixel in the image contains either a full spectrum/pattern allowing for the extraction of more detailed information on the sample by post-hoc analysis. This allows for the physicochemical state of the catalyst to be determined and correlated to its catalytic activity and selectivity.[1,2]

Here we report on a series of chemical imaging developments on the microfocus beamline (I18) at Diamond Light Source. Microfocus X-ray fluorescence computed tomography (μ-XRF-CT), microfocus X-ray diffraction computed tomography (μ-XRD-CT) and microfocus X-ray absorption near edge spectroscopy computed tomography (μ-XANES-CT) methodologies have been developed to allow for 3-dimensional imaging of elemental distribution, crystal phase and local chemical environment with 2x2 μm spatial resolution. By careful choice of the incident X-ray beam energy, μ-XRF-CT and μ-XRD-CT data may be collected simultaneously.

The design and construction of a capillary cell allow for this combined imaging to be performed under reaction conditions and in combination with monitoring the reactions by Raman spectroscopy or mass spectrometry. We present results on 2 commercial catalytic systems: 1) the heterogeneous catalysis of nitrobenzene to aniline by Mo promoted colloidal Pt/C3,4, and 2) the effect of Re promotion on Co/SiO2 Fischer Tropsch catalysts. We thank Diamond Light Source for access to beamlines B18 and I18 (proposals SP4939, SP10242, NT11043 and NT12064) that contributed to the results presented here, and the EPSRC for additional funding.

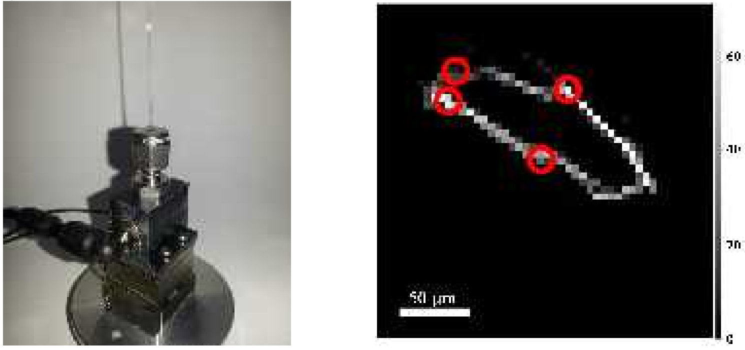

Figure: (Left) Capillary microreactor for liquid phase catalysis. (Right) XRF-CT slice of Pt location on carbon support with approximate crystalline Pt (111) location (circles), recorded under reaction conditions.

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O3 - 5

Speciation of adsorbates on surface of solids by operando IR spectroscopy and chemometrics: application to the description of reactivity at the silica / silane interfaces

Franck Vilmin [a,b,*] *Philippe Bazin,*[a] *Frédéric Thibault-Starzyk,*[a] *and Arnaud Travert* [a]

[a] Laboratoire Catalyse et Spectrochimie, ENSICAEN – Université de Caen – CNRS, 6 Boulevard Maréchal Juin, 14050, Caen, France
[b] Manufacture Française des Pneumatiques Michelin, place des Carmes, 63040 Clermont Ferrand Cedex 9, France
[*] Corresponding Author: franck.vilmin@fr.michelin.com

Speciation, i.e. identification and quantification, of surface species on heterogeneous surfaces by infrared spectroscopy is important in many fields but remains a challenging task when facing strongly overlapping spectra of multiple adspecies.

Here, we propose a new methodology, combining state of the art instrumental developments for quantitative infrared spectroscopy of adspecies, standard chemometric tools (Principal Component Analysis, Evolving Factor Analysis, Multivariate Curve Resolution, multivariate calibration) and innovative multivariate algorithms (baseline correction, soft and hard modeling, spectral decomposition). The whole chemometric approach, built on a formal transposition of the general linear mixture model to adsorption spectral data, is closely intertwined with spectroscopic and physico-chemical insights.

As an illustration of its relevancy for quantitatively studying complex systems, the methodology was applied to a real industrial solid/liquid system widely used in the rubber industry to produce high mechanical performances nanocomposites: hydrated precipitation silica used as reinforcing filler and bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) used as coupling agent between silica and rubber matrix.[1]

A series of non-isothermal operando experiments, including the recently developed Analysis by Gravimetry and IR spectroscopy (AGIR) technique, were designed to be representative of the industrial process at the molecular scale in various environmental conditions, in particular in presence of water.

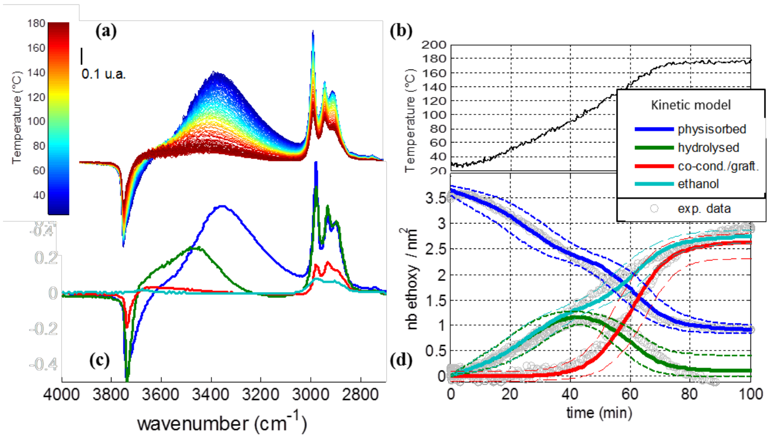

Figure 1: non-isothermal operando experiment on TESPT / hydrated silica system. (a) preprocessed time resolved difference spectra IR spectra of both silica / silane interface and cell gas phase; (b) recorded time - temperature profile; (c) resolved gas phase and surface species spectral profiles;(d) Superposition of kinetic model predictions with resolved experimental concentration profiles

After full chemometrical processing of the huge amount of spectral data generated, we were able as illustrated figure 1, (i) to identify physisorbed, grafted and co-condensed silane adspecies through their unraveled pure spectral profile and, (ii) to propose and implement a chemical kinetic model which fairly fits their respective pure concentration profile. Hence the methodology, by allowing for the first time a surface speciation on the real system in operating conditions, revealed a reaction scheme which contrasts with previous mechanisms proposals.

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Unique correlative optical imaging approach to link catalyst composition to catalytic performance

Eva Plessers[1], Johan Hofkens[2], Dirk E. De Vos[1] and Maarten B.J. Roeffaers[1]
[1]Dept. of Microbial & Molecular Systems, Centre for Surface Chemistry and Catalysis, KU Leuven
[2] Dept. of Chemistry, Molecular Imaging and Photonics, KU Leuven
eva.plessers@biw.kuleuven.be

Supported metal nanoparticles are widespread in heterogeneous catalysis, as they combine both high activity and stability. Because of the direct impact of nanoparticle size, shape and structure on the catalytic performance much attention has been paid to optimize the synthesis conditions. Rationalization of the obtained results often relies on insights generated by high resolution transmission electron micrographs obtained on a limited subset of the material and often misses a direct link to the measured catalytic performance at the ensemble averaged level.

In contrast to elaborate techniques like electron tomography, we used a straightforward optical imaging method that interlinks high resolution SEM, SEM-EDX and catalytic performance measurements at the single support particle level. This unique correlative approach allows for the first time to uncover the effect of supported catalyst composition onto the catalytic performance. The studied Ag/SiO_2 catalysts is a typical yellowish powder, looking seemingly homogeneous. However close inspection using optical microscopy revealed an unexpected large variability in color between different support particles. By a correlative approach, the optical appearance could be successfully linked to silver loading, displaying a 10-fold variation in loading between different silica support particles, and to silver nanoparticle size as was validated by electron microscopy.

Furthermore, our straightforward imaging approach allows us to perform single particle experiments and directly relate optical appearance and catalytic performance at the same single support particle. Analysis of experiments conducted in reaction conditions revealed an unanticipated structure-activity relationship, with 20-50nm as optimal size-range for the AgNPs. Interestingly, combining fast optical screening and traditional catalyst impregnation optimization can lead to the development of a material with an optimal catalyst composition.

The proposed catalyst screening method is technically straightforward and widely applicable in catalysis research; also supported Ag on alumina or Pt on silica was studied with this approach and similar heterogeneities could be observed.

O3 - 7

Wavelet-based XAS as a tool to disclose mechanistic insight into Pt-In catalyst formation

Matthias Filez, Hilde Poelman*, Evgeniy A. Redekop, Vladimir V. Galvita, Guy B. Marin
Laboratory for Chemical Technology (LCT), Technologiepark 914, 9052 Ghent, Belgium
* e-mail: hilde.poelman@ugent.be

Since the pioneering work of Röntgen on the discovery of X-rays, spectroscopic characterization methods have acquired a role of utmost importance in the field of natural sciences. Nanometre scale information obtained through systematic application of novel spectroscopies has revolutionized chemistry, materials science and biology. In catalysis, novel X-ray absorption spectroscopic (XAS) techniques – including (S)XMT, μ-XAFS, QXAS – aspire to unravel structure-performance relations through increased spatio-temporal resolution.[1-2] Besides applying these new spectroscopies, novel mathematical methods for *a posteriori* data treatment are being developed for intelligent information filtering of measured signals. Although these methods are employed after the experiment, their development and use can be as valuable for disclosing nanoscale information as applying novel types of spectroscopies.[3]

In this work, wavelet transformed XAS analysis is shown to be an effective mathematical method for exploiting unrevealed nanoscale mechanisms governing Pt-In catalyst formation. By providing simultaneous k- and R-space resolution, wavelet-based XAS analysis succeeds in the elemental discrimination and spatial localization of Pt neighbours. Impregnation of a $Pt(acac)_2$-toluene solution on a $Mg(In)(Al)O_x$ support and subsequent drying to 110 °C leads to the adsorption of $Pt(acac)_2$ precursor molecules on the support surface. Subsequent calcination to 650 °C results in acac ligand decomposition and the complete oxidation of Pt, yielding atomically dispersed Pt^{4+} species at the support surface. H_2 reduction to 650 °C is accompanied by Pt clustering, In migration to these Pt clusters and Pt-In alloying. Eventually, this results into the formation of In-rich 1.5 nm Pt-In nanoparticles, showing high-performance during selective alkane dehydrogenation (Figure 1).

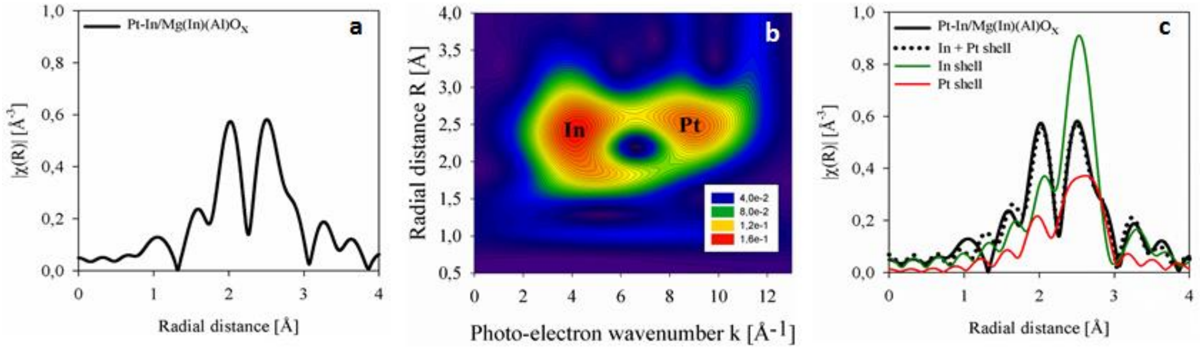

Figure 1: XAS data of $Pt/Mg(In)(Al)O_x$ after H_2/He reduction to 650 °C (no phase correction): a) k -weighted Fourier transformed EXAFS magnitude showing two intense but undefined peaks; b) wavelet transformed XAS contour plot allowing to allocate the chemical nature to the R-space peaks based on k-space location; c) results acquired through wavelet-based analysis serve as input for EXAFS modeling yielding good convergence between model and data.

Acknowledgements: This work was supported by the Fund for Scientific Research Flanders, the Flemish Government Methusalem Funding and the IAP7/05 Interuniversity Attraction Poles – Belgian State – Belgian Science Policy. E.A. R. acknowledges a Marie Curie International Incoming Fellowship granted by the European Commission.

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O3 - 8

Observing the solid-state chemistry inside a working catalytic membrane reactor

A. Vamvakeros[1, 2], A. M. Beale[1, 2*], S. D. M. Jacques[3], M. Di Michiel[4], F. Gallucci[5] V. Middelkoop[6]
[1] Department of Chemistry, University College London, 21 Gordon Street, WC1H 0AJ London, UK
[2] UK Catalysis Hub, Rutherford Appleton Laboratory, Research Complex at Harwell, Harwell, Didcot OX11 0FA, UK
[3] School of Materials, University of Manchester, Manchester, Lancashire M13 9PL, UK
[4] European Synchrotron Radiation Facility, F-38000 Grenoble, France
[5] Department of Chemical Engineering, Eindhoven University of Technology, The Netherlands
[6] Flemish Institute for Technological Research, VITO NV, Boeretang 200, Mol, Belgium
*corresponding author: andrew.beale@ucl.ac.uk

Natural gas, whose main component is methane, is considered to be an abundant hydrocarbon source compared to crude oil and there is a lot of interest in producing higher value bulk chemicals from it. This is the reason why the oxidative coupling of methane (OCM) for the production of ethylene and ethane has been studied extensively during the last 30 years. Catalytic membrane reactors present a promising route to achieve the required high C_2 yield for the industrial application of OCM. In this type of reactor, the membranes are mixed ionic and electronic conducting (MIEC) perovskite-type ceramics whose role is to provide oxygen ions to the catalyst. Maintaining the oxygen partial pressure low and homogeneously distributing the oxygen over the catalytic reactor can lead to an increase in C_2 selectivity by preventing the total oxidation of methane. This is the first time that these catalytic membrane reactors have been tested under operando conditions with X-ray Diffraction Computed Tomography (XRD-CT) at station ID15A of the ESRF. XRD-CT is a non-destructive and non-invasive technique which can provide local structure information with high spatial resolution (beam size between 2 – 100 μm) and resolve microstructure heterogeneities [1].

The catalytic membrane reactors that were used in this study consisted of hollow fiber $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ (BCFZ) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) membranes packed with 2%Mn1.6%Na3.1%W/SiO2 catalyst supported by glass wool [2]. Investigating this OCM system under operando conditions has allowed us to get unprecedented information about both the structure-activity relationship for this catalyst and the reasons behind the deactivation of the catalytic membrane reactor (Figure 1).

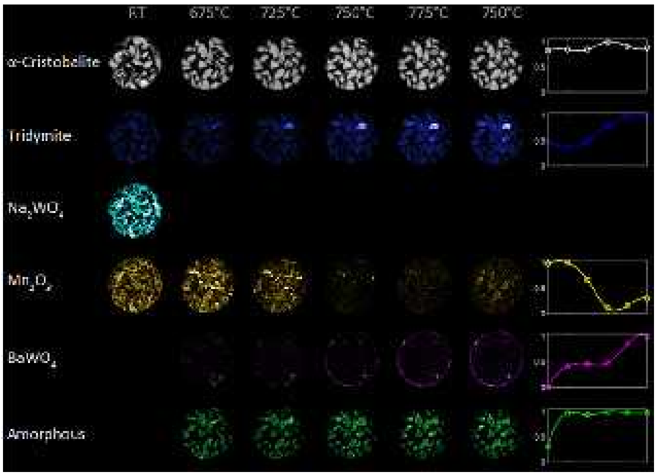

Figure 1. Phase maps for α-cristobalite and tridymite (SiO_2 polymorphs), Na_2WO_4, Mn_2O_3, $BaWO_4$, and an amorphous phase as determined from the XRD-CT data.

Acknowledgements

The development of the catalysts and membranes for the catalytic membrane reactor used in this work is funded within the DEMCAMER project as part of the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement nº NMP3-LA-2011-262840. Note: "The present publications reflect only the authors' views and the Union is not liable for any use that may be made of the information contained therein." The authors would like to thank the European Synchrotron Radiation Source for beam time, CerPoTech AS for providing the ceramic powders and the Boreskov Institute of Catalysis for preparing the catalyst.

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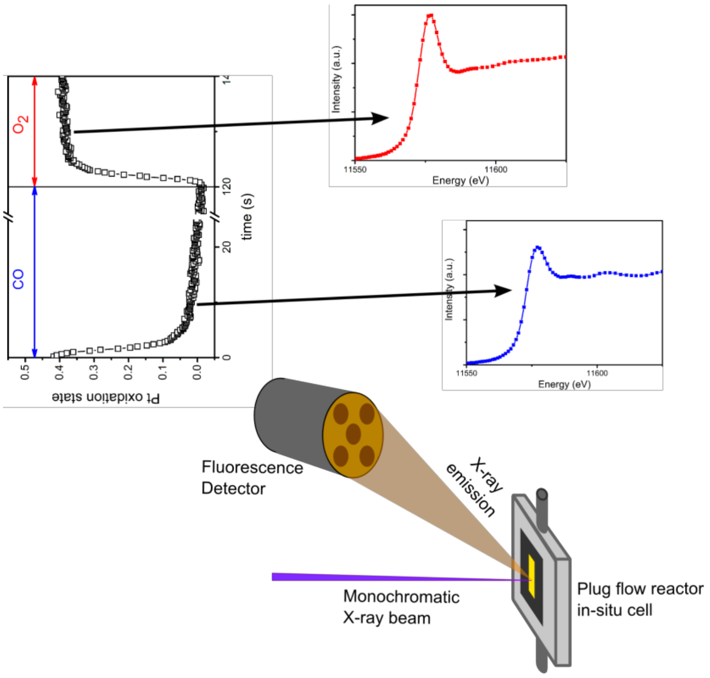
O4 - 1

Transient fluorescence-detected X-ray absorption spectroscopy for probing kinetics of catalytic processes with subsecond time-resolution.

O. V. Safonova[1], R. Kopelent[1], G. Smolentsev[1], A. Guda[2], A. Bugaev[2], J. A. van Bokhoven[1,3], M. Nachtegaal[1]

[1]Paul Scherrer Institute, 5232 Villigen, Switzerland
[2]Research Center for Nanoscale Structure of Matter, Southern Federal University, 344090 Rostov-on-Don, Russia
[3]Institute for Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland
olga.safonova@psi.ch

We report on novel transient X-ray absorption spectroscopic (XAS) method for fast data acquisition in fluorescence mode available at the superXAS beamline at the Swiss Light Source for probing the kinetics and mechanisms of catalytic reactions. Time-resolved XAS of various chemical elements in a working catalyst can be acquired in fluorescence mode with a resolution of 0.1-1 s, which allows probing the kinetic behavior of different species involved in the catalytic process. The important advantage of fluorescence-detected XAS with respect to XAS measured in transmission mode is the possibility to study catalytic materials with highly absorbing/scattering nature, such as ceria, and obtain quantitative and element specific information on the solid state kinetics.



First studies were performed on automotive catalysts containing ceria-based materials promoted by metal nanoparticles, which are used for low-temperature CO oxidation. We investigated the kinetics of 1.5% Pt/CeO_2 catalyst transformation in a plug flow reactor upon CO/O_2 cycling at 30-150°C with 100 ms time-resolution at the Ce L_3 and Pt L_3 edges. Upon exposure to CO the kinetics of PtO_x reduction is faster than the rate of the reduction of ceria. At the same time, CeO_{2-x} oxidation upon exposure to oxygen starts earlier than the oxidation of platinum and then proceeds with a similar rate. These results suggest that reduction of the Pt/CeO_2 catalyst is slow because CO reduces ceria only at the Pt/CeO_2 interface. Nevertheless, oxidation of CeO_{2-x} is fast because the reaction is not taking place at the Pt/CeO_2 interface but on the whole surface of ceria. Already at 47°C and a space velocity of 880 ml g^{-1} h^{-1} for CO and oxygen we observed that the kinetics starts to depend on the concentration gradient in the catalyst bed, which we demonstrate by space resolved measurements.

This transient spectroscopic method can be widely used to study three-way catalysts and other materials where reversible cycling is relevant for catalyst operation.

O4 - 2

Multi-technique Approach to Understand Selective Oligomerisation Mechanisms

Dr. Moniek Tromp, Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, P.O. Box 94215, 1090 GE Amsterdam, The Netherlands, m.tromp@uva.nl

The industrially relevant ethylene oligomerisation reaction known for more than five decades is more than ever of prime interest for both academic and industrial actors. Catalyst developments, for which 10 to 20 years are mandatory, have always been a direct consequence of scientific discovery. The Cr success story started in the 1960s with ethylene polymerisation reactions to afford in the 1990s and 2000s highly selective catalysts for trimerisation and tetramerisation reactions. This led to process development for linear alpha olefin (LAO) production as 1-hexene or 1-octene used as comonomers in polyethylenes. However, exciting questions raised from these discoveries as what oxidation states are involved in the selective and non-selective catalytic cycles and how to switch from one mechanism to another, which intermediates will promote alpha olefin formation versus side products. Answering these questions is crucial for complex design and elucidation of chemical mechanisms.

Characterisation techniques are thus required that provide detailed structural and electronic information on the working catalytic system. Ideally, the changing active site is monitored and characterised during the catalytic reaction, in situ / operando and in a time-resolved mode. An experimental technique that can provide structural as well as electronic analysis and that can be applied in situ and in a time-resolved mode, is X-ray spectroscopy. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is powerful in determining the local structure of compounds including amorphous materials and solutions, since long-range order is not required. Combined X-ray Absorption and X-ray Emission spectroscopy (XAS and XES resp.) provides detailed insights in the electronic properties of a material. Detailed information about the catalysts in their dynamic chemical active environment can thus be obtained and structure/electronic – performance relationships and reaction mechanisms derived. Moreover, a combination of spectroscopic techniques (e.g. UV-Vis) gives complementary information about the system under investigation.

Here, we will report on the development of our stopped-flow methodologies for mechanistic and spectroscopic studies in homogeneous catalysis [1]. Combined time-resolved UV-Vis and XAS (down to millisecond time-resolution) have been successfully applied to identify the activated species in industrial selective oligomerisation Cr catalysts, i.e. Sasol's Cr(SNS)Cl_3 [2] and Cr(PNP)Cl_3 [3] (for ethene trimerisation and tetramerisation resp.) upon activation with aluminium reagent, and their Mo [1d] and Sc [1e] analogues. Continued work incl. further developments in spectroscopic methodologies required for homogeneous catalysis will be discussed.

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O4 - 3

Operando Studies on PdZn, Co_3O_4/CoO and Ni-ZrO_2: Synergies of Surface Science Based Model Systems and Technological Catalysts

Günther Rupprechter, Christoph Rameshan, Karin Föttinger, Yuri Suchorski, Andrey Bukhtiyarov, Hao Li,
Kresimir Anic, Astrid Wolfbeisser, Liliana Lukashuk

Institute of Materials Chemistry, Vienna University of Technology, 1060 Vienna, Austria
guenther.rupprechter@tuwien.ac.at

Our group´s philosophy is to study catalytic surface reactions on heterogeneous catalysts *via a two-fold approach,* employing both *surface science based planar model catalysts* as well as *industrial-grade catalysts* [1-3]. For both, the focus is on examining *active functioning catalysts* under *operando* conditions, at (near) ambient pressure and at elevated temperature.

In particular for ultrahigh vacuum (UHV) based model catalysts that has been a challenge, requiring application of *in situ surface spectroscopy*, such as sum frequency generation (SFG) laser spectroscopy, polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) and near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) [1]. To image ("see") ongoing surface reactions by *in situ surface microscopy*, photoemission electron microscopy (PEEM) was applied to polycrystalline samples [2]. For technological catalysts, analogous *operando* studies were performed by Fourier transform infrared spectroscopy (FTIR), x-ray absorption spectroscopy (XAS), near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS), and x-ray diffraction (XRD) [3]. Most of the operando studies were performed at synchrotron sources (BESSY (DE), MaxLab (SE), SLS (CH)), and in lock-step with theory.

This two-fold approach yields a more "*holistic*" view of the catalytically relevant atomic and electronic surface structure of catalysts, as well as of molecular details that steer reaction activity and, even more important, reaction selectivity. Comparing surface science based single crystals with nanoparticle model catalysts elucidates the *materials gap*, and comparing UHV to ambient pressure studies reveals the *pressure gap*. In particular, synergisms between studies on model and technological catalysts often provide access to atomistic details.

Among the systems studied are
i) hydrogen generation by methanol steam reforming on alloy (intermetallic) catalysts, i.e. PdZn surface alloys on Pd(111) single crystals [4] and PdZn nanoparticles supported on ZnO [3],
ii) CO oxidation on (oxide-supported) noble metals [2], and on cobalt oxides (Co_3O_4 and CoO),
iii) CO and water adsorption, and methane reforming on Ni-ZrO_2, employing an ultrathin ZrO_2 trilayer (O-Zr-O) film on $Pt_3Zr(0001)$ [5] as well as commercial ZrO_2 as support [6].

The combined studies provide detailed mechanistic insight, e.g. on i) the effect of PdZn thickness, surface corrugation and valence band structure on selectivity, ii) locally-resolved catalytic ignition, surface oxide formation/reduction, oxygen vacancy formation as well as carbon balance, iii) electronic structure of ultrathin oxides, and gas-induced oxide and nanoparticle reconstructions.

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O4 - 4

Structural and Charge Inhomogeneities in Supported Pt Clusters Under *Operando* Conditions*

F. D. Vila[1] (fdv@uw.edu), J. J. Rehr[1] and A. I. Frenkel[2]

[1]Department of Physics, University of Washington, [2]Department of Physics, Yeshiva University

Nanoparticle materials are ubiquitous in heterogeneous catalytic processes and there is broad interest in their physical and chemical properties. However, global probes such as XAS and XPS reveal their ensemble characteristics, obscuring details of their internal structure. We have previously shown [1] that a combination of theoretical and experimental techniques is needed to understand the intra-particle heterogeneity of these systems [2], and their changes under operando conditions [3]. DFT/MD simulations revealed that the nanoscale structure and charge distribution are inhomogeneous and dynamically fluctuating over several time-scales, ranging from fast (200-400 fs) bond vibrations to slow fluxional bond breaking (>10 ps). In particular the anomalous behavior of the mean-square relative displacement is not static, but rather is driven by the stochastic motion of the center of mass over 1-4 ps time-scales, resulting in “dynamic structural disorder” (DSD) [2]. In addition the nanoparticles exhibit a semi-melted cluster surface which for alloy clusters can be atomically-segregated. Recent studies of CO- and H-covered Pt nanoclusters on C and SiO_2 supports exhibit a variety of spectral and structural trends as a function of temperature. DFT simulations show that adsorption drives local electronic structure changes that are responsible for the opposite energy shifts, as a function of temperature, of absorption edge and off-resonant emission line. Moreover, desorption results in local bond contraction, thus explaining the observed negative thermal expansion. For example, upon single CO adsorption, the Pt-Pt bonds formed by coordinated Pt atoms are locally expanded by ~5%, with little change in the rest of the particle. Coordination also has a large effect on the net charge of the Pt atoms (Figure 1), with a net loss of charge upon adsorption. Finally, we show how high coverage inverts the charging structure of the cluster, turning the negative surface (positive interior) of the clean cluster to positive surface (negative interior) in the fully covered case.

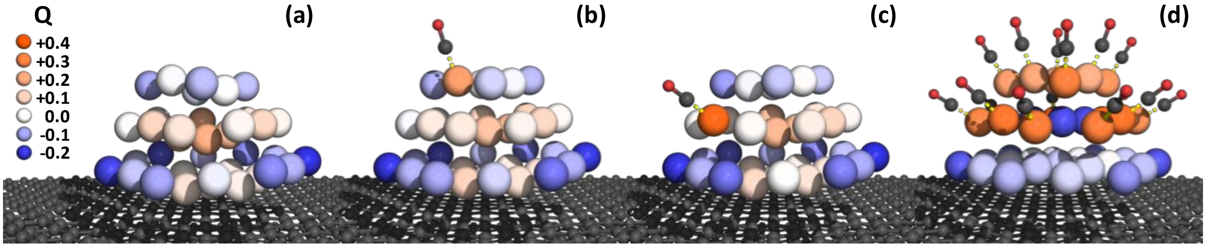

Figure 1: Net charge changes upon CO adsorption for a Pt_{37} cluster on carbon. a) Clean cluster, b) edge adsorption, c) face adsorption, d) full-top coverage.

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ATR-IR/EXAFS of catalytic solid-liquid interfaces in a single cell

Mark A. Newton, Maarten Nachtegaal, Oliver Kröcher, Davide Ferri
Paul Scherrer Institut, CH-5232 Villigen, Switzerland; davide.ferri@psi.ch

Liquid phase heterogeneous catalysis is a key technology for a number of segments in chemical industry. A liquid phase environment near a solid phase is also characteristic for biomass treatment and photocatalysis. However, catalysis by solid materials immersed in a solution is still considered difficult to study using common spectroscopic and diffraction methods. It has been repeatedly shown that extended X-ray absorption fine structure (EXAFS) spectroscopy in liquid environments is feasible in transmission and fluorescence mode. Despite the strong interference from the liquid environment, adsorption and reaction at catalyst surfaces can also be followed by infrared spectroscopy in the attenuated total reflection mode (ATR-IR) [1]. Combination of EXAFS and ATR-IR spectroscopy was demonstrated using an ATR-IR probe inserted in a stirred reactor cell [2] similarly to other well-known combinations of Raman, UV-vis and ATR-IR spectroscopies [3].

Here we want to show that the same portion of the catalyst can be analyzed by EXAFS and ATR-IR. This offers the unique possibility to obtain information from the adsorbate layer on the catalyst surface and from the active element (oxidation and coordination states) of the catalyst simultaneously that is ambiguous in the existing combinations of the two methods. Commercially available ATR-IR cells typically use horizontal internal reflection elements (IRE). On the contrary, the homemade ATR-IR cells available at PSI are based on the original design by Specac and possess a vertical IRE. This arrangement is ideally suited to allow coupling X-rays from the side of the flowing solution (Figure 1) in contact with the solid catalyst deposited onto the IRE. However, only EXAFS in fluorescence mode can be exploited.

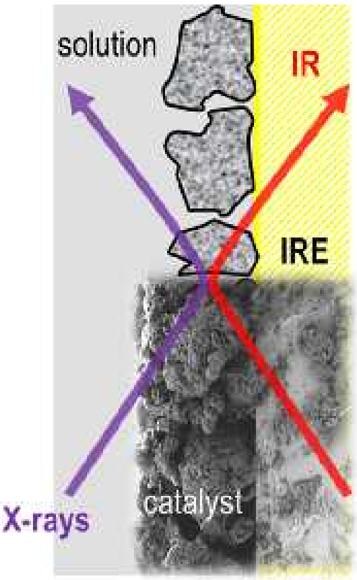

Figure 1. cell geometry for combined EXAFS/ATR-IR spectroscopy.

We have designed, manufactured and tested in preliminary experiments a combined ATR-IR/EXAFS cell. High quality XANES and EXAFS spectra at the Pd K-edge have been obtained on a 5 wt% Pd/Al_2O_3 catalyst layer deposited on the ZnSe IRE. This configuration is typical of ATR-IR experiments. Quantitative reduction of Pd at room temperature was followed by XANES while flowing H_2-saturated cyclohexane solvent over the catalyst layer. The subsequent adsorption of CO from the saturated solvent was followed by ATR-IR spectroscopy.

Because of the intrinsic potential for homogenous catalysis of metal complexes, the detection limit of both methods within the cell was determined using a solution of $CuSO_4$ in the concentration range 0-0.1 mol·L^{-1}. The cell can be operated in a variable temperature range, the liquids can be admitted using a peristaltic pump and solvent/solutions can be saturated by various pure gases.

As a consequence, a dedicated set-up has been built to allow for typical ATR-IR measurements at lab scale that can be transferred to the SuperXAS beamline of the SLS for EXAFS measurements of liquids in contact with solids. The cell seems to be ideally suited for extension to time-resolved experiments using X-rays and for high pressure liquid phase experiments [4].

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O5 - 2

High temperature and pressure ATR-IR spectroscopy study of Aqueous Phase Reforming of Hydroxyacetone on zirconia and boehmite supported Pt catalysts

*Kamila Koichumanova, Anna Kaisa K. Vikla, K. Seshan, Barbara L. Mojet, Leon Lefferts**
*Catalytic Processes and Materials, MESA+ Institute for Nanotechnology, University of Twente, PO BOX 217, 7500AE, Enschede, the Netherlands; *l.lefferts@utwente.nl*

Growing interest in the development of new catalytic technology for biomass processing is raising new challenges in the field of *in-situ* spectroscopy. Different reaction conditions as well as new reaction environments require to reconsider the approach used for catalytic studies with *in-situ* techniques. For instance, in Aqueous Phase Reforming (APR), which is suggested as a substitute for Steam Reforming [1], high pressure liquid conditions are a challenge for vibrational spectroscopy. Presence of large amounts of hot compressed water, absorbing most of the infrared radiation, requires new infrared technique to replace the traditional transmission spectroscopy technique.

This study reports on a new approach in Attenuated Total Reflection Infrared (ATR-IR) spectroscopy which makes it possible to perform *in-situ* studies at the required higher temperatures (up to 230°C) and pressures (up to 80 bar) for the APR reaction, in order to observe and study reaction intermediates and catalysts while performing the reaction. Figure 1 presents a scheme of the newly designed ATR-IR cell. Internal total reflection phenomenon at the surface of the ZnSe element covered with a thin catalyst layer is limiting the pathway of light through bulk water [2]. Thus, only a layer of just a few microns of the solid-liquid interface is probed.

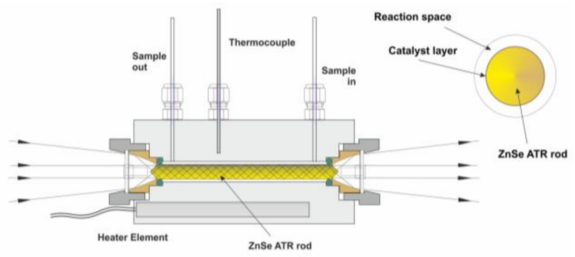

Fig.1 Drawing of the ATR-IR tunnel cell and cross section of the catalyst layer coated on the internal reflection element [3].

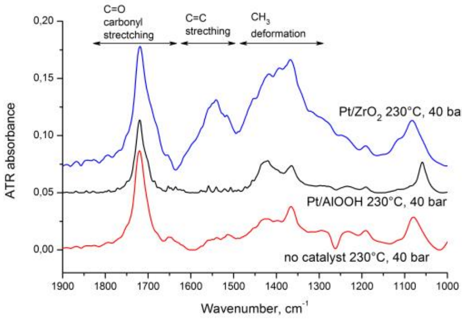

Fig.2 *In-situ* ATR-IR spectra of hydroxyacetone adsorption on Pt/AlOOH and Pt/ZrO_2 catalysts at 230°C, 40 bar.

The aqueous phase fraction formed during flash-pyrolysis of biomass, containing C_1-C_3 oxygenates, is converted to hydrogen and alkanes via APR. Hydroxyacetone was used as a model compound in this study due to its abundance in aqueous phase of pyrolysis bio-oil. IR spectra of hydroxyacetone interacting with platinum catalysts supported on zirconium oxide and boehmite are obtained at ambient as well as reaction conditions (Fig. 2). Formation of species containing C=C, C=O bonds and their reactivity will be discussed in the presentation.

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O6 - 1

Adsorption and thermal decomposition of methyl iodide using silver-exchanged zeolites: an *operando* study on the trapping mechanism

Mouheb Chebbi[1*], Bruno Azambre[1], and Laurent Cantrel[2]
[1]Université de Lorraine, Laboratoire de Chimie et Physique-Approche Multi-Echelle des Milieux Complexes (LCP-A2MC- EA n°4632), Institut Jean-Barriol FR2843 CNRS, r, France
[2]Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SAG, 13115 Saint-Paul Lez Durance, France.
*Corresponding author, e-mail mouheb.chebbi@univ-lorraine.fr

During a severe accident in a Nuclear Power Plant, fission products such as CH_3I and I_2 are released from the degraded fuel and can reach the environment [1]. In order to avoid the release of radioactive ^{131}I isotope, an improvement may consist in combining current filtration devices with an inorganic porous adsorbent, such as metal-loaded zeolites [1].

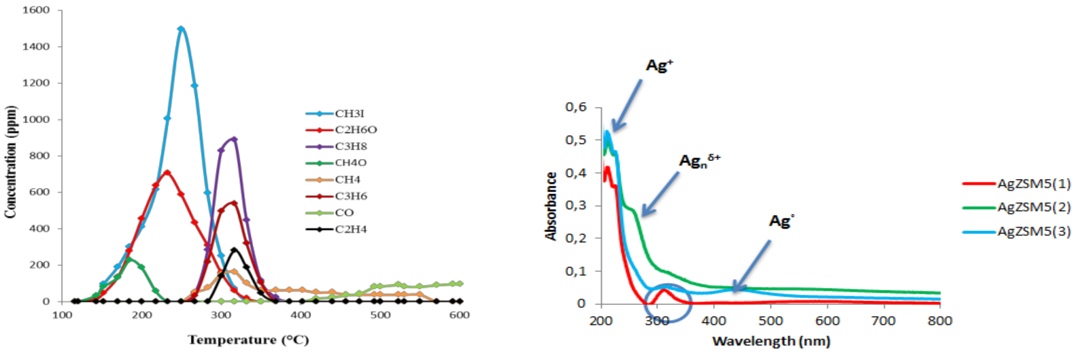

Figure 1: TPD profile of CH_3I adsorbed at 100 °C over Ag23%/Y (left); and (right) Silver speciation by DR-UV-visible spectroscopy for Ag/ZSM-5 zeolites

Our preliminary experiments on silver-exchanged zeolites of different structural types have shown that the adsorption capacity of CH_3I depends mostly on the Ag content that could be introduced by ion exchange. Because of their interesting adsorption properties, Ag/Y zeolites (with Si/Al = 2.5) were chosen to study the effect of silver loading on the trapping mechanism of methyl iodide and its catalytic thermal decomposition. For the first time, a combination of several *operando* spectroscopic techniques was used to gain insight onto these aspects. In the adsorbed phase, time-resolved infrared (Varian Excalibur 4100 spectrometer, Graseby Specac accessory and Spectra-Tech environmental cell) and diffuse reflectance UV-Vis spectroscopies (Agilent Cary 4000 spectrometer with Harrick Praying Mantis DR accessory) were used in order to plot the kinetic evolution of organic species and the silver speciation, respectively. These data were then correlated to those monitored from quantitative gas-phase FTIR spectroscopy in order to elucidate the pathways involved in the trapping and catalytic decomposition. The formation of crystalline AgI (β) phase co-existing with CH_3I in molecular form was observed after methyl iodide adsorption at 100 °C. The AgI formation suggests a precipitation reaction between the Ag cationic species and the iodide ions I^- after a first step involving the dissociation of CH_3I. In addition, dimethyl ether and methanol were the primary products formed during the catalytic decomposition of methyl iodide. Their production involves the participation of Brönsted acid sites and surface methoxy species as intermediates. Moreover, higher alkanes and alkenes were formed at medium temperatures from coupling reactions catalyzed by protonic and silver sites (Figure 1) as well as I_2 release from AgI decomposition above 500 °C.

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O6 - 2

Alumina layer on metallic structured catalyst carriers studied by in situ Raman, XRD and coupled AFM/Raman techniques

J. Łojewska[1], A. Knapik[1], P. Jodłowski[2], A. Kołodziej[3]
[1]Jagiellonian University, Faculty of Chemistry, Krakow, Poland, lojewska@chemia.uj.edu.pl
[2] Cracow University of Technology, Department of Chemical Engineering and Technology, Poland
[3] Technical University of Opole, Faculty of Civil Engineering, Poland

Short channel structured catalysts carriers in form of wire meshes, metallic foams or stripes used as reactor internals offer much higher heat and mass transport parameters than ceramic monoliths [1]. With this reference it results in substantial shortening of the catalytic reactor length (upto 50 times). The metallic internals can thus be applied in all processes of high reaction kinetics (fast reaction rate). The application of metallic internals is, however, dependent on the development of the methods of catalyst layering on metallic surfaces. One of the steps in catalyst preparation is formation of washcoat layer. If the carriers are made of kanthal type steel (alloys containing aluminium) than the alumina layer can be formed both in high temperature calcination and chemical digestion of the surface. In both cases two questions arise: i) what phases of alumina are formed under certain treatment (e.g. calcination conditions) and ii) what kinds of species are present on the very surface of the carrier after the treatment. The first question is important from the point of view of surface development and alumina stability at high temperature. In this study the problem has been approached by the in situ Raman and low angle XRD analyses of the kanthal steel surface upon oxidation at various temperatures (100-1000°C). The second question is connected with the problem of the surface heterogeneity or more precisely the composition of active centres (after catalyst layering on alumina surface). This information has been provided by both micro Raman and coupled AFM/Raman micro analyses [2] of the surface of the formed alumina matrix and, for a reference, the alumina deposited with cobalt spinel and ceria catalysts.

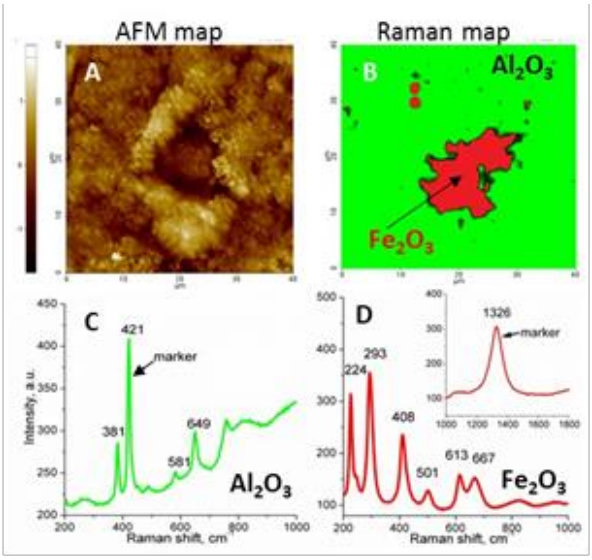

Fig. 1 Heterogeneity of precalcined kanthal steel (imaged by interfaced AFM/Raman microscopy: A) AFM topography map 40x40 µm, B) Raman map 40x40 µm of the same area obtained using 2 marker bands of α-Al_2O_3 (421 cm^{-1}) and α-Fe_2O_3 (1321 cm^{-1}) shown in C) and D), respectively.

An example of the AFM/Raman micro analysis of the kanthal steel surface precalcined at 1000°C are shown in Fig. 1. As it can be seen the surface is composed not only of α- and γ- Al_2O_3 (γ phase detected by XRD) but also α-Fe_2O_3 phase.

In all, The study show comprehensive results on the evolution and composition of the kanthal steel surface at various temperatures upon its calcination, which fills the gap existing in the subject literature. The results demonstrate that by varying calcination conditions (temperature and calcination time) different phases of alumina can be formed on the steel surface as shown by in situ Raman and low angle XRD results. Both in situ and mapping studies confirm the presence of additional α-Fe_2O_3 phase at various temperatures. The uniqueness of the results is also the results of the in situ Raman microscopy gathered at very high temperature (1000°C)

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O6 - 3

Solid/solution interfaces probed by ATR-IR: in situ speciation of molybdate and tungstate ions onto iron (hydr)oxides

A. Davantès, D. Costa, G. Lefèvre

CNRS-ENSCP, IRCP – UMR8247, 11 rue Pierre et Marie Curie 75231 Paris Cedex 05, France

gregory.lefevre@chimie-paristech.fr

Infrared spectroscopy is a widespread tool for analysis of catalyzed reaction in operational conditions. The gas phase or the gas/solid interfaces are suitable systems to be probed by mid-IR beam. To use the same approach for aqueous solutions or solid/solution interfaces, the problem of the strong absorption of infrared beam by water should be solved. Accessories based on Attenuated Total Reflectance effect allow to record spectra of aqueous solutions, due to a small probed depth of the water (about 1 μm). Beyond the possibility of recording spectra of aqueous solutions, a protocol has been developed in the 90's [1] to probe the whole solid/solution interface : a deposit made by drying a colloidal suspension is formed onto the ATR crystal, and a circulation cell is clamped. Thus, the spectra of adsorbed species can be recorded in situ, and in real time.

We have applied this method to determine the sorption mechanism of molybdate ions onto several ferric (hydr)oxides: goethite, hematite, lepidocrocite, akaganeite. Our previous works on sorption on hydrotalcite [2] have shown that ATR-IR is a tool of choice to determine the speciation of aqueous molybdate, easily distinguishing MoO_4^{2-} ion from polyoxomolybdate ions (mainly heptamolybdate). In this study, we have followed the formation of different geometries of sorbed complexes as a function of surface structure of the iron (hydr)oxide phase. In addition, periodic DFT calculations at 0K have been conducted in order to get insight into the local bond formation between the complex and the surfaces, identify the most stable adsorption mode, and calculate vibrational spectra. We thus benefit from a double check (energetics and theory-assisted IR interpretation) of the Mo adsorption. Thus, molybdate ions can adsorb as isolated inner sphere species, or can form surface polymers with a 2D or 3D structure. An important conclusion is that the geometry is controlled by the iron (hydr)oxides phase rather than the speciation in solution.

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POSTER PRESENTATIONS

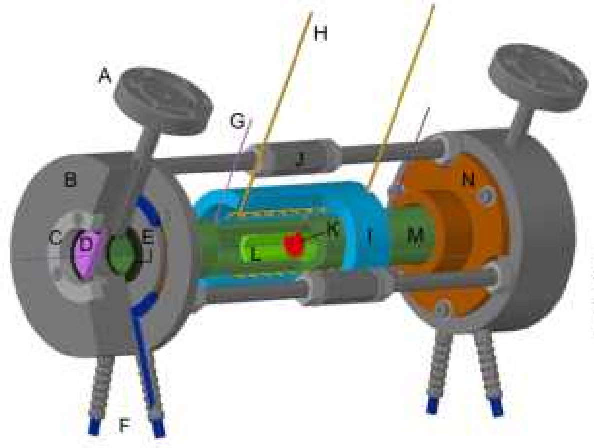
P 1

A high-temperature, ambient-pressure ultra-dry operando reactor cell for FT-IR Spectroscopy

Eva-Maria Köck, Michaela Kogler, Reinhold Pramsoler, Bernhard Klötzer, Simon Penner

Institute of Physical Chemistry, University of Innsbruck, Innrain 80-82, A-6020 Innsbruck
simon.penner@uibk.ac.at

The construction of a newly designed high-temperature, high-pressure FT-IR reaction cell for ultra-dry in-situ and operando operation is reported (Figure 1). The reaction cell itself as well as the sample holder is fully made of quartz glass, with no hot metal or ceramic parts in the vicinity of the high-temperature zone. Special emphasis was put on chemically absolute water-free and inert experimental conditions, which includes reaction cell and gas-feeding lines. Operation and spectroscopy up to 1273 K is possible in reactive gases at pressures up to ambient conditions. The reaction cell exhibits a very easy and variable construction and can be adjusted to any available FT-IR spectrometer. Its particular strength lies in its possibility to access and study samples under very demanding experimental conditions. This includes studies at very high temperatures, e.g. for solid-oxide fuel cell research or studies where the water content of the reaction mixtures must be exactly adjusted. The latter includes all adsorption studies on oxide surfaces, where the hydroxylation degree is of paramount importance. The capability of the reactor cell is highlighted in Figure 2, matching the operando-obtained FT-IR spectra in methane up to 1143 K on Y_2O_3 with corresponding conductivity measurements by electric impedance measurements. The FT-IR spectra at the highest temperature reflect the formation of a conductive carbon layer by methane decomposition encapsulating the oxide grains. This setup therefore provides both the possibility to perform highly specific infrared experiments in transmission mode and offers at the same time the great advantage to directly follow and hence to correlate experiments performed by other in-situ/operando methods such as electrochemical impedance spectroscopy, volumetric adsorption or even catalytic investigations.



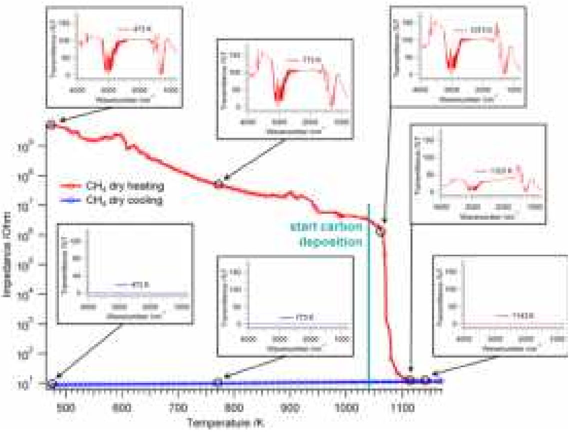


Figure 1 (left): Scaled schematic 3D drawing of the in-situ/operando IR cell. (A) CF flange for gas supply, (B) multi-purpose side flange, (C) IR-window holder, (D) IR-window, (E) Viton seal, (F) water cooling lines, (G) Ni/NiCr thermo element, (H) heating wire, (I) ceramic heat shield, (J) threaded rod, (K) sample disc, (L) quartz sample holder, (M) quartz tube, (N) cooled copper shield.

Figure 2 (right): Electrochemical impedance spectroscopy measurement on Y_2O_3 in dry CH_4 (flow ~0.7 ml s^{-1}) at linear heating and cooling rates of 10 K min^{-1} up to 1173 K and back to 470 K (large panel). For these measurements an excitation signal of 20 mV and a frequency of 1 Hz were used. The correlating FT-IR spectra were also performed at a flow rate of 0.7 ml s^{-1} up to 1143 K and back to 470 K at linear heating and cooling rates of 10 K min^{-1}.

P 2

An *Operando* Molecular Spectroscopic Study of Ethylene Polymerization by Supported CrO_x/SiO_2 Catalysts

Anisha Chakrabarti* and Israel E. Wachs
Operando Molecular Spectroscopy & Catalysis Laboratory,
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015 USA
*anc412@lehigh.edu

Ethylene polymerization by the supported CrO_x/SiO_2 catalysts was discovered in the 1950s at Phillips Petroleum by J.P. Hogan and R.L. Banks. The main product of this system is high-density polyethylene (HDPE) and is responsible for a large share of the HDPE produced globally. Advantages to using this system include that it functions without the use of activators and can synthesize many types of PE. Additionally, the reaction works at relatively low temperatures (80-180°C) and pressures (<50 bar).

Although supported CrO_x/SiO_2 ethylene polymerization catalysts have been extensively studied over the years, the same fundamental structural and mechanistic questions are still being debated today with researchers being no closer to a common view. For example, the initial molecular structure of the oxidized surface $Cr^{+6}O_x$ site has been proposed to be present as isolated surface dioxo CrO_4, isolated surface mono-oxo CrO_5, and dimeric surface Cr_2O_7, while the chromia oxidation state during ethylene polymerization has been proposed to be reduced Cr^{+2} and Cr^{+3}. Additionally, the structure-activity relationships are absent, and the reaction mechanism, particularly the initiation mechanism, remains elusive. The objective of this study has been to determine the structure-activity relationship for the SiO_2-supported catalytic active chromia surface sites for ethylene polymerization.

To address the molecular details of ethylene polymerization by supported CrO_x/SiO_2 catalysts, modern *in situ* and *operando* molecular spectroscopic techniques were applied before and during reaction conditions. The initial supported CrO_x/SiO_2 catalyst was found to only contain isolated chromia sites (very high UV-vis edge energy value), a significant fraction of CrO_4 coordinated sites (pronounced XANES pre-edge feature) and two distinct surface chromia sites (dioxo $(O=)_2CrO_2$ and mono-oxo $O=CrO_4$). *In situ* Raman spectroscopy during ethylene polymerization revealed that the surface dioxo CrO_4 site reduces and becomes activated more easily than the surface mono-oxo CrO_5 site. The corresponding *in situ* UV-vis and *in situ* XANES experiments verified the reduction of Cr^{+6} to Cr^{+3} for both the dioxo and mono-oxo surface chromia sites during ethylene polymerization. *Operando* IR spectroscopy detected the formation of active sites, surface intermediates, and the condensed PE product allowing structure-activity relationships.

This study has addressed confusion in the literature for ethylene polymerization by the supported CrO_x/SiO_2 catalysts. Employing the same experimental conditions for each *in situ* and *operando* spectroscopic measurement has allowed now for the determination of the molecular and electronic structures of the CrO_x sites on SiO_2 for the initial oxidized catalyst as well as the catalyst during ethylene polymerization. This presentation will address the catalytic roles of the two distinct surface CrO_x species on SiO_2 in the ethylene polymerization reaction.

P 3

Operando DRIFTS investigation of cobalt-based Fisher-Tropsch catalysts exposed to trichloroethylene.

Anaelle Paredes-Nunez, Davide Lorito, Nolven Guilhaume, Yves Schuurman and Frederic Meunier*
Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne (France)
*E-mail: fcm@ircelyon.univ-lyon1.fr

Introduction

Biomass-derived syngas contain significant concentrations of chlorine that may contaminate downstream Fisher-Tropsch catalysts. We report herein an operando diffuse reflectance FT-IR spectroscopy (DRIFTS) study in which the hydrogenation of CO is monitored in the presence of 150 ppm of chlorine (introduced as 50 ppm of trichloroethylene, noted "TCE") at ambient pressure.

Results and Discussion

The experimental setup was described elsewhere [1]. The rates of formation of the main products of interest sharply decreased upon the introduction of the chlorinated compound, typically showing a 10-fold drop (Fig. 1, left). Interestingly, the drop in the carbonyl band area was far less marked and mostly due the removal of bridged/multi-bonded carbonyls (Fig. 1, middle 1950-1750 cm^{-1} region). This suggests that each Cl atoms poisoned several surface sites and/or selectively poisoned the most active sites. The effect of Cl was partly and slowly reversible. Surprisingly, the Cl poisoning hardly affected the position of the on-top CO(ads) IR band, in contrast to the effect of surface coverage when CO was removed from the feed (Fig. 1, right). In addition to site poisoning, our operando DRIFTS data highlights a strong electronic effect of Cl, which is able to counteract the effects of surface coverage of CO on the position of the IR band (Fig. 1, right). Similar effects were observed on a silica-supported cobalt catalyst (data not shown).

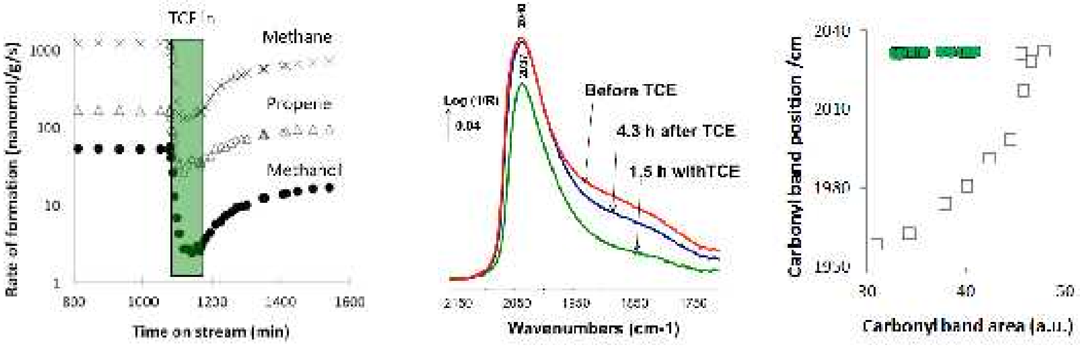


Figure 1. (Left) Rate of formation of products as a function of time before, during and after exposure to TCE. (Middle) DRIFTS spectra collected before, during and after exposure to TCE. Feed: 30% CO + 60 % H_2 (+ 50 ppm C_2HCl_3 if any) in Ar. T = 220°C, P = 1 atm. (Right) Wavenumber of the on-top CO(ads) band as a function of band area during (open square) CO removal and (full circle) chlorine removal.

Acknowledgements

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P 4

Baseline artifacts and correction of gas-phase species signal during diffuse reflectance FT-IR analyses of catalysts at variable temperatures.

Anaelle Paredes-Nunez, Imen Jbir, Daniel Bianchi and Frederic Meunier*
Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne (France)
*E-mail: fcm@ircelyon.univ-lyon1.fr

Summary

Diffuse reflectance FT-IR spectroscopy (DRIFTS) is commonly used to investigate catalytic reactions. CO is a reagent of many reactions of interest for environmental catalysis and fuel and chemical synthesis, as well as being a surface probe to investigate the structure and oxidation state of metal-based particles by *in situ* and *operando* FT-IR spectroscopy. It is crucial to avoid IR signal distortion that may affect the IR spectrum in the region corresponding to adsorbed CO, which spans from ca. 2250 cm^{-1} down to 1600 cm^{-1}. Such bands can appear in the DRIFTS spectra of silica-based solids when the temperature and/or the hydration level of the sample are modified (Fig. 1, left). These bands are merely due to variations in the vibrations modes of the silica solids and are not related to adsorbed CO. Accurate correction of gas-phase CO signal during DRIFTS analyses can be obtained by collecting a subtrahend spectrum under identical reaction conditions over an inert material such as SiC. Spurious bands may otherwise arise if a subtrahend is collected at a different temperature (Fig. 1, right).

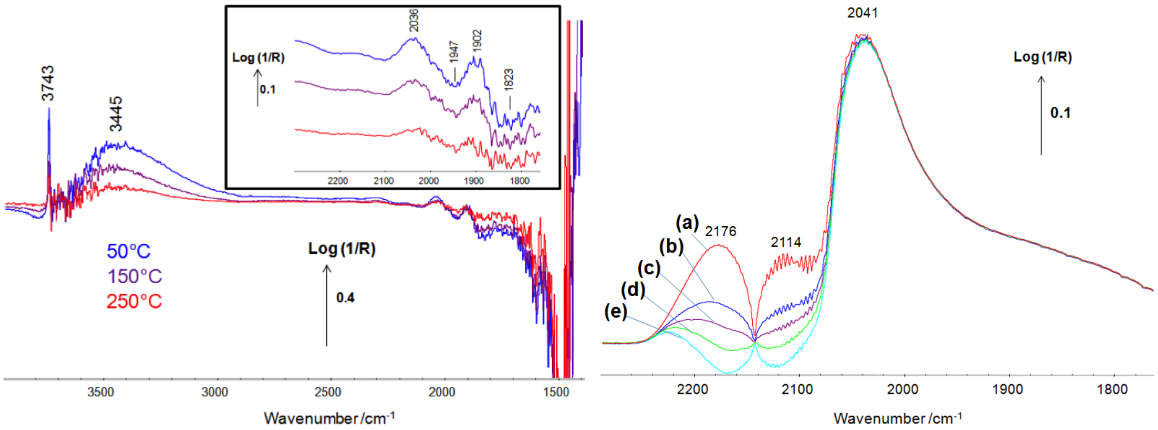

Figure 1. (Left) *In situ* DRIFTS spectra recorded over silica at various temperatures during sample cooling from 250°C down to 50°C. The spectrum obtained over the same sample pre-treated at 350°C was used as background to calculate the pseudo-absorbance. Feed: Ar. (Right) **.** *In situ* DRIFTS spectra recorded over 15% Co/alumina at 220°C (a) in the presence of 30 % CO + 60 % H_2 + 10 % Ar at steady-state. The spectrum (b), (c) (d) and (e) are equal to (a) to which a gas-phase spectrum of CO recorded over SiC at 50°C was subtracted to different proportions, i.e. 0.5, 0.7, 0.9 and 1.1-fold respectively. The spectra obtained over SiC at the corresponding temperatures under pure Ar were used as background to calculate the pseudo-absorbance.

Acknowledgements

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An *Operando* Molecular Spectroscopic and Density Function Theory (DFT) Calculation Investigation of Methane Aromatization by Supported Mo/ZSM-5 Catalysts

Israel E. Wachs[1]*, Yadan Tang[1], Jih-mirn Jehng[2], James Gallagher[3], Jeffery Miller[3], Jie Gao[4], Simon Podkolzin[4]
[1]*Operando Molecular Spectroscopy & Catalysis Lab, Lehigh University, Bethlehem, PA 18015 (US)*
[2]*Department of Chemical Engineering, National Chung Hsing University 402 (Taiwan)*
[3]*Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60429 (US)*
[4]*Department of Chemical Engineering and Material Science, Stevens Institute of Technology, Hobboken, NJ, 07030(US)*
*iew0@lehigh.edu

Supported Mo/ZSM-5 catalysts are able to convert methane to aromatics, but despite intensive studies many fundamental issues still remain unresolved: the nature of the initial Mo^{6+} oxide species and the active Mo phase during CH_4 activation (MoO_x, MoO_xC_y, MoC_y or Mo_2C).

This study aims to resolve the fundamental issues for CH_4 dehydroaromatization (DHA) by supported Mo/ZSM-5 catalysts with the application of *in situ* and *operando* spectroscopy (Raman, IR, UV-vis, X-ray adsorption spectroscopy) and DFT calculations for a systematic series of catalysts (Si/Al molar ratio from 15-140 and 1-5 wt% MoO_3). Combined *in situ* FT-IR/UV-vis/Raman/XAS/DFT studies have revealed the presence of four distinct isolated surface MoO_x structures: 1) isolated dioxo $(O=)_2MoO_2$ species over two Brønsted acid sites at low Mo loading and high Al content; 2) isolated dioxo $(O=)_2MoO_2$ species over one Brønsted acid site and an adjacent Si-OH group at increasing Mo loading; 3) isolated dioxo $(O=)_2MoO_2$ species over two Si-OH groups at low Al content; 4) isolated mono-oxo $O=MoO_4$ surface site over extra framework Al-OH groups at almost no Al content. The reactivity of these initial Mo oxides and the nature of the active Mo phases during CH_4 DHA are investigated *via operando* Raman-MS spectroscopy, XAS spectroscopy and DFT calculations. The results indicate that: (1) surface dioxo MoO_x species are more reactive than mono-oxo MoO_x species during methane activation; (2) MoO_x species become reduced to poorly-ordered MoO_xC_y nanoparticles (~4 Mo atoms) with predominated oxidation state of Mo^{2+} when aromatics are formed during CH_4 DHA reaction. The MoO_xC_y species activates CH_4 to C_2 hydrocarbons and the ZSM-5 Brønsted acid sites oligomerize the C_2 fragments to aromatics; (3) the *operando* Raman-MS experiments of regenerated Mo/ZSM-5 catalysts during CH_4 DHA reaction implies an important structure-activity correlation: the extent of recovered surface dioxo MoOx species affects the CH_4 DHA reactivity of the regenerated catalysts. These new studies demonstrate how *operando* experiments are able to resolve the fundamental structure-reactivity issues of complex catalytic systems.

Effective bulk and surface temperatures of the catalyst bed of FT-IR cells used for in situ and operando studies.

Frederic Meunier[1,*], Haoguang Li[2], Mickael Rivallan[2], Frederic Thibault-Starzyk[2], Arnaud Travert[2]
[1] Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne, France.
[2] Laboratoire Catalyse et Spectrochimie, ENSICAEN, University of Caen, CNRS, 6 Bd Mare´chal Juin, 14050, Caen, France.
*E-mail: fcm@ircelyon.univ-lyon1.fr

Summary

The temperature prevailing in the catalyst bed of three different IR spectroscopic reaction cells was assessed by the means of thermocouples, an optical pyrometer and reaction rate measurements. One of the cells was a custom-made transmission FT-IR cell for use with thin wafers and the two others were commercial Harrick and Spectra-Tech diffuse reflectance FT-IR (DRIFTS) cells used for the analysis of powdered samples. The rate of CO methanation measured over a 16 wt.% Ni/alumina catalyst was used as a means to derive the effective temperature prevailing in the IR cells from that existing in a traditional (non-spectroscopic) reactor having a well-controlled temperature.

The sample bed of these three IR cells exhibited a significantly lower temperature than that of the corresponding measure thermocouple, which was yet located in or close to the sample bed. The comparison of Arrhenius plots enabled to determine a temperature correction valid over a large temperature range.

The use of an optical pyrometer was assessed with a view at determining the temperature of the surface of the powdered beds and that at the centre of the wafer. The optical pyrometer proved useful in the case of the catalyst powder, which behaved as a black non-reflecting body. On the contrary, the temperature reading was inaccurate in the case of the pressed wafer, probably due to the shiny surface and minute thickness of the wafer, which led to a significant portion of the IR radiation of the surroundings being reflected by and transmitted through the wafer.

The optical pyrometer data showed that the temperature of the surface of the powdered beds was significantly lower than that the bulk of the bed, but that total flow rate and composition did not affect this value.

This work emphasises that the effective bed temperature in spectroscopic cells can be significantly different from those given from measure thermocouples, even when located in the vicinity of the sample, but that the use of calibration curves derived from rate measurements can be used to overcome this problem [1].

Acknowledgements

This work was supported by the French national agency for research (BioSyngOp, ANR-11-BS07-026).

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Liquid-phase cyclohexene epoxidation over X wt % ZrO_2-TiO_2 (X =5, 10, 15 and 20 % Zr) anatase xerogel.

Lahcene Driss [1,2] *, Abderrahime Choukchou-Braham[2], Laurence Pirault-Roy[3] and Charles Kappenstein[3].

[1]*Département de technologies, Faculté des Sciences et Technologies, Université de Bechar, BP 417 Route Kenadsa Béchar 08000, Algeria.*
[2]*Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, Université A. Belkaid, B.P. 119 Tlemcen 13000, Algeria.*
[3]*IC2MP UMR-CNRS 7285, Institute of Chemistry of Mediums and Materials of Poitiers, Faculty of Science, 86022 Poitiers, France.*
(e-mail) drissino@yahoo.fr*

Abstract

Epoxidation reactions are indispensable for the chemical industry in order to produce important chemical intermediates. Catalytic liquid-phase epoxidation of cyclohexene is a commercially important reaction used to produce cyclohexene oxide, which is an essential organic intermediate in the production of fine chemicals. Production of epoxides paves the way to the development of mild and green chemical processes for the synthesis of adipic acid, the raw material used in the production of nylon 6,6[1].

To prepare binary or multicomponent oxide solid solutions by the sol–gel method, the key is to control the hydrolysis and condensation rates of the various molecular precursors used. The difference in reactivity can be minimized by controlled prehydrolysis of the less reactive precursor or by chemical modification of the precursors [2].The aim of the current work was to investigate the additive effect of TiO_2 to ZrO_2 on the structure, morphology and textural properties. Ceramic materials based on zirconium titanate (ZrTiO4) are extensively used in humidity sensors, resonators for microwave telecommunications and catalysis [3].

In this work, we report the sol–gel synthesis of X wt % ZrO_2–TiO_2 mixed oxides, calcined at 500 °C under air. The prepared catalysts are characterized by physico-chemical techniques like infrared spectroscopy (IR), X-rays diffraction (XRD), Analyses ICP-OES, thermal analysis (ATG-ATD) and specific surface determination (BET) to undestand their behavior, and their use as solid catalysts for epoxidation of cyclohexene using Tert-butyl hydroperoxyde (TBHP) as oxidizer.

X wt % ZrO_2–TiO_2 mixed oxides presents a crystalline structure with the presence of TiO_2 anatase phase. This system are strong solid acids showing catalytic activity in different acid catalyzed reactions The best catalytic performance was observed at 6 h reaction time with 15 wt.-% ZrO_2–TiO_2 catalyst in heptane as solvent at 70 °C. The conversion of cyclohexene was 33 % while the selectivity to cyclohexenol was higher (87 %).

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P 8

Near-Ambient Pressure Photoelectron Spectroscopy Investigations for Electronic Structure Changes on Metal Surfaces : UVPES Valence Band Study

Chinnakonda S. Gopinath,* Kanak Roy, Ruchi Jain and Manojkumar Ghosalya
Centre of Excellence on Surface Science, National Chemical Laboratory, Pune 411 008, India
cs.gopinath@ncl.res.in http://nclwebapps.ncl.res.in/csgopinath

Near-ambient pressure photoelectron spectroscopy (NAPPES) is available for a decade, and number of literature reports is increasing fast with this analysis method, although a vast majority is yet to reap its potential (in our opinion). It is also to be mentioned that most of such work reported has been measured at one of the synchrotron radiation centres. Laboratory-based NAPPES systems are very few, and the details of the custom-built NAPPES system (Prevac, Poland) utilised for the present study is available in Roy et al., *J. Phys. Chem. C* **117**, 4717 (2013). For the high inelastic scattering expected/observed at higher pressures (≥0.01 mbar), there has been no reports on valence band photoelectron spectral (VBPES) studies with photon energies less than 100 eV. Needless to say that VBPES with different photon energy gives complementary information; especially with low photon energies, more precise details are possible due to high resolution at low photon energies, including molecular vibrations of reactant/product under in-situ reaction conditions.

Our efforts to explore the VBPES under NAP conditions was very successful and the first report on systematic Cu oxidation to Cu_xO between 300 and 625 K and 0.3 mbar O_2 partial pressure with He I (21.2 eV) and x-ray photons was published recently (K. Roy, C. S. Gopinath, *Anal. Chem.* **86**, 3683 (2014)). Characteristic energy divide between fully filled Cu $3d^{10}$ and O $2p^6$ bands was observed for Cu_2O; on the contrary, a significant energy overlap between Cu $3d^9$ and O $2p^6$ bands was observed for CuO (Fig. 1-left). This provides the direct chemical bonding information. Further, the change in surface potential (from Cu to Cu_2O to CuO) is reflected in the shift in binding energy of gas-phase molecules that are close to the surface, which is very relevant information to understand many phenomena, such as catalysis.

Figure 1: Open-reactor in NAPPES and Cu oxidation to Cu_2O and CuO.

We continued our work in VBPES area of research under NAP conditions to explore other surfaces, namely Pd and Ag. Both surfaces are vulnerable to oxygen diffusion into the sub-surfaces. A change in surface nature from metallic to mild-cationic character upon oxygen diffusion induces significant changes in surface electronic nature as well as the ensuing catalysis. Necessary results obtained from a molecular beam instrument also will be compared.

For the present talk, a brief review of how VBPES works under NAP conditions with an open-reactor design, in spite of low kinetic energy electrons (≤ 15eV), will be explained with Cu oxidation as an example (Fig. 1). This will be followed by the VBPES under NAP conditions on Pd and Ag surfaces. Oxygen interaction with Pd and Ag surfaces under NAP conditions and high temperatures will be presented to demonstrate the changes in surface electronic nature under oxidizing conditions. CO oxidation catalysis carried out on Pd, and epoxidation measured on Ag surfaces will be presented. A correlation between surface changes with catalysis to be presented.

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In Operando Studies of Catalyst Materials by Neutron Scattering

Martin Owen Jones[1], Stewart Parker[1], Zheng Jiang[2]

1. ISIS Neutron Spallation Facility, STFC Rutherford Appleton Laboratory Harwell Oxford, Didcot, OX11 0QX, UK
2. Engineering and the Environment, University of Southampton, Highfield, Southampton, SO17 1BJ

The ISIS neutron spallation facility is a world-leading centre for neutron scattering. The technique is applicable to a great diversity of subjects spanning condensed matter physics, engineering, materials science, chemistry and soft matter. ISIS has a formidable selection of elastic and inelastic neutron scattering instruments to study the physical properties solids and liquids by a number of techniques that include diffraction, total scattering and molecular spectroscopy. In addition, complex sample environment apparatus may be utilised with these instruments that allows materials to be studied under controlled gas environments as a function of temperature, pressure and gas flow. Here we discuss the application of these instruments and various sample environments to materials challenges within the field of catalysis, describe some of the more recent catalysis and catalysis-related experiments, including studies of methane reforming catalysts and highlight the capabilities of the ISIS facility in tackling catalytic challenges.

P 10

Chemical Imaging of Catalysis in Etched Silicon Microreactors with Synchrotron IR

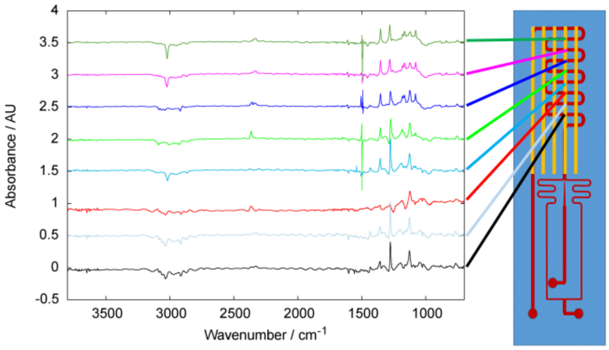
I. P. Silverwood,*[1,2] D. J. Nelson,[3] A. Chutia,[1,2] N. Al-Rifai,[4] E. Cao,[4] P. P. Wells,[1,2] S. P. Nolan,[3] A. Gavriilidis,[4] C. R. A. Catlow[1,2]

*ian.silverwood@rc-harwell.ac.uk
[1]Rutherford Appleton Laboratory, UK Catalysis Hub, Research Complex at Harwell (RCaH), Harwell, Oxon OX11 0FA, UK
[2]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[3]EaStCHEM School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife, KY16 9ST Scotland, UK
[4]Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

In situ reactors on the milligram scale are regularly used for the study of catalysis. In most cases these designs are optimised for the ease of spectroscopic measurement, rather than the fidelity of reaction conditions. It has been shown that great care is therefore needed to provide accurate measurement of in situ catalysts to provide true operando measurement.[1]

Infrared spectroscopy is a cheap and powerful technique to interrogate catalysts, although reactor design must be approached with care to eliminate issues such as high dead volume, catalyst bypass, and poor heat and mass transfer. In addition, the commonly-used diffuse reflectance geometry allows sampling only of part of the catalyst bed. Etched silicon microfluidic reactors offer an improvement in reaction control, as they can eliminate the problems described above. In addition, they have the advantages of flexible design, safe operation at elevated temperature and pressure, and they allow reaction with low quantities of catalyst and reactants.[2] Although such reactors are ideal for measurement of kinetic parameters they have largely been overlooked for spectroscopy due to their more complex manufacture and optical characteristics. Silicon's transparency in the infrared offers the opportunity to couple IR spectroscopy with an idealised environment for catalysis rather than compromising reactor performance by optimising for spectroscopic measurement.

We have performed preliminary experiments using an infrared microscope with synchrotron IR to follow a Ru-catalysed alcohol isomerisation[3] as a function of distance along an etched silicon reactor. With good mixing and idealised continuous flow at known rate, the distance along the channel can be related to time after mixing and thus temporal data can be accessed. Further experiments to be performed at an awarded beamtime session in February investigating both homogeneous and heterogeneous catalysis will also be described. Reactor design, challenges in data analysis, and future directions, including coupling with other techniques will be covered. These reactors are broadly applicable for measurement of heterogeneous and homogeneous catalysis and allow imaging of chemistry along the full reaction path.



Difference IR spectra as a function of position

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P 11

Inner Shell Spectroscopy Beamline – a New X-Ray Tool for Operando Catalysis Research at National Synchrotron Light Source II

Eli Stavitski,* Klaus Attenkofer. William Loo, Cynthia Longo
Photon Sciences Directorate, Brookhaven National Laboratory
Upton, NY 11973, *istavitski@bnl.gov

Introduction

Inner Shell Spectroscopy (ISS) beamline at the National Synchrotron Light Source II is slated to start operations in fall 2016.[1] It is s a damping wiggler beamline which will provide X-ray radiation in the range of 4 to 36 keV and the resolution of 10^{-4} and the flux of $\sim 10^{15}$ photons/s . Quick energy scanning capabilities, together with the wide energy spectrum will allow ISS to provide world-class capabilities for X-ray spectroscopic measurements. The key instrument at ISS is a sample chamber, which integrates detection system and sample environment allowing high detection efficiency and exceptional opportunities to develop in-situ and operando experiments for heterogeneous applications.

Discussion

The concept of the Photon Delivery System (PDS) of ISS beamline includes low-energy filter to manage significant wiggler heat load, a two-mirror system (an internally cooled flat and the collimating mirror), the dual monochromator and a toroid mirror to deliver focused light into the experimental endstation. The heart of the PDS is a direct drive LN2 cooled direct drive monochromator, which allows for fast scanning (1-10 Hz) over a full EXAFS energy range. High harmonics contribution is reduced with a set of harmonics rejection mirror to be installed at the endstation. The beam of 50-100 μm at the sample is achieved by using polycapillary optics.

From the heterogeneous catalysis application perspective two unique developments at ISS are the sample chamber and integrated gas handling system. The sample chamber integrates sample environment, which allows to rapidly changing capillary reactor temperature, by means of laser heating and liquid nitrogen-based cryostat, as well as the X-ray detectors. Gas handling system delivers reactive mixtures to the catalytic sample in the reactor. A variety of gases will be available, covering significant fraction of possible experiments. In addition, liquids can be delivered to the reactors as vapors. The mixture composition will be defined using mass flow controllers, with up to 8 gases per channel and two independent channels; fast (under 1 s) switching between the channels will be possible for kinetic and modulation measurements. Gas handling system controls will be fully integrated into the beamline controls system.

Several X-ray detector configurations will be available at ISS, including traditional Silicon Drift Detector array as well as X-ray emission spectrometers in van Hamos and Spherical Backscattering analyzer geometries. Extraction of the emitted light will be performed with polycapillaries, dramatically increasing solid angle coverage. With this detector selection, X-ray absorption, emission, resonance scattering as well as X-ray energy loss spectroscopy to probe light element will become possible.

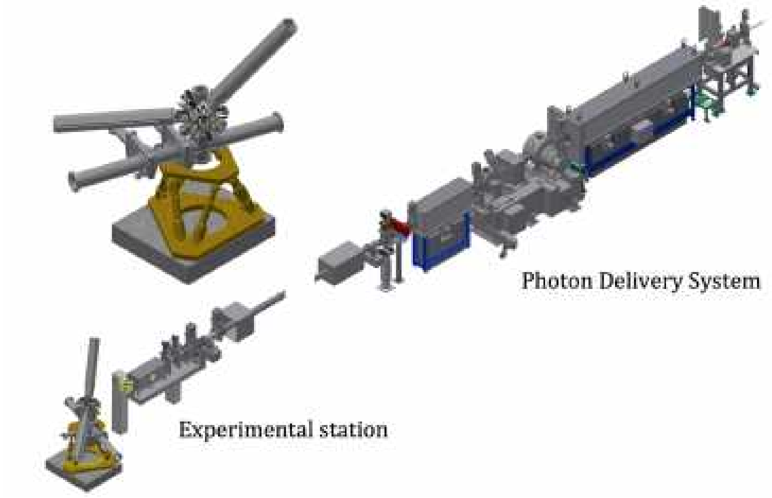

Figure 1. Conceptual layout of the ISS beamline. Upper left corner shows the sample chamber with automated sample loader systems and two X-ray emission spectrometers (other spectrometers are removed for clarity)

Significance

ISS beamline is a novel tool many scientists in catalysis will benefit from. Given the startup day in 2016, the time is ripe to develop first-science experimental program for the beamline in coordination with the community.

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P 12

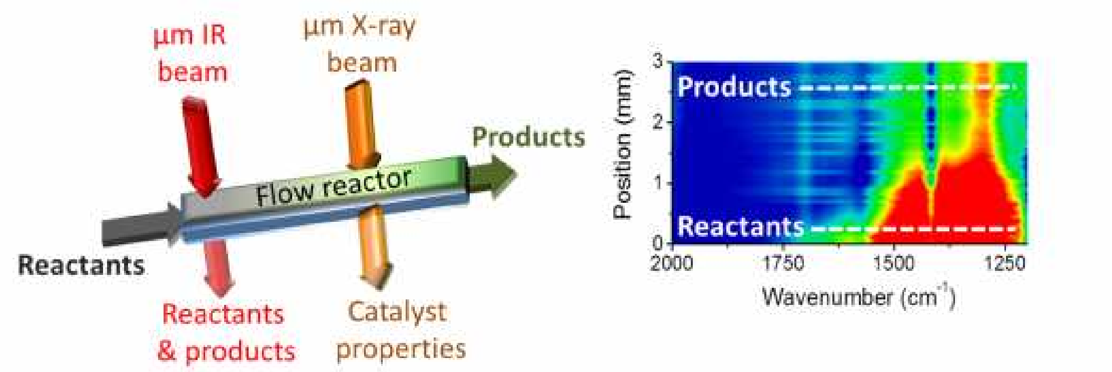
High Spatial Resolution *Operando* IR and X-ray Microspectroscopy Measurements of Multistep Catalytic Reactions in Flow Reactor

Elad Gross

Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Elad.gross@mail.huji.ac.il

Molecular-level analysis of catalytic reactions in flow reactors and detection of short lived intermediates are essential for optimization of complex reactions. In this study, multistep catalytic reaction in flow reactor was analyzed by spectral mapping of the catalyst and the organic phase with a spatial resolution of 15 μm, employing micrometer-sized synchrotron-sourced IR and X-ray beams. The catalyst in this reaction was two nanometer sized Au nanoclusters that were encapsulated within a dendrimer matrix and loaded on mesoporous SiO_2 support. The catalyst was packed within a flow microreactor and its reactivity was tested toward the cascade reaction of dihydropyran formation. *In-situ* synchrotron-sourced IR microspectroscopy detected the reactant-into-product transformation along the flow reactor. By tuning the residence time of the reactants, full kinetic analysis of the catalytic reaction was achieved. X-ray absorption microspectroscopy scan along the flow reactor correlated locally-enhanced catalytic conversion, as detected by IR microspectroscopy, to areas with high concentration of Au(III), the catalytically active species. This study demonstrates the fundamental understanding of mechanism of catalytic reactions that can be gained by detailed *in-situ* mapping of multistep reactions in flow reactors.



P 13

Investigation of oxidation catalysts by *in situ* electrical conductivity measurements in correlation with their catalytic performances

Ionel Popescu[a], Ioan-Cezar Marcu[a,b]

[a] Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018 Bucharest, Romania
[b] Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018 Bucharest, Romania.
E-mail: ioancezar.marcu@chimie.unibuc.ro

The electronic and redox properties of oxide-based catalysts strongly influence their catalytic performance in both selective and total oxidation reactions [1]. This is why, establishing relationships between the electronic and redox properties of oxide catalysts and their activity and/or selectivity is essential for a better understanding of the reaction mechanism and, consequently, for improving their catalytic performances on a scientific basis or for a rational design of new efficient catalysts. *In situ* electrical conductivity measurements constitute a powerful technique for the investigation of electronic and redox properties of oxidation catalysts and can help understanding their catalytic behavior [2].

Oxidation or reduction of semiconducting oxide-based catalysts can be evidenced by following the evolution of their electrical conductivity as a function of the nature of the gas phase in contact with the solid. Thus, exposure of a p-type semiconducting oxide to oxygen leads to the increase of its electrical conductivity with respect to that in inert atmosphere, according to the following equilibrium:

$$O_{2(gas)} \leftrightarrows h^{\bullet} + O^{-}_{2(ads)} \leftrightarrows h^{\bullet} + 2O^{-}_{(ads)} \leftrightarrows 2h^{\bullet} + 2O^{2-}_{(ads)} \leftrightarrows 2O^{\times}_{O} \qquad (1)$$

where $h^{\bullet}$ represents a hole and $O^{\times}_{O}$ a lattice oxygen anion of the solid. The electrons trapped by the adsorbed oxygen are provided by the valence band of the oxide where new positive holes are created. On the contrary, exposure to a reducing gas such as a hydrocarbon leads to the consumption of lattice oxygen with the subsequent formation of oxygen vacancies. In this case electrons are released in the valence band of the oxide resulting in the decrease of the positive holes concentration and thus in the decrease of the electrical conductivity.

In contrast with the p-type oxides, the exposure of a n-type semiconducting oxide to oxygen leads to the decrease of its electrical conductivity with respect to that in inert atmosphere, according to the equilibrium depicted in Eq. (2):

$$O_{2(gas)} + e' \leftrightarrows O^{-}_{2(ads)} + e' \leftrightarrows 2O^{-}_{(ads)} + 2e' \leftrightarrows 2O^{2-}_{(ads)} \leftrightarrows 2O^{\times}_{O} \qquad (2)$$

where e' represent free electrons provided by the conduction band of the oxide. The exposure to a reducing gas leads to the consumption of lattice oxygen with the subsequent formation of oxygen vacancies but, in this case, electrons are released in the conduction band of the oxide resulting in the increase of the free electrons concentration and thus in the increase of the electrical conductivity.

The electrical conductivity of oxide-based catalysts was studied as a function of temperature and oxygen partial pressure and temporal responses during sequential exposures to air, hydrocarbon-air mixture (reaction mixture) and pure hydrocarbon in conditions similar to those of catalysis were analyzed. Correlations between their semiconductive and redox properties and their catalytic performance in oxidative dehydrogenation of light alkanes or total oxidation of methane reactions have been established and the origin of differences in their catalytic behavior was elucidated.

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P 14

EXAFS study under reaction conditions of V-based catalytic materials

M.O. Guerrero-Pérez[1], E. Mikolawska[2], R. López-Medina[2], E. Rojas[2], M.A. Bañares[2]

[1] Departamento de Ingeniería Química. Universidad de Málaga. E-29071- Málaga (Spain).
oguerrero@uma.es. [2] Catalytic Spectroscopy Laboratory, Instituto de Catálisis y Petroleoquímica; CSIC;
Marie Curie 2; E-28049-Madrid (Spain).

Introduction and objectives

X-Ray Absorption Spectroscopy has been used to analyze the oxidation state and environmental structure around vanadium atoms in three different catalytic systems: VPO, VSbO, and MoVNbTeO, which are well known as active and selective for light alkane partial oxidation reactions. These studies have been performed under reaction conditions with an in situ cell (Figure 1A).

Results

Figure 1B shows the results obtained for the alumina supported VPO catalysts, together with the compounds that are used as reference. Comparing these main-edge and pre-edge positions it may be concluded that the 8V9PAl precursor contains mainly V^{4+} species under reaction conditions, whereas the value of the main-edge position in the case of the catalyst suggests oxidation state of vanadium between +4 and +5, indicative of a mixture of both. In the case of VSbO catalysts, only V^{5+} appears to be present under reaction conditions at room temperature, whereas V^{4+} species appear when temperature is increasing, and, again, a mixture of both oxidation states is detected. Some changes in vanadium environment are observed under reaction conditions in the case of MoVNbTeO catalysts. The results clearly shows how this technique is useful for underlining changes in oxidation state and environment of vanadium species under reaction conditions.

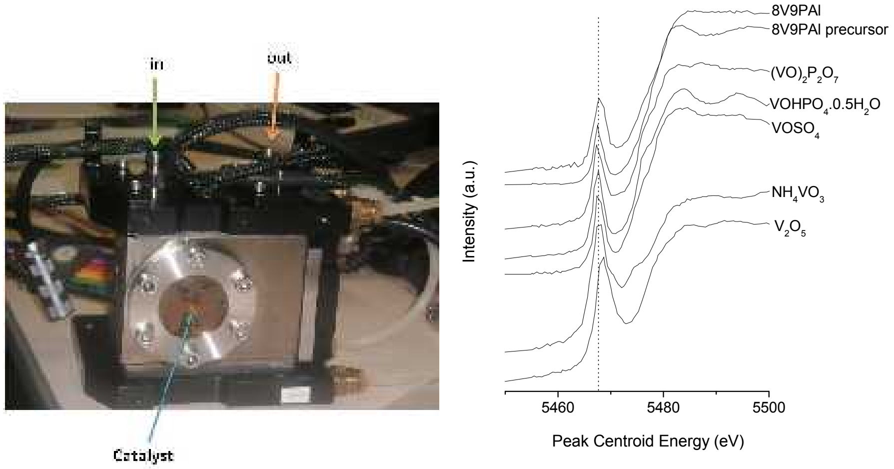

Figure 1A. In situ cell. 1B XANES spectra of bulk and supported VPO catalysts, their precursors and reference samples

A universal reactor cell for operando experiments?

V. Marchionni,[1] M. Nachtegaal,[1] G.L. Chiarello,[2] Oliver Kröcher,[1] D. Ferri[1],
[1] Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland; [2] Università degli Studi di Milano, I-20133 Milano, Italy

The understanding of structure-performance relationships under working conditions by the combination of various in situ spectroscopic and diffraction methods is crucial for catalyst and process development. However, each technique requires specific sample geometry and environment. The combination of two or more methods in a single reactor cell is highly desirable in order to guarantee identical experimental conditions. We describe a novel cell specifically designed to combine X-ray methods with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in a single experiment. The novelty of the cell design compared to currently available examples is that both radiations are passed through an X-ray window and an IR transparent window in direct contact with the sample.[1] The cell was designed to represent a plug flow reactor, has reduced dead volume in order to allow for fast exchange of gases and is therefore suitable for experiments under fast transients, e.g. according to the concentration modulation approach, where a short residence time is required. The cell is always coupled to the same gas feeding system ensuring that an identical measurement can be performed with different spectroscopic and diffraction methods. The cell was tested at SuperXAS beamline at the SLS studying CO oxidation on Pt-based three way catalysts by synchronously recording transmission X-ray absorption (XAS) and DRIFT spectra.[1] In order to avoid interference from the crystalline IR transparent material (e.g., CaF_2, MgF_2, diamond) on the XAS spectra a 500 μm carbon-filled hole was laser drilled in the center of the window. High quality time-resolved XAS and DRIFTS data of a 2 wt% Pt/Al_2O_3 catalyst were obtained in concentration modulation experiments where CO (or H_2) pulses were alternated to O_2 pulses at given temperatures. Additional information could be obtained on the Pt redox dynamics under working conditions because of the improved sensitivity provided by coupling of the modulation approach with phase sensitive detection (PSD).

High energy resolution off-resonant spectroscopy (HEROS) experiments were conducted at the Pt L_3-edge with Pt/Al_2O_3 and $Pt/CeO_2/Al_2O_3$ samples.[2] PSD provided high chemical sensitivity and allowed for the identification of adsorbed species, i.e. CO adsorbed on Pt and an intermediate state attributed to chemisorbed O on Pt as confirmed by simulations. Similarly, time-resolved resonant X-ray emission spectroscopy (R-XES) data were collected at the Ce L_3-edge to study the influence of ceria on the reducibility of Pt. The fluorescence geometry of the emission spectroscopy method enables high time resolution that cannot be achieved in conventional fluorescence measurements.

The cell was also utilized in synchrotron high energy X-ray diffraction (XRD) experiments that confirmed the results obtained with a modified DRIFTS cell.[3] Analysis of 2 wt% Pd supported on $Ce_{1-x}Zr_xO_2$ by high energy XRD during repeated CO and O_2 pulses demonstrated the suitability of the modulation approach to obtain details of structural changes associated with Pd nano-particles of 1-2 nm. The temporal evolution of the Pd(111) and Ce(111) reflections revealed that Ce maintained Pd oxidized in the CO pulse, whereas reduction was detected at the beginning of the O_2 pulse. The range and the quality of the XRD data allow in principle for pair distribution function (PDF) experiments.

The cell windows can be further exchanged to enable for Raman and UV-visible spectroscopy measurements thus making the cell suitable for various spectroscopic and diffraction methods typically used in the operando analysis of materials under representative operation conditions.

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P 16

Transient XANES of CO oxidation: from spectroscopy to reactor level kinetics

Urs Hartfelder (urs.hartfelder@chem.ethz.ch)[1] , Jeroen A. van Bokhoven[1,2]

[1]Institute for Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich

[2]Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

In situ spectroscopy of heterogeneous catalysts is key in understanding catalytic activity and thus designing better catalysts. It is however limited by the spectator problem, i.e. the fact that the most abundant species is not necessarily the most active or even active at all. In fact, since highly active species tend to be short-lived, they might be only a minority of the observed species. Transient spectroscopy, i.e. the observation of the reaction under non steady-state conditions, circumvents that problem, since reactive species should adapt to altered conditions much faster than spectators. In addition, transient spectroscopy has the advantage of providing the equivalent of multiple steady-state experiments in terms of kinetic data.

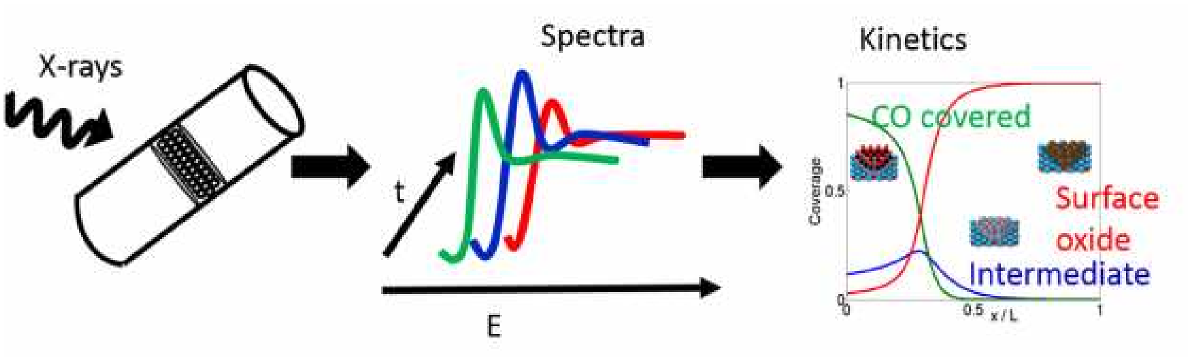

Figure 1: Time –resolved x-ray absorption spectroscopy is applied during a transient experiment. The resulting spectra are analyzed, including extraction of any intermediate spectra. The obtained data permit the fitting of detailed, reactor level models of reaction kinetics, which are necessary for the interpretation of transient results. The figure on the right shows the measured surface fractions of carbon monoxide covered platinum (green), the intermediate (blue) and the surface oxide (red) through the reactor in the steady state after the switch.

In this work, we apply transient kinetics to light-off in CO oxidation over platinum nanoparticles supported on aluminum oxide triggered by a concentration switch. The formation and decay of a short-lived phase with low coverage of adsorbates was observed. Two distinct reaction mechanisms (through surface oxide and chemisorbed oxygen) are used to describe the kinetic data. A reactor level simulation based on the spectroscopic results is able to independently reproduce the mass spectrometry results. It is shown how the combination of transient spectroscopy with mass spectrometry and chemometric analysis can be used to achieve reactor level kinetic understanding.

P 17

Insight into CO_2 methanation mechanism over NiHNaUSY zeolites: an *Operando* IR study

A. Westermann[a], B. Azambre[b], M.C. Bacariza[a], I. Graça[a], J.M. Lopes[a], C. Henriques[a]

[a] CQE, Centro de Química Estrutural, Instituto Superior Técnico, UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

[b] Université de Lorraine, Laboratoire de Chimie et Physique Approche Multi-échelle des Milieux Complexes (LCPA2MC), EA 4632, Institut Jean Barriol, Rue Victor Demange, 57500 Saint-Avold, France

corresponding author: westermann.alexandre@hotmail.fr

Nowadays, CO_2 emissions arising from fossil fuels are becoming more and more critical for the ecosystem regarding the greenhouse gases effect. Among several solutions CO_2 hydrogenation appears to be one of the possible sustainable solutions to reach EU objectives. In this way, CO_2 hydrogenation has been studied over a wide range of supports (e.g., Al_2O_3, Ce-Zr mixed oxides) and using VIIIB metals (e.g., Rh, Ru, Pd and Ni). Despite the existence of several mechanistic studies, the active surface species and reaction pathways are still under debate. Some information relative to intermediates and actives sites are now mandatory to improve the catalytic activity and selectivity to methane of Ni-based zeolites.

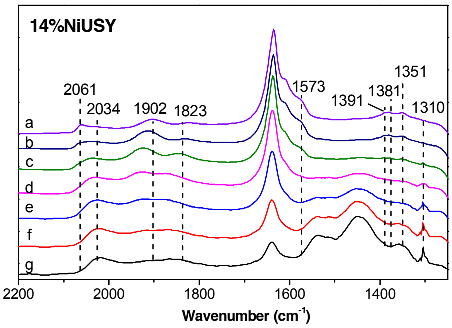

Figure 1 – FTIR spectra under $Ar/H_2/CO_2$ (75:20:5) mixture over 14%NiUSY zeolite; (a) 150°C, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, (f) 400°C, (g) 450°C.

In this study, several *Operando* IR measurements were performed under CO_2/Ar or $CO_2/H_2/Ar$ onto Ni-impregnated zeolites (with Ni contents from 5 to 14 $\%_{wt.}$). It appears that, in absence of hydrogen, CO_2 is almost not adsorbed but formates and carbonyls were detected in presence of hydrogen. Hence, the CO_2 hydrogenation mechanism does not probably pass through the carbonate formation as intermediate, but rather passes through the formate dissociation onto Ni^0 particles leading at temperatures below 300°C to the formation of adsorbed CO and at higher temperature to methane. Considering the absence of basic sites, CO seems to be the “true” intermediate in the CO_2 methanation reaction. This mechanism can explain the better activities obtained for the higher Ni contents ($14\%_{wt.}$), since the increase of reduced Ni offers new adsorption sites for CO adsorption and CO/H_2 dissociation. A detailed mechanism of the pathways involved in CO_2 methanation over NiHNaUSY catalysts was elaborated in accordance with infrared spectroscopic data.

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Operando Molecular Spectroscopy during Catalytic Biomass Pyrolysis

Christopher J. Keturakis,[1*] Olga B. Lapina[2], Victor V. Terskikh[3], and Israel E. Wachs[1]
[1]*Operando Molecular Spectroscopy and Catalysis Laboratory, Chemical Engineering Department, Lehigh University, Bethlehem, PA 18015 USA*
[2]*Boreskov Institute of Catalysis, SB RAS, Prosp. Lavrentieva 5, 630090 Novosibirsk, Russia*
[3]*Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N6N5*
*CJK209@lehigh.edu

Perpetually increasing petroleum prices and finite petroleum resources have become large societal concerns in recent decades, causing a search for new, renewable and energy-efficient sources of liquid hydrocarbon fuel. With biomass being the only sustainable source of carbon, advances in technology for biomass conversion are critical for the development of renewable fuel sources. Significant scientific understanding and improvement of catalysts for biomass pyrolysis can only come from a fundamental research approach to all aspects of biomass conversion.

We have developed an *operando* Raman/IR-MS spectroscopy system for catalytic biomass pyrolysis that simultaneously monitors catalyst structure, biomass structure, surface reaction intermediates, coking, char formation, and over 40 major gas phase pyrolysis products (determined by GC-MS). Model supported 1-10% Al_2O_3/SiO_2 catalysts were synthesized and characterized (*in situ* Raman, *in situ* IR, and high field (21.1T) *ex situ* dehydrated ^{27}Al NMR spectroscopy). The chemical nature (Brönsted or Lewis acid sites; BAS or LAS) of specific surface AlO_x acid sites was determined from *in situ* IR-CO adsorption. These well-defined catalysts were employed during the catalytic pyrolysis of cellulose, hemicellulose (xylan), lignin, their monomers (glucose and xylose), and woody biomass to determine correlations between specific value-added chemicals, required acid site nature, and surface AlO_x active site coordination. Results were also compared to popular HZSM-5 catalysts (Zeolyst) with different Si/Al ratios (15 to 140).

Results of *operando* spectroscopy experiments during catalytic biomass pyrolysis revealed that there are several intermediates on the catalyst surface depending on the biomass source, including furans, conjugated alkenes, alkenes conjugated to aromatics, and small cyclic rings with carbonyl groups. Demethylation of small aromatics (such as toluene or xylene) was determined to be the pathway for benzene production while methylation is the route to larger methylated aromatics such as 1-methylnaphthalene. The catalytically assisted dehydration of xylose into furfural was observed to be a key step in furfural production. Aromatic polymerization into graphite-like coke was observed to be the major catalyst deactivation mechanism. The production of furfural, benzene, toluene, and xylene correlated with the presence of BAS associated with AlO_5 while large aromatics, such as naphthalene, correlated with AlO_6 LAS. Similar correlations were found for glucose and cellulose catalytic pyrolysis. In general, cellulose and xylan (polymers) pyrolysis trends indicate that greater acid site strength is needed than for glucose and xylose (monomers) pyrolysis. For lignin pyrolysis, strong AlO_4 BAS selectively cleaved the C_1-C_α propenyl ligand bond and enhanced demethoxylation.

This talk will explore the developed correlations for value-added chemicals from each major fraction of biomass (cellulose, hemicellulose, lignin and whole woody biomass). This is the first application of *operando* spectroscopy to biomass conversion and the method developed here paves the way for definitively establishing catalytic structure-activity relationships for catalytic biomass pyrolysis in future studies.

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An *Operando* Molecular Spectroscopic Study of Ethylene Polymerization by Supported CrO_x/SiO_2 Catalysts

Anisha Chakrabarti* and Israel E. Wachs
Operando Molecular Spectroscopy & Catalysis Laboratory,
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015 USA
*anc412@lehigh.edu

Ethylene polymerization by the supported CrO_x/SiO_2 catalysts was discovered in the 1950s at Phillips Petroleum by J.P. Hogan and R.L. Banks. The main product of this system is high-density polyethylene (HDPE) and is responsible for a large share of the HDPE produced globally. Advantages to using this system include that it functions without the use of activators and can synthesize many types of PE. Additionally, the reaction works at relatively low temperatures (80-180°C) and pressures (<50 bar).

Although supported CrO_x/SiO_2 ethylene polymerization catalysts have been extensively studied over the years, the same fundamental structural and mechanistic questions are still being debated today with researchers being no closer to a common view. For example, the initial molecular structure of the oxidized surface $Cr^{+6}O_x$ site has been proposed to be present as isolated surface dioxo CrO_4, isolated surface mono-oxo CrO_5, and dimeric surface Cr_2O_7, while the chromia oxidation state during ethylene polymerization has been proposed to be reduced Cr^{+2} and Cr^{+3}. Additionally, the structure-activity relationships are absent, and the reaction mechanism, particularly the initiation mechanism, remains elusive. The objective of this study has been to determine the structure-activity relationship for the SiO_2-supported catalytic active chromia surface sites for ethylene polymerization.

To address the molecular details of ethylene polymerization by supported CrO_x/SiO_2 catalysts, modern *in situ* molecular spectroscopic techniques were applied before and during reaction conditions. The initial supported CrO_x/SiO_2 catalyst was found to only contain isolated chromia sites (very high UV-vis edge energy value), a significant fraction of CrO_4 coordinated sites (pronounced XANES pre-edge feature) and two distinct surface chromia sites (dioxo $(O=)_2CrO_2$ and mono-oxo $O=CrO_4$). *In situ* Raman spectroscopy during ethylene polymerization revealed that the surface dioxo CrO_4 site reduces and becomes activated more easily than the surface mono-oxo CrO_5 site. The corresponding *in situ* UV-vis and *in situ* XANES experiments verified the reduction of Cr^{+6} to Cr^{+3} for both the dioxo and mono-oxo surface chromia sites during ethylene polymerization. *Operando* IR spectroscopy detected the formation of active sites, surface intermediates, and the condensed PE product.

This study has addressed confusion in the literature for ethylene polymerization by the supported CrO_x/SiO_2 catalysts. Employing the same experimental conditions for each *in situ* technique has allowed now for the determination of the molecular and electronic structures of the CrO_x sites on SiO_2 for the initial oxidized catalyst as well as the catalyst during ethylene polymerization. This presentation will address the catalytic roles of the two distinct surface CrO_x species on SiO_2 in the ethylene polymerization reaction.

P 20

Real-time X-Ray Diffraction Computed Tomography on a Cobalt-based Fischer-Tropsch catalyst

P. Senecal[1,2], S. D. M. Jacques[1,3], M. Di Michiel[4], J. Paterson[5], E. Ferguson[5], A. M. Beale[1,2*]
[1]*UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell, OX11 0FA, UK*
[2]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK*
[3]*School of Materials, University of Manchester, Manchester, Lancashire M13 9PL, UK*
[4]*The European Synchrotron Facility, 6 Rue Jules Horowitz, 38000, Grenoble, France*
[5]*BP Chemicals, Conversion Technology Centre, HRTC-DL10 Saltend, Hedon, Hull, HU12 8DS, UK*
**corresponding author: andrew.beale@ucl.ac.uk*

X-Ray Diffraction computed tomography (XRD-CT) is a relatively recent synchrotron-based diffraction measurement technique capable of imaging materials undergoing chemical change under *operando* conditions [1]. Here, the method has been used for the first time on a cobalt based Fischer-Tropsch (FT) catalyst while under reduction and then under real FT conditions (250 °C, CO/H_2) in order to follow the 2 dimensional evolution of the cobalt phases during these steps. This necessitated mounting the catalyst body in a quartz cell with a gas delivery connector and following the exhaust gases with a mass spectrometer. This experiment was carried out at station ID15A of the ESRF (Grenoble, France) using a high energy monochromatic pencil beam.

Through the reduction and FTS on the Co/Al_2O_3 catalyst, three cobalt phases are observable: Co_3O_4, CoO, and Co fcc. Figure 1 shows the reconstructed images of those cobalt phases.

As expected, the catalyst presents a lower amount of cobalt oxide after reduction. However, CoO and Co_3O_4 are still visible after a high temperature under H_2. This shows that not all the cobalt is reduced to fcc Co during this step. Furthermore, during FTS, the cobalt on the outer circumference undergoes a major re-oxidation (CoO and Co_3O_4) which has been reported as a potential effect of the presence of water in the FT products [2]. This significantly reduces the metallic Co fcc in this area. There is ambiguity in the current literature over the occurrence of this re-oxidation. Some authors [3] claim that no re-oxidation occurs but this could be due to the small size of the particle under investigation. Others [2] do observe re-oxidation however their measurements have no spatial component. Using XRD-CT to obtain the spatial distribution of each cobalt phase over the catalyst pellet during reaction may lead to an explanation of these opposing experimental observations.

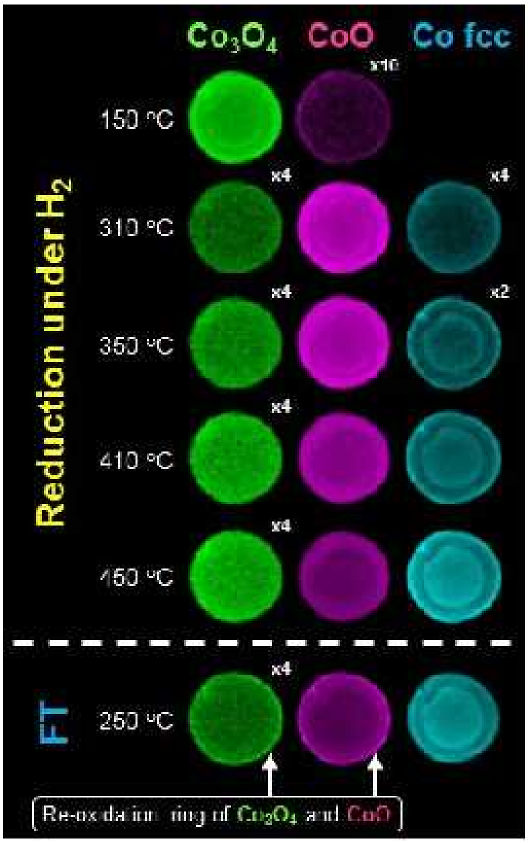

Figure 1: Reconstructed images of cobalt phases observed under reduction and during FTS (250 °C) of a γ-Al_2O_3 supported Co catalyst precursor

This experiment shows the large potential of using XRD-CT as an *operando* spectroscopic technique for the understanding of the formation and evolution of active phases inside a catalyst body under real conditions of gas and temperature. XRD-CT is a powerful tool to follow spatial chemical evolution over time and could greatly benefit the understanding of other catalytic systems.

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P 21

The Role of Brønsted and Lewis Acid Sites in the Selective Dehydration of Glycerol

Guo Shiou Foo, John R. Copeland, Daniel Wei, David Sholl, Carsten Sievers
Georgia Institute of Technology, School of Chemical & Biomolecular Engineering, Atlanta, GA, USA,
carsten.sievers@chbe.gatech.edu

Glycerol is the major by-product from biodiesel production by transesterification. To ensure economic viability, it is crucial to convert glycerol to value-added chemicals. Acrolein can be produced by dehydration of glycerol. It is currently produced by selective oxidation of propylene and used in the syntheses of acrylic acid and DL-methionine. Dehydration of glycerol has been studied over many catalysts including zeolites, heteropoly acids, niobia and alumina. However, controlling the selectivity of this reaction remains a challenge because the relevant surface reactions are not understood in detail. In the present work, in-situ IR spectroscopy is used to identify surface intermediates to deduce reaction paths.

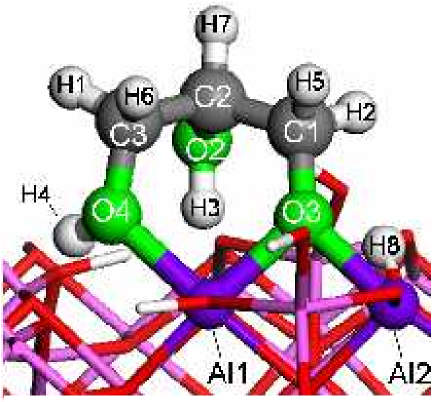

Figure 1: Most stable surface species formed from glycerol on γ-Al_2O_3 based on DFT calculations.

When glycerol was adsorbed on γ-Al_2O_3, blue shifts of the C-O stretching bands indicated that all alcohol groups interact with the surface [1]. By forming multiple bonds with the surface, glycerol can compete favourably with co-adsorbed water for surface sites. The most stable surface species from glycerol was identified by DFT calculations (Figure 1): One of the primary alcohol groups forms a bridging alkoxy bond on a Lewis acid site (LAS), while the other primary alcohol group interacts non-dissociatively with the same site. In addition, the secondary hydroxyl group forms a hydrogen bond with the surface. The vibrational frequencies from experimental and theoretical studies were in very good agreement [1].

Glycerol formed the same surface species on various Nb_2O_5 samples with different concentrations of Brønsted and Lewis acid sites [2]. In case of Na^+-exchanged niobia, which contained no Brønsted acid sites (BAS), only very small bands corresponding to dehydration products were observed. When a monolayer of glycerol was impregnated on niobia with BAS and heated up, chemisorbed glycerol and hydroxyacetone were the main surface species (Figure 2). This indicates that the interaction with the LAS polarizes the primary alcohol group sufficiently to render it susceptible to dehydration, producing 2-propene-1,2-diol, which can easily tautomerize to hydroxyacetone. However, the dehydration step still requires the aid of a Brønsted acid site. Hydroxyacetone is commonly considered a less desired product.

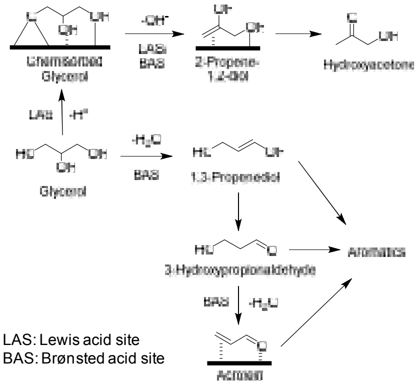

Figure 2: Scheme for dehydration of glycerol over Brønsted and Lewis acid sites.

When more than a monolayer of glycerol was present, the IR spectra also contained characteristic peaks of acrolein and monoaromatics. The formation of acrolein requires the secondary alcohol group of glycerol to be eliminated first (Figure 2), which is the favored over BAS in the absence of steric factors due to the higher stability of the secondary carbenium that is formed in the transition state. The primary dehydration product of this reaction, 1,3-propenediol, can tautomerize to 3-hydroxypropionaldehyde, which is readily converted to acrolein in a second dehydration step. Oligomerization and formation of aromatics occur if the density of unsaturated surface species is sufficiently high.

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P 22

An operando IR study of the synergetic effect between $C_{10}H_{22}$ and NH_3 for NOx-SCR over a silver-alumina catalyst

Kévin BECHOUX[a], Olivier MARIE[a], Philippe BAZIN[a], Asima Sultana[b], Hideaki Hamada[b] Motoi Sasaki[b] and Marco DATURI[a]
olivier.marie@ensicaen.fr
[a] Laboratoire Catalyse et Spectrochimie, UCBN, UMR CNRS 6506, ENSICAEN 6 Bd Mal Juin 14050 Caen France.
[b] Research Center for New Fuels and Vehicle Technology, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Japan.

In the upstream of the SCR catalyst, several reducing agents are present such as unburnt hydrocarbons, which can potentially reduce NOx species. This study aims at understanding the effect of feeding both a hydrocarbon ($C_{10}H_{22}$) and ammonia on the NOx conversion. To distinguish the route for each reducing agent, isotopic experiments using ^{15}N-labeled ammonia ($^{15}NH_3$) were undertaken. Moreover, the progressive introduction of the components in the reaction flow made possible to identify several phenomena that enhance or poison the deNOx capacity of the catalyst.

It thus appears that ammonia is strongly oxidized in presence of a high concentration of oxygen. This oxidation leads to several products such as N_2O or N_2 but also NO (Figure 1).

Obviously, the formation of nitrogen monoxide by ammonia oxidation should negatively impact the deNOx capacity of the catalyst. Moreover, when only $^{15}NH_3$ was used as a reducing agent, the conversion of NO was extremely weak due a strong water inhibiting effect.

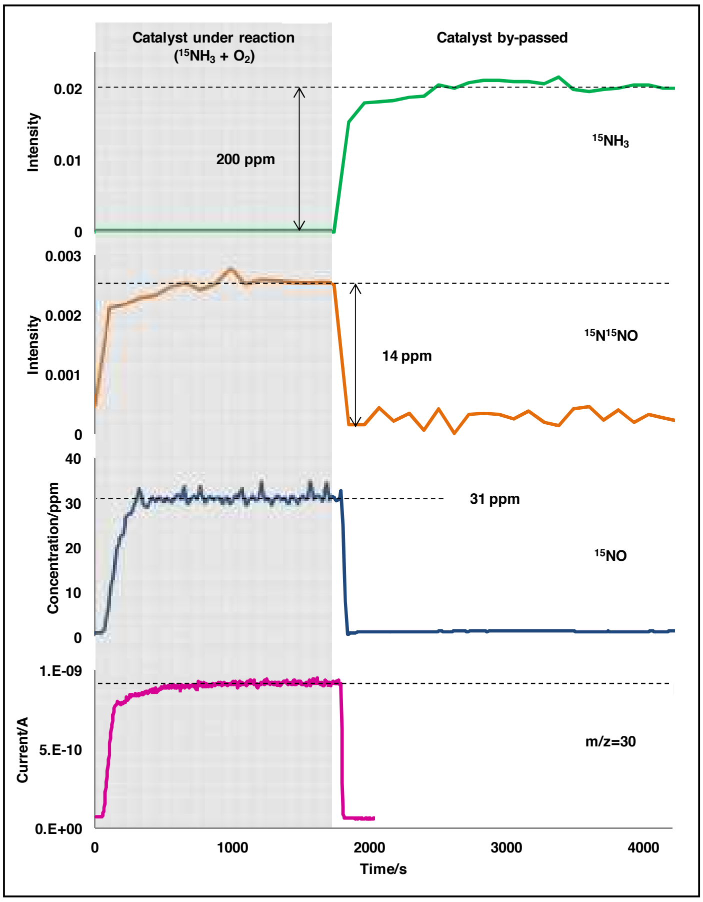

Figure 1: Evolution of the $^{15}NH_3$, $^{15}N^{15}NO$, ^{15}NO and $^{15}N^{15}N$ concentrations during the reaction involving 200 ppm $^{15}NH_3$ + 5% O_2 at 653K over Ag/Al_2O_3 as measured by IR gas, chemiluminescence and MS respectively.

In parallel, when $C_{10}H_{22}$ was used only as a reducing agent, the carbon monoxide generated by its oxidation allowed to produce isocyanates upon reaction with nitrogen monoxide. These species are primarily formed on the silver particles and then migrate onto the alumina support. When H_2O is added to the reaction flow, isocyanates are quickly hydrolyzed to ammonia that further reduces NOx into N_2 with a high selectivity (no N_2O was observed by gas phase FTIR). The SCR involving the locally formed NH_3 is however still slow in presence of water as revealed by the detection of non-reacted ammonia at the outlet of the reactor cell.

Finally, with both $^{15}NH_3$ and $C_{10}H_{22}$ as reducing agents, the "decane" route still allows the NO reduction via the formation of in situ ammonia produced upon isocyanates hydrolysis. Moreover, it was observed that the ^{15}NO formed by the O_2 assisted oxidation of $^{15}NH_3$ reacts with CO to give ^{15}NCO that further gives back $^{15}NH_3$ upon hydrolysis. In wet conditions, the total amount of 'in situ' produced ammonia (thus in the close vicinity of active sites) is thus higher in the simultaneous presence of ammonia and decane than with only decane as a reducing agent. This phenomenon consequently leads to an increased NO conversion due to the above mentioned synergetic effect.

P 23

Operando DRIFTS investigation of the preferential oxidation of CO over bimetallic Pt-Sn catalysts: evidence of surface segregation.

Alina Moscu[1,*], Laurent Veyre,[2] Chloé Thieuleux,[2] Frederic Meunier,[1] Yves Schuurman[1]
[1]Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne (France)
[2]Université de Lyon, Institut de Chimie de Lyon, LC2P2, UMR 5265 CNRS-CPE Lyon-UCBL, CPE Lyon, 69100 Villeurbanne, France
*E-mail: alina.moscu@ircelyon.univ-lyon1.fr

Introduction

PEM fuel-cell technology requires virtually CO-free hydrogen feedstocks. Preferential oxidation (PROX) aims at removing small amounts of CO in H_2-rich streams by catalytic oxidation of CO at low temperatures, with minimal production of water. Bimetallic Pt-Sn catalysts have shown much higher activities for CO oxidation and PROX than those based solely on Pt. The actual state of the active phase under reaction conditions is still a matter of debate. To further explore this issue, operando DRIFTS (Diffuse Reflectance Infrared Fourier Transformed Spectroscopy) experiments under PROX conditions were performed on alumina-supported Pt-Sn and Pt exhibiting both well-controlled particle sizes.

Results and Discussion

An Agilent 3000 A microGC was used to analyze the reaction effluent collected after a modified Spectra-Tech DRIFTS reaction cell described elsewhere [1]. The Pt-Sn/alumina was pre-reduced at 400°C, which was demonstrated to lead to a Pt-Sn alloy phase characterized by a Pt-bound CO(ads) stretching band at ca. 2050 cm^{-1} [1]. The PROX feed was introduced at 50°C and the activity was monitored over a temperature cycle up to 250°C and back to 50°C. The sample showed a CO_2 selectivity of ca. 30%, which is consistent with those reported in the literature over similar samples.

The corresponding $CO_{(ads)}$ signal followed by DRIFTS showed a complex evolution over the temperature cycles, which can be rationalized by a marked reconstruction of the bimetallic particles under the reaction feed, probably related to the oxidation and segregation of Sn [1]. The $CO_{(ads)}$ wavenumber always remained around 2070 cm^{-1}, which was well above the 2050 cm^{-1} value associated with the Pt-Sn alloy. The marked increase of the $CO_{(ads)}$ band during the cycle showed that the Pt dispersion was increased ca. 4-fold.

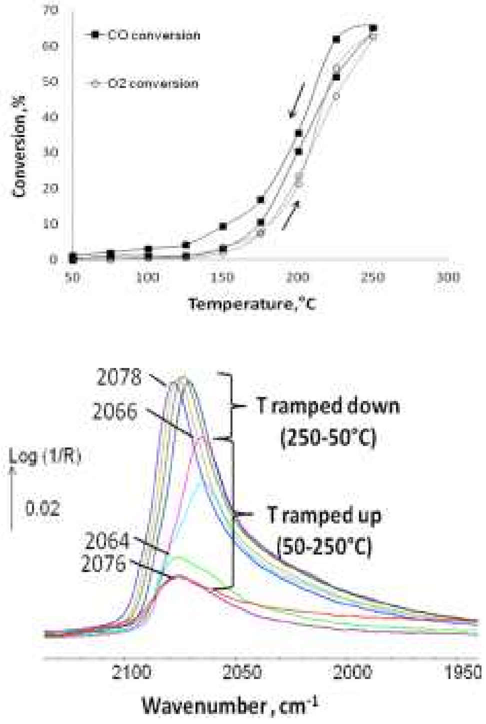

Figure1. (Top) PROX activity of the Pt-Sn/alumina sample as a function of temperature. Feed: 1% CO, 2% O_2, 80 % H_2 in N_2. (Bottom) Corresponding DRIFTS spectra collected over the sample at temperatures ramped by 50°C steps

Conclusions

No surface alloy could be observed under reaction condition, suggesting that the active catalyst involves a pure Pt phase alongside oxidized Sn, rather than a surface Pt-Sn alloy.

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P 24

Application of Raman Analysis in a Multichannel Micropacked-Bed Reactor System for Catalyst Evaluation and Reaction Optimization

Enhong Cao[1], Simon Barrass[1], Gemma Brett[2], Peter J. Miedziak[2], John M. Douthwaite[2], Paul F. McMillan[3,4], Graham J. Hutchings[2], Asterios Gavriilidis[1*]

*a.gavriilidis@ucl.ac.uk
[1]Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK
[2]School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
[3]Materials Chemistry Centre, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[4]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

The integration of spectroscopic technologies with microstructured reactors has been demonstrated to be an attractive approach for monitoring catalytic reactions and active species, providing molecular insight and better understanding of the reaction mechanism and helping in catalyst development and improvement[1]. In our previous work, Raman spectroscopy integrated silicon/glass microreactor systems have been developed for in- situ catalyst characterization for the gas phase oxidation of methanol to formaldehyde on silver catalyst[2] and on-chip monitoring and reaction profiling for the gas-liquid phase benzyl alcohol oxidation with O_2 in a micropacked-bed reactor[3]. Here we report the extension of this approach to a multichannel packed-bed reactor system to develop a microreactor platform with a portable Raman spectrometer for fast catalyst evaluation and reaction optimization.

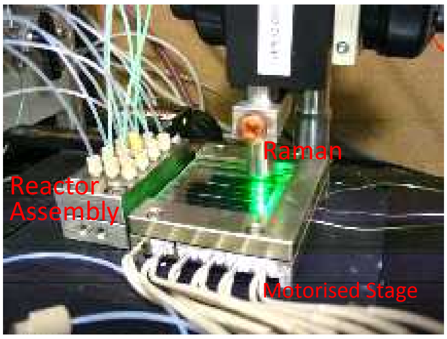

Fig. 1 Microreactor platform set-up

The microreactor platform consists of a four-reactor chip assembly, a Ventana-532 portable Raman spectrometer (Ocean Optics), a motorised positioning stage, a gas-liquid supply unit, a set of gas-liquid separators and a temperature controller (see Fig. 1). The whole setup is placed in a dark enclosure. The four-reactor microreactor chip was designed in such way that for each reactor there was a liquid trapping structure after the catalyst retainer to facilitate the Raman measurement. Raman sampling and the stage movement were controlled by Labview. Using the oxidation of benzyl alcohol as a model reaction, the calibration of the Raman was carried out by performing the reaction in one of the four reactors and correlating the Raman peak ratio 1700 $cm^{-1}/1000\ cm^{-1}$ (indicating benzaldehyde yield) against GC analysis. Using this procedure the effect of water produced by the reaction on the Raman spectrum was accounted for. Subsequently the four reactor chip was loaded with four 1%(wt) $AuPd/TiO_2$ catalysts with different ratio of Au/Pd. The reaction was carried out at 120°C at benzyl alcohol flow rates of 5, 8 and 12 µl/min with an O_2/liquid ratio of 200. Fig. 2 shows a good agreement between Raman and GC analysis, verifying the validity of the calibration procedure. The on-chip Raman sampling required only 1 s to determine benzaldehyde yield, compared to 20 min run-time for GC.

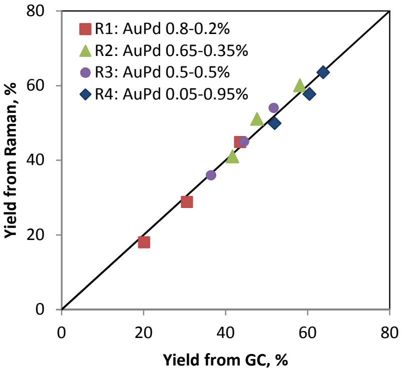

Fig. 2 Comparison of benzaldehyde yield from Raman and GC

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The effect of copper loading on the carbide phase formation in iron based catalysts during CO_2-rich Fischer-Tropsch synthesis: In situ X-ray absorption spectroscopy/high-resolution X-ray powder diffraction studies.

D. Peña[1]*, L. Saue Jensen[1], A. Cognigni[1], N. E. Tsakoumis[1], W.van Beek[2], M. Rønning[1]
[1] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway
[2] The Swiss-Norwegian Beamlines (SNBL) at ESRF, BP 220, F-38043 Grenoble, France
*Presenting author. E-mail address: diego.a.p.zapata@ntnu.no

Introduction

Fischer-Tropsch (FT) syntheses for synthetic hydrocarbons production applied to coal and natural gas and biomass-derived syngas (X to liquids XTL processes) are well-established industrial processes being the subject of considerable fundamental and applied research over the last few decades. The syngas (H_2/CO) feed originated from biomass is CO_2 rich, therefore operating FT reaction without syngas purification could result in a simpler, lower cost process since CO_2 has negligible influence on FT kinetics at H_2/CO higher than 0.8 [1,2]. Fe catalysts are attractive for BTL applications, in view of their capacity to manage non-stoichiometric syngas, to work at higher temperatures, and their lower cost, although they have lower FT activity[3]. For that reason, it is very important optimize the catalytic activity. The activation of the iron oxide catalyst precursors in H_2, CO, H_2/CO seems to be a very important issue with the aim to increase stability and activity[4]. On the other hand the use of promoters can also enhance those features. In particular, copper is added to improve the reducibility, metal dispersion and to improve the water-gas shift activity. However the effect of copper loading on the formation of different carbide phases has not been studied in detail. In the current work high-resolution X-ray powder diffraction (HR-XRPD) was combined with X-ray absorption spectroscopy (XAS) in order to reveal the changes occurring during the experimental FTS revealing the effect of copper loading on the active iron phase under different gas pre-treatments and FT performance.

Experimental details

15 wt% Fe catalysts with varying Cu loading (0.6, 1, 2, 5 wt%) supported on a commercial alumina (-Al_2O_3) were prepared by incipient wetness impregnation. The prepared catalysts were ex situ characterized by SEM, TEM, TPR, TGA-MS, and textural properties. A quartz capillary *in situ* experimental cell was used in a setup configuration similar to that employed previously [6]. *In situ* experiments were performed at the Swiss–Norwegian Beamlines (SNBL) station BM01B at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. XAS was performed on the Fe K-edge (7112 eV) while HR-XRPD data were collected using a wavelength of 1.781 Å (6.980 keV). *In situ* studies were carried out during pretreatment and FTS steps. An online mass spectrometer was used to detect reactants and products in the capillary effluent gas stream.

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TiO_2 photoreactivity investigated by *operando* FTIR spectroscopy under UV-Vis irradiation

Lorenzo Mino, Chiara Negri, Adriano Zecchina, Giuseppe Spoto

Department of Chemistry, NIS Reference Centre, University of Turin, via P. Giuria 7, 10125 Torino, Italy
lorenzo.mino@unito.it

In the last decades TiO_2 has been extensively investigated for its widespread application in photocatalysis and in dye-sensitized solar cells. Concerning air and water remediation, the mechanism of photodegradation of the most common organic pollutants on TiO_2 has been studied by several experimental techniques [1], however in most cases a detailed knowledge of the processes occurring at the catalyst surface is still lacking.

To try to achieve deeper insights into this issue, we developed a set-up allowing to acquire FTIR spectra in transmission mode (with all the advantages that this technique offers in terms of sensitivity and spectral quality with respect to the ATR and DRIFT ones generally used so far for photoreactivity studies) while simultaneously irradiating the sample with a UV-Vis source. The possibility to operate in controlled atmosphere and at variable temperature allowed us to investigate in greater detail the photodegradation of model organic compounds (e.g. phenol, methylene blue) on different TiO_2 nanoparticles (pure anatase, Evonik P25) and to identify the intermediates that are formed on the TiO_2 surface at the different reaction steps. This information, combined with an accurate investigation of the surface active sites using suitable probe molecules and electron microscopy (see Figure 1) [2-4], allowed us to better clarify the complex processes occurring at the TiO_2 surface during the photocatalytic reactions.

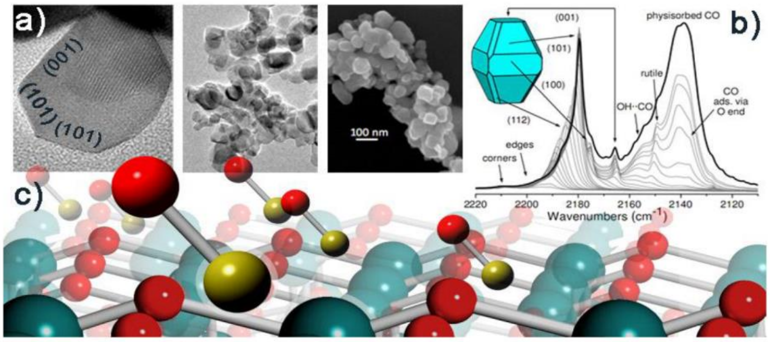

Fig. 1. a) HR-TEM images of the TiO_2 P25 sample in which the interference fringes originated by the (101) and (001) planes are clearly visible. b) Complete assignment of the FT-IR spectra of CO adsorbed at 60 K on Degussa (Evonik) P25, achieved combining the experimental results with periodic DFT calculations (see pictorial representation in part c). This approach allows to obtain the average P25 anatase nanoparticle morphology and to disclose the correlations between surface properties, particle morphology and photoactivity.

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Operando AGIR spectroscopy and NNMF techniques applied to the study of coke formation on ZSM5 catalysts with hierarchical porosity.

Christian Fernandez, Louwanda Lakiss, Philippe Bazin and Jean-Pierre Gilson,
Laboratoire Catalyse et Spectrochimie,
ENSICAEN, Université de Caen, CNRS, France
christian.fernandez@ensicaen.fr

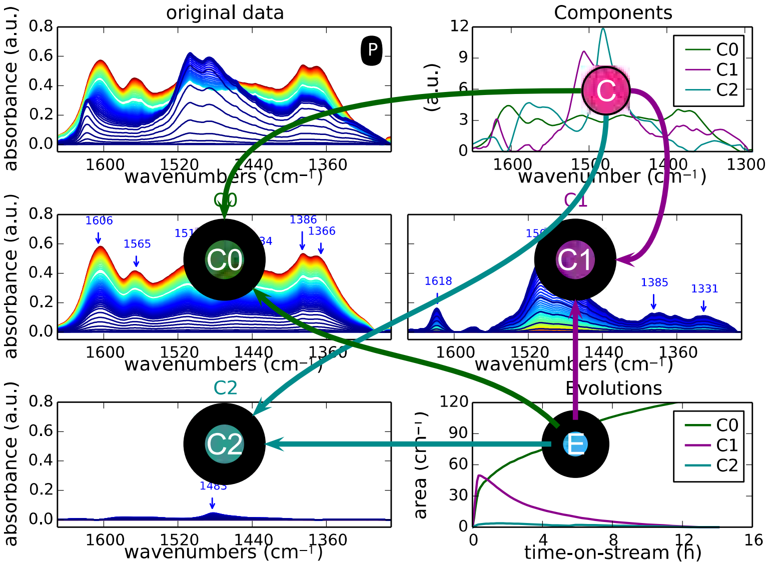
The AGIR technique, hyphenating thermo-gravimetrical analysis (TGA) and Fourier transform infrared spectroscopy (FTIR), is employed for the first time to study the deactivation behavior of zeolite with hierarchical porosities during the methanol to hydrocarbons (MTH) reaction.

Two kind of zeolite materials, which present micro- and macroporosity (fluoride leaching) or micro- and mesoporosity (alkaline leaching) hierarchical porosity are investigated and compared to the parent ZSM-5.

The novelty of the AGIR method is that it allows the simultaneous chemical analysis and mass measurement of the carbonaceous species ("coke") formed during the course of reaction, leading to real quantitative information about the coke formation.

The major difficulty however in such experiment is to easily extract relevant parameters from a large amount of spectroscopic data, because for the coke species strong overlaps of the band occur. Therefore, we have used numerical methods such as principal component analysis (PCA) and the less common non-negative matrix factorization (NNMF) to decompose the spectra and extract the evolution of the detected species. This results, in combination with the gravimetric data, to the possibility to calculate extinction coefficients, which are mandatory for the quantitative analysis of the IR spectra.

In this communication we will describe the technique and show its power to understand the mechanism of coke formation and its relation with the nature of the zeolite porosity. We will also show that it can be rather easily extended to other spectroscopy such as operando NMR.



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Reaching enzyme activities with size controlled supported gold clusters of low atomicity

P. Concepción[a], *M. Boronat*[a], *A. Corma*[*], *M.J. Sabater*[a], *J. Navas*[a], *M.J. Yacaman*[b], *E.Larios*[b],

[a] *Instituto de Tecnología Química (UPV-CSIC), 46022 Valencia-SPAIN*

[b] *Department of Physics University of Texas at San Antonio One 1604 circle San Antonio Texas 78249 Texas, USA*

**pconcepc@upvnet.upv.es*

Gold has attracted wide interest as catalyst in the last years due to its unexpected activity and, specially, to its high selectivity in organic reactions.[1] Unexpected high catalytic activity associated to gold clusters composed by few number of atoms have been reported[2,3]. These results open a new front in catalytic studies associated to metal clusters, i.e. metal aggregates composed of few atoms.

Isolated gold atoms in absence of gold clusters and/or nanoparticles have been synthesized by a very easy process[4]. Cs-corrected high resolution STEM analysis confirms the presence of isolated gold atoms. The chemical nature of these isolated atoms has been investigated by X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) Raman and IR analysis. Following the evolution of the catalyst during reaction we have shown that isolated gold atoms are not active in the aerobic oxidation of thiophenol with air, but atomic aggregates with 5 to 10 atoms are extremely active for the reaction, with turnover frequencies (TOF) as high as $7*10^5$ h^{-1}, which are of the same order of magnitude than those found with sulfhydryl oxidase enzymes. When clusters grow into nanoparticles of diameter ≥ 1nm, the catalytic activity drops to zero.

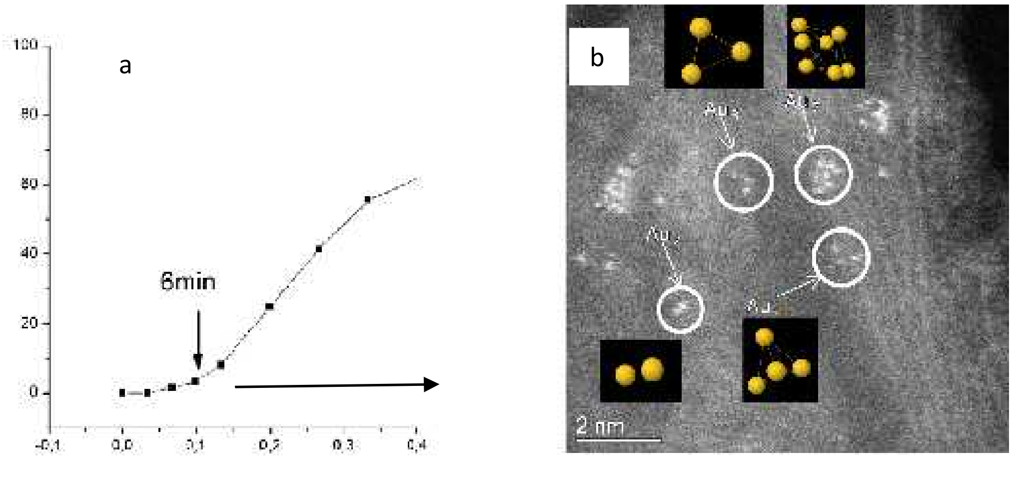

Figure 1 a) yield to disulfide with reaction time on isolated gold atoms b) HAADF-STEM image of atomic gold aggregates

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Transient kinetic investigations of the partial oxidation of (meth-)acrolein to (meth-)acrylic acid

*M. Heid, S. Knoche, N. Menning, N. Dürr, A. Drochner and H. Vogel**
Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie,
*Alarich-Weiss-Straße 8, D-64287 Darmstadt (Germany), *H.Vogel@tc1.tu-darmstadt.de*

Introduction

Acrylic acid (AA) as well as methacrylic acid (MAA) are important intermediates. Both are produced by heterogeneously catalyzed partial oxidation starting from the corresponding aldehydes[1] and molecular oxygen. Even though the difference between both aldehydes (acrolein (ACR) and methacrolein (MAC)) is located in only one additional methylgroup at the β–carbon atom, the catalysts for the industrial processes are quite different. While Mo/V/W-oxides (MOX) are used for the ACR oxidation towards AA, heteropolyacid compounds (HPA) such as $H_{((3+n)-x)}Cs_xPMo_{(12-n)}V_nO_{40}$ are the most common catalysts used for the MAC-oxidation to MAA[2]. This contribution is focused on the different behavior between the partial oxidations of MAC and ACR on MOX and HPA and on possible reasons for the discrepancies.

Materials and Methods

Different transient kinetic methods, i.e. temperature- and concentration-programmed (TP and CP) methods were used for a comparative study on the reactivity of both aldehydes on both catalysts. Therefore, notably SSITKA ($^{18}O_2$ and $H_2{}^{18}O$) and in situ educt replacement (MAC vs. ACR) were exploited.

The experiments were performed in a tubular reactor equipped with an online mass-spectrometer for the time resolved analysis of the gas-phase.

The investigations were carried out on a hydrothermal prepared mixed oxide ($Mo_8V_2W_{0,5}O_x$) and on spray dried HPAs ($H_{(4-x)}Cs_xPVMo_{11}O_{40}$)[3].

Results and Discussion

Results from SSITKA experiments with $^{18}O_2$ and $H_2{}^{18}O$ give an evidence that both aldehydes (MAC and ACR) adsorb on hydroxyl groups on the catalysts surface (no matter if MOX or HPA) by the formation of an acetalic species. Accordingly, the first reaction intermediates are only discriminated by the substituent at the β-carbon atom. Nevertheless, an intrinsic reaction pattern follows for each kind of acetalic species. This becomes clear by observing the byproduct spectrum for the different aldehydes with both catalysts (MOX and HPA) in TP reactions. The major byproducts of the ACR oxidation on MOX are the total oxidation products, whereas on HPAs a significant value of acetic acid (AcOH) can be detected. On the contrary, AcOH is determined to be the major product at higher temperatures (> 360 °C) during MAC oxidation on MOX.

Interesting results arise from educt exchange experiments. As part of these experiments, ACR was in situ exchanged by MAC, stepwise, by another. We found that both aldehydes react with similar activities on HPA but with quite different selectivities. The selectivity towards AA is nearly constant during the investigated temperature range (300 – 360 °C). In contrast to that the selectivity towards MAA decreases from 95 to less than 50 % while increasing the temperature.

This is remarkable to the experiments on MOX, where strong distinctions in activity and also selectivity can be monitored for the different aldehydes. Under the chosen conditions (300 °C) the conversion of ACR is nearly 100 %, while the conversion of MAC is similar to that on HPA at this temperature (~12 %). Nevertheless, MAA selectivity is lower than in to the comparable HPA experiments.

The different performance of both catalysts dependent on the aldehyde in the feed, the role of water and coke-layers towards this behavior, will be discussed.

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Operando Raman-GC Study of Heteropoly Acids during the Selective Oxidation of Methacrolein to Methacrylic Acid

*K. Kantchev, D. Ohlig, A. Drochner and H. Vogel**
Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie,
*Alarich-Weiss-Strasse 8, Darmstadt, D-64287 (Germany), h.vogel@tc1.tu-darmstadt.de**

Introduction

Methacrylic acid (MAA) is an important intermediate in the chemical industry for the production of polymethyl methacrylate (PMMA). Partially salified Keggin-type heteropoly acids (HPA) are the state of the art catalysts for the partial oxidation of methacrolein (MAC) with molecular oxygen to MAA. Among the formation of lacunary structures, the migration of the vanadyl species (Raman band at ~1032 cm^{-1}) is discussed to play a key role in the formation of the active catalyst.[1,2] In this context *operando* Raman measurements of various HPA catalysts during the oxidation of MAC to MAA have been realized.

Experimental

The tests were performed on self-made, spray dried and calcinated HPA catalysts with the formal composition $H_{(4-x)}Cs_xPVMo_{11}O_{40}$.[3] For *operando* Raman studies, a tubular quartz cell was used which was installed in a confocal Raman microscope system (Bruker Senterra). A 532 nm laser with a power of 0.5 mW was used for excitation. The standard feed composition was 5 vol% MAC, 10 vol% O_2, 7 vol% H_2O and N_2 as balance at a total flow rate of 20 mL/min (STP). The reactions were carried out at 330 °C and the product stream was analyzed via an online gas chromatograph.

Results and Discussion

A first benchmark test showed that completely salified HPAs (i.e., $Cs_4PVMo_{11}O_{40}$) have nearly no activity and are characterized by the complete absence of a band related to a vanadyl species. This correlates to the high thermal stability of these systems, which was shown via thermogravimetric analyses. In contrast, the partially salified HPA catalysts showed MAC conversion and evolved a band around 1032 cm^{-1} in addition. For these partially salified systems the vanadyl band could only be observed at non reductive atmospheres and after thermal activation of the catalyst. In reductive atmospheres the vanadyl band is absent which indicates a participation in the oxidation process. For further studies model catalysts were prepared where additional vanadium was applied on the surface of HPAs via incipient wetness impregnation.

In tests with standard feed at 330 °C an additional band at ~187 cm^{-1} was observed in the Raman spectra. Further tests showed that the band evolves under reductive atmospheres (5 vol% MAC in N_2 / 5 vol% H_2 in N_2), whereas the band remained absent in non-reductive atmospheres (10 vol% O_2 in N_2 / 7 vol% H_2O in N_2) (see Fig. 1). In cyclic experiments, where alternating reactive and oxidative feeds were used, it was possible to reproduce this observation in a reversible manner.

Among further observations, the impact of the obtained Raman features on the catalytic performance will be discussed in this contribution.

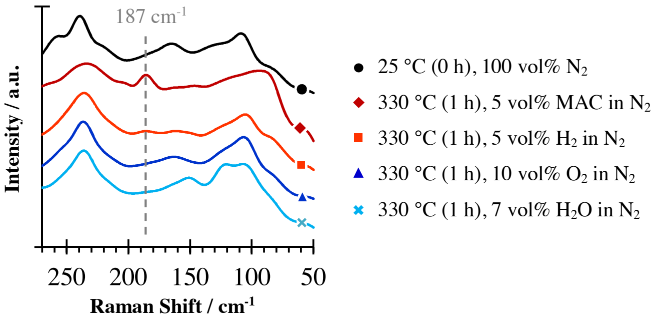

Figure 1. Raman spectra of HPA catalyst ($H_2Cs_2PVMo_{11}O_{40}$) under five different atmospheres.

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Steady state isotope transient tracing in an isothermal tubular differential heterogeneous catalytic reactor in laminar flow

Masood Otarod[a,1] and Ronald M. Supkowski[b]
[a]Department of Mathematics, University of Scranton, Scranton, PA 18510
[b]Department of Chemistry and Physics, King's College, Wilkes-Barre, PA 18711

Transport properties of a fluid [1] play an important role in the interpretation of the kinetic parameters of heterogeneous catalytic reactions in differential tubular reactors under steady state isotope transient tracing [2]. A novel method is presented for the analysis and interpretation of steady state isotope transient tracing data in a differential tubular reactor with low particle Reynolds numbers and large aspect ratios. The model is derived from the mean cross sectional transformation of the fundamental kinetic equations governing the operation of differential reactors. The application of the model does not require the advanced knowledge of the velocity distribution in packed beds as the mean cross sectional transformation maps the velocity distribution into a constant which is to be estimated along with other kinetic parameters from a curve fitting procedure. It is shown that for a differential reactor operating at steady state rate of V with a fractional conversion of ξm, a mean residence time of τ, the mass conservation equations for fluid phase and adsorbed species are as shown in Eqs. (1) and (2).

$$\frac{1}{\xi_m}\frac{\partial\ 1-\xi\ z^{\text{fluid}}\ \ \xi,\theta}{\partial\theta}+\Omega_1\frac{\partial\ 1-\xi\ z^{\text{fluid}}\ \ \xi,\theta}{\partial\xi}-\frac{\xi}{\text{Pe}_{\text{a}}}\frac{\partial^2\ 1-\xi\ z^{\text{fluid}}\ \ \xi,\theta}{\partial\xi^2}$$

$$=\frac{\Omega_2}{V}{}_0^1\ 2\rho\,\square^{\text{fluid}}(\xi,\rho,\theta)\ d\rho \qquad (1)$$

$$\frac{C^{\text{ads}}}{\tau}\frac{\partial z^{\text{ads}}\ \ \xi,\theta}{\partial\theta}={}_0^1\ 2\rho\,\square^{\text{ads.}}\ \ \xi,\rho,\theta\ \ d\rho \qquad (2)$$

$z^i\ \ \xi,\theta$ (*i* = fluid, ads.), represents the mean cross sectional fractional concentration of the traced compound; $\square^i$, the rate function; $C,^{\text{ads}}$ the concentration of the adsorbed species; ξ, the dimensionless axial coordinate, ρ; the dimensionless radial coordinate; θ, the dimensionless time coordinate (number of reactor space times); Pe$_a$, the axial Peclet number. $_1$ and Ω_2 are given by

$$\Omega_1=\frac{{}_0^1\ 2\rho\frac{U_{\text{a}}\ \ \rho}{u_0}\psi_z\ \ \rho,\rho_z\ \ \psi_F\ \ \rho,\rho_F\ \ d\rho}{{}_0^1\ 2\rho\psi_z\ \ \rho,\rho_z\ \ \psi_F\ \ \rho,\rho_F\ \ d\rho},\quad \Omega_2=\frac{1}{{}_0^1\ 2\rho\psi_z\ \ \rho,\rho_z\ \ \psi_F\ \ \rho,\rho_F\ \ d\rho},$$

$$\psi_i\ \ \rho,\rho_i\ \ =\frac{1}{2\rho_i}+\frac{1-\frac{1}{2\rho_i}}{\frac{2}{3\rho_i}-1}\ \ \frac{\rho}{\rho_i}-1\ \ ,i=z,F;\quad 0<\rho_z,\rho_F\neq\frac{2}{3}<1$$

$U_{\text{a}}(\rho)$, is the steady state axial velocity. For plug flow $\rho_z = \rho_F = 0.5$, and Ω1 = Ω_2= 1. The method, without additional assumptions, is applicable to the study of all mechanisms whose material balance equations are linear in the fractional concentration of the tracer. For others, the assumption of independency of the fractional concentration of the tracer from the radial position of the flow will suffice for data interpretation.

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[1] masood.otarod@scranton.edu

Example. The following mechanism is widely used for CO adsorption on several catalyst.

$$CO + \ell \rightleftharpoons CO\ell$$
$$CO\ell + \ell \rightarrow C\ell + O\ell$$

The first equation is at equilibrium and ℓ represents adsorption on a lattice site. These equations are to be solved with the initial and boundary conditions $z\ 0,\theta = 0, z\ \xi,0 = 1, \frac{\partial z(\xi,\theta)}{\partial \xi}|_{\xi_m} = 0$. The model was simulated for CO adsorption by using the data for CO hydrogenation on Pd/Al_2O_3 [3]. Fig. 1 shows the impact of $_1$, Ω_2 on $z^{CO}(\theta)|_{\xi_m}$ for two axial Peclet numbers of 5 and 30. The blue curve represents plug flow.

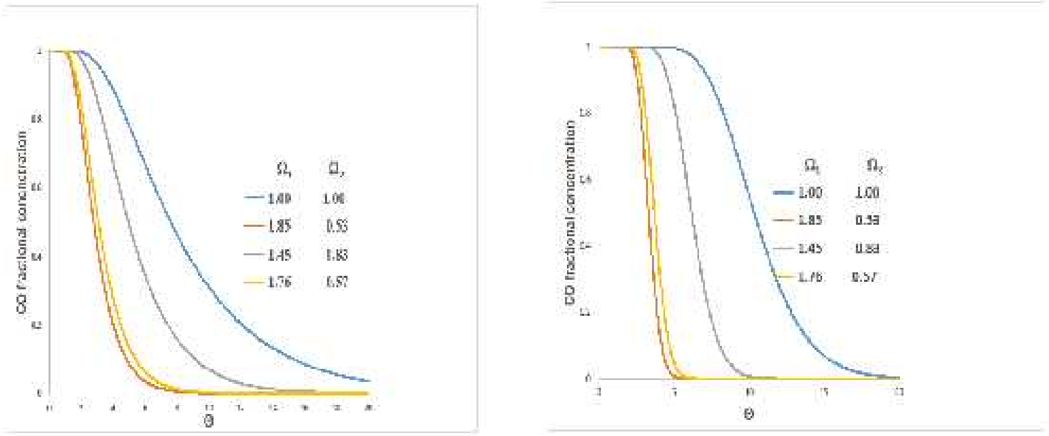

Fig. 1: Effect of $_1$, Ω_2 on the fractional marking of CO for (left) $Pe_a = 5$, and (right) $Pe_a = 30$

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A promoting effect of Pd site isolation on supported Pd-Au catalysts generated under "in situ" reaction conditions for the Selective Hydrogenation of 1,5-Cyclooctadiene.

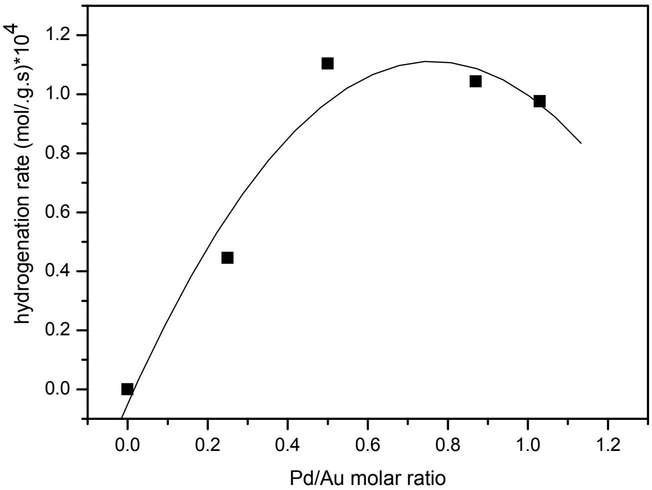
S. García[a*], *P. Concepción*[a], *A. Corma*[a], *J.J. Calvino*[b](*sagarga3@itq.upv.es)
[a]*Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia, 46022 Valencia, Spain.*
[b]*Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica. Universidad de Cádiz. Facultad de Ciencias, Caumpus Río San Pedro, Puerto Real, 11510, Cádiz, Spain.*

The selective hydrogenation of alkadienes and/or alkynes to monoalkenes attract attention due to both their practical importance and their theoretical interest.[1] While Pd catalysts exhibit the highest activity-selectivity their selectivity towards monoalkenes decreases when working at high conversion levels.[2] Thus considerable attention has been paid to improve the selectivity of Pd catalysts. In this work the promotional effect of gold on Pd/CeO_2 catalysts has been studied. Isolation of Pd sites, by alloy formation has been evidenced.

Au/CeO_2 samples have been impregnated with different Pd loadings. XPS data shows that the presence of Au favors the reduction of Pd. Moreover, under reaction conditions a modification of the oxidation state of the metal surface sites and gold surface restructuration is observed, favoring alloy formation with enhanced Pd dispersion on the surface (Table 1).

Sample	t(min)	C(%)[a]	Surface composition[b]				Pd3d5/2[c]		Au4f7/2[c]		
			Au	Pd	O	Ce	Pd^{2+} (%)	Pd^0(%)	Au^0 (%)	Au^+ (%)	Au^{3+}(%)
0.10Pd-0.36AuCe	0	--	0.05	0.37	75.36	24.21	53.3	46.7	100	0	0
0.10Pd-0.36AuCe	**15**	**94.5**	0.14	0.36	78.46	21.03	27.8	72.2	67.8	0	32.2

Table 1: XPS data of H_2-reduced $Pd-Au/CeO_2$ samples after catalytic reaction ([a] Conversion of COD (C) at reaction time (t) at which the sample has been characterised, [b] Surface composition determined by XPS (atomic ratio), [c] Atomic percent of each oxidation state determined by XPS



The variation of the reaction rate with Pd loading in $Pd-Au/CeO_2$ samples, displayed in Figure 1, shows a volcano type curve with a maximum at Pd/Au molar ratio of 0.5. HRTEM analysis shows alloy formation with a Pd/Au molar ratio of 0.13. Pd dilution due to alloy formation could explain the enhanced catalytic activity.

Figura1: Variation of the reaction rate with Pd loading.

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In situ and operando X-ray absorption and emission spectroscopies: characterizing SCR-relevant Cu species in Cu-SSZ-13 zeolite under controlled conditions

Kirill A. Lomachenko[1, 2], Elisa Borfecchia[1], Filippo Giordanino[1], Hanne Falsig[3], Pablo Beato[3], Ton Janssens,[3] Alexander V. Soldatov[2], Silvia Bordiga[1], Carlo Lamberti[1, 2]

[1] University of Turin, Department of Chemistry, NIS and INSTM Reference Centers, Via P. Giuria 7,10125 Turin, Italy
[2] Southern Federal University, International research center "Smart materials", Zorge str. 5, 344090 Rostov-on-Don, Russia
[3] Haldor Topsøe, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

kirill.lomachenko@sfedu.ru

X-ray absorption and emission spectroscopies (EXAFS, XANES, XES) are known to be very powerful tools for structural and electronic characterization of catalytically active metal centers in various types of materials. Making use of high penetrative power of hard X-rays combined with the high flux, ultimate stability of the beam and impressive flexibility of sample environment available at the modern state-of-the-art synchrotron sources, these methods are perfectly suited for various kinds of *in situ* and *operando* catalytic experiments[1]. Element selectivity of XAS and XES techniques represents a significant advantage as well, since minor or disordered species are often the focus of interest in catalysis.

Novel Cu-SSZ-13 zeolite, which attracts a lot of attention due to its outstanding performance in NH_3-assisted selective catalytic reduction (SCR) of NO_x, has been an example of a very successful application of X-ray absorption and emission techniques. Since catalytically active sites in this material are relatively low-abundance single Cu ions incorporated without any long-range order in the cavities of the zeolite framework, element selective methods were a logical choice for the characterization task.[2] In the present study we used EXAFS, XANES and XES methods not only for shedding light Cu local environment in the activated material, but also for the identification and characterization of intermediate Cu species, that form at different stages of SCR reaction cycle under *operando* conditions.

Cu-SSZ-13 sample under study was synthesized and characterized by laboratory techniques as described elsewhere.[3] Si/Al and Cu/Al ratios were 13.1 and 0.444 respectively. X-ray characterization was performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). EXAFS and XANES measurements were carried out at the BM23 beamline, while XES and high energy resolution fluorescent detection (HERFD) XANES data were collected at the ID26 experimental station. Measurements at both beamlines were conducted in a closed reactor cell connected to gas supply rig, which allowed controlling precisely the temperature of the sample and the atmosphere inside. Subsequent DFT calculations of different Cu-SSZ-13 structures together with the simulation of the corresponding XANES and XES spectra were carried out in the ADF2012 software. EXAFS data were analyzed using the Demeter package.

Obtained EXAFS, XANES and XES data suggest, that during the heating from room temperature to 400 °C both in oxygen and in helium Cu cations lose the coordinated water molecules present in the hydrated sample and coordinate to the zeolite framework. However, in case of O_2-activation OH^- ligand is likely to stay coordinated to copper, which remains Cu^{2+}, whereas in He atmosphere it goes away above 250 °C causing the reduction to Cu^+. Analogously, other species, including $Cu(NH_3)_x$ complexes and Cu nitrates, that form at different stages of the catalytic cycle, were characterized.

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Catalytic reduction of polar substrates using Frustrated Lewis pairs. An operando calorimetry approach to measure kinetics and thermodynamics under catalytic operating conditions

Sean Whittemore, Don Camaioni, Abhi Karkamkar, Mark Bowden, Tom Autrey
Pacific Northwest National Laboratory, Richland, WA 99352, USA
tom.autrey@pnnl.gov

The combination of Lewis acid and Lewis base pair that is sufficiently steric to encumber quenching provides a unique environment to activate H_2 heterolytically to enable the catalytic reduction of polar substrates at ambient temperature and moderate pressure without using metals. In this presentation we demonstrate how we have modified mixing cells fitted for reaction calorimetry to measure the rates, TOF, TON and thermodynamics for catalytic reduction of imine using a phosphane/borane Frustrated Lewis Pairs (FLP). Figure 1 shows a comparison of the heat flux resulting from the stoichiometric and catalytic reduction of tert-butylbenzaldimine, (IM) with the Frustrated Lewis acid-base pair (FLP), 2-(dimesitylphosphino)ethyl] bis(pentafluorophenyl)borane (PBCat) at 298 K and 13.8 bar H_2 pressure. Using a three step kinetic modeling (Scheme 1) to fit the experimental data we can extract the rate of H_2 transfer, $k_3 = 2.2\ M^{-1}s^{-1}$, that is in excellent agreement with the rate obtained in the stoichiometric experiment, $2\ M^{-1}s^{-1}$, and the corresponding reaction enthalpy, $\Delta H_2 = 6.7$ kcal/mol as well as the rate of H_2 activation, $k_2 = 1\ M^{-1}s^{-1}$, and overall thermodynamic driving force for the reduction of the imine to the corresponding amine, ΔH ca. 17.7 kcal/mol. The model is also constrained to fit the drop in H2 pressure due to the reduction of imine.

Scheme 1.
(1) $H_2(g) \Leftrightarrow H_2(s)$
(2) PBCAT + $H_2(s) \rightarrow$ PBCATH2
(3) PBCATH2 + IM $\rightarrow$ PBCAT + amine

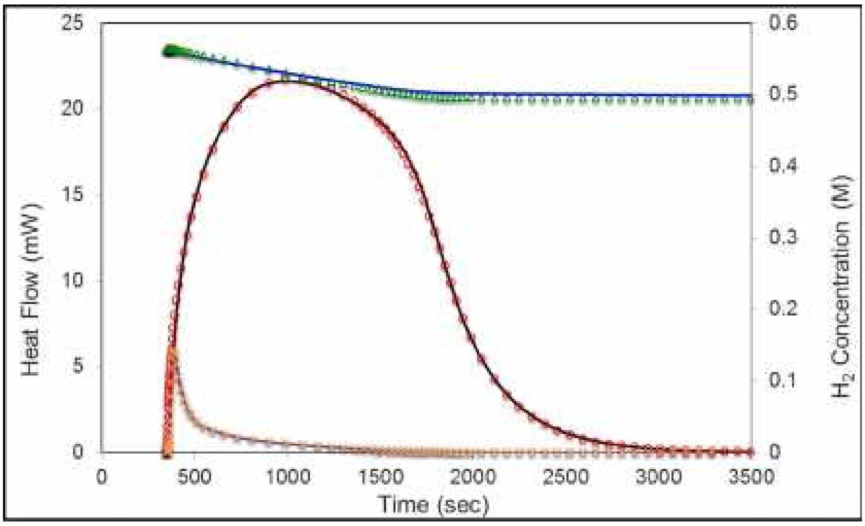

Figure 1. Comparison of heat flux measured in calorimeter and best fit to kinetic model (-) for stoichiometric reduction (o), catalytic reduction (o) and H_2 pressure drop (o). Not that the area under the catalytic reaction is ca 25x the stoichiometric reaction as the reduction is cycled 25x with 4 mol% catalyst.

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ATR-FTIR Quantitative Spectrokinetic Analysis at Liquid/Solid Interface

Alejo Aguirre, Claudio L.A. Berli, Sebastián E. Collins

Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral, CONICET, Güemes 3450, S3000GLN Santa Fe, Argentina

Attenuated total reflection (ATR) infrared (IR) spectroscopy is a powerful tool to investigate reaction pathways in liquid(reactive)/solid(catalyst) systems, because it provides the detection of adsorbed species on a catalyst under reaction conditions [1]. Catalysts are commonly deposited on an internal reflection elements (IRE) as layers of powders or as films (e.g. metal film), and they are exposed to the liquid phase reactants. In order to study the evolution of adsorbed intermediates, transient techniques are usually applied, such as stop-flow and concentration-modulation excitation spectroscopy (c-MES) [1-2]. However, to obtain quantitative information, that is, determining intrinsic reaction rates, the chemical engineering aspects of an ATR flow-through cell must be developed. Particularly, mass transport in the ATR cell has to be characterized. We present here an optimized flow-through ATR microfluidic cell to assess intrinsic kinetic parameters of reactions under chemical control. This ATR cell possesses no dead-volume and has a uniform fluid velocity profile across the cell. The mass transport dynamic from the bulk solution to the surface of the ATR crystal -where the catalyst is deposited- is described by a convection-diffusion transport model [3]. The mass-transfer limitation in the ATR cell is investigated comparatively using the simplest case of adsorption/desorption in both a non-porous and a porous catalyst layer (Fig. 1). A Pt thin film deposited on a ZnSe IRE by vapor deposition and the layer of Pt(0.38%)/Al_2O_3 was prepared by evaporation of a dispersion of the catalyst. The operational limit of the cell is characterized by means of a non-dimensional analysis in terms of Péclet (Pe), diffusive Biot (Bi_D) and Sherwood numbers (Sh_M) for the porous film case. Suitable criteria to determine kinetic parameters under chemical control were develop considering the geometry and experimental flow rates. Results show that, for the porous film case, the internal mass transport (e.g. the diffusion in the porous layer) could be neglected for low Bi_D; and the external mass transport (e.g. the transport from the liquid phase to the film) is limiting for $Bi_D/Sh_M > 0.1$ (Fig. 2). This condition allows the determination of elemental kinetic constants under chemical control.

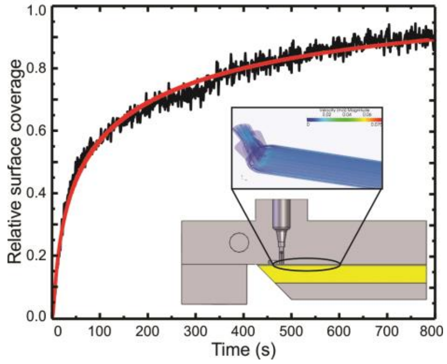

Figure 1: Evolution of the normalized IR signal of Pt-CO (2048 cm^{-1}) on Pt/Al_2O_3 as a function of time (black line) during transient adsorption of CO(aq). Red line is the best fit using the complete convection-diffusion model.

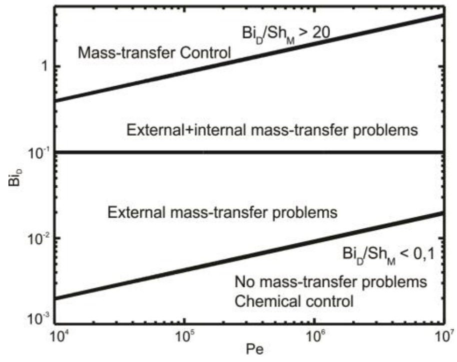

Figure 2: Operational limits of the ATR cell for a layer of porous catalyst deposit on the IRE.

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In situ studies of the carburization process of the tungsten carbides catalysts: influence of the surface functionalization and nickel addition

Débora M. Meira[a,*] *Beatriz D. Moreno*[b] *and Cristiane B. Rodella*[a]
[a]Brazilian Synchrotron Light Laboratory - LNLS, C.P. 6192, 13083-970, Campinas, São Paulo, Brazil
[b]Canadian Light Source Inc. – CLS, SK S7N2V3, Saskatoon, Canada
**debsmeira@gmail.com – cristiane.rodella@lnls.br*

The production of value-added chemicals and biofuels from renewable resources is a vital way to feed the high demanded energy from industry and transport sectors. The catalytic conversion of lignocellulosic biomass and derivate can be an environmental and economic sustainable route to obtain bio-based products [1,2]. Tungsten carbide has shown to be an effective catalyst for cellulose and cellulosic derivate hydrogenation reaction to obtain valuable commodities. It is known that particle size, dispersion and promoters have influence in the carburization process as well as in the catalytic performance of tungsten carbides catalysts [3,4]. In the case of biomass conversion, it is also important to consider acid and basic properties of the catalyst because it has a direct influence in the reaction pathways and selectivity. Although the catalytic behavior of Ni-promoted tungsten carbides catalysts have been successful explored in the biomass conversion, the interaction among promoter/tungsten carbide/support and the carburization process has not been deeply explored. Thus, the aim of this work was to investigate the influence of the Ni-promotion and the functionalization of the carbon with SO_3H and KOH groups in the carburization processes of the tungsten carbides catalysts. *In situ* X-ray absorption and diffraction were carried out at the DXAS beamline at the LNLS and 11-ID-B beamline at the APS, respectively. Samples were placed in a capillary cell reactor and heated up to 850 ^{0}C (10 ^{0}C/min), under 10mL/min flow of 90%H_2/10%CH_4 gas mixture. According to the XANES analysis at Ni K-edge, the formation of Ni^0 started around 450^{0}C for the sample supported on commercial or functionalized carbon with SO_3H (C-SO_3H). On the other hand, metallic Ni was formed 150^{0}C lower when carbon was modified by KOH. The results indicate that the functionalization with KOH leaded to a better dispersion nickel nanoparticles. The functionalization of the support seemed to act in the same way for W dispersion. The W L_1-edge showed that the carburization temperature decreased for the non-promoted sample supported on C-KOH. In the case of the samples promoted with Ni, the results at W L_1-edge, showed that changes started at higher temperatures for the sample supported on C-KOH (663^{0}C), when compared to the samples supported on C-SO_3H (577^{0}C) and commercial carbon (381^{0}C). Thus, despite Ni contribution in the hydrogen spillover, which promotes the CH_x species formation, which are the carburization agents, the excess accumulated on the surface forms polymeric carbon, reducing the carburization rate. *In situ* XRD results showed that the Ni-promoted tungsten carbide supported on C-KOH presented WC and W_2C phases. However, the other two samples exhibited only the metastable W_2C phase being the crystalline domain bigger in the sample supported on commercial carbon than in the same sample supported on C-SO_3H. Thus, highly dispersed Ni nanoparticles lead the transformation of a W metastable phase (W_2C) to a more stable phase (WC). In conclusion, the structural and electronic transformation from the tungsten oxide to carbide phase (W_2C, WC), crystal size as well as the Ni reduction ($Ni^{2+} \rightarrow Ni^0$) are influenced by the functionalization of the support. It seems that KOH groups improves Ni and W dispersion and WC formation. However, it could increases the polymeric carbon deposition on the surface. The structural and electronic characterization of the tungsten carbides catalysts will be correlated with the catalytic performance in a reaction related with biomass conversion.

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Preferred form of presentation: oral – Scientific session: Reaction mechanisms (1)

Operando Raman spectroscopy of $H_3PW_{12}O_{40}$ in the dehydration of methanol: Laser-induced growth of coke seeds into polyaromatic coke

J. Schnee*, E.M. Gaigneaux
Institute of Condensed Matter and Nanosciences (IMCN) – MOlecules Solids and reactiviTy (MOST) – Université catholique de Louvain. Croix du Sud 2, box L7.05.17 1348 Louvain-la-Neuve, Belgium
*josefine.schnee@uclouvain.be

Introduction and Objectives

Heteropolyacids (HPAs) are well defined molecular clusters showing a large variety of structures. They are commonly studied as acid catalysts owing to their very strong Brönsted acidity, approaching the superacid region [1]. The main issue preventing a widespread use of HPAs for gas phase reactions is their rapid deactivation due to the formation of carbonaceous deposits, the so-called "coke" [2]. In our work, we investigate the formation of coke on HPAs in the gas phase dehydration of methanol to dimethylether by means of *operando* Raman spectroscopy. Our current research focuses on the most acidic Keggin-type HPA: $H_3PW_{12}O_{40}$. In the present contribution, we demonstrate how the continuous laser irradiation in an *operando* Raman investigation of $H_3PW_{12}O_{40}$ can itself promote the formation of coke and so distort the vision we get of the operating catalyst.

Results and Discussion

We have monitored the coking behavior of $H_3PW_{12}O_{40}$ under a flow of methanol (10 vol% in nitrogen) at 50°C by *operando* Raman spectroscopy. When only one single spectrum was measured after 3 hours of exposure to methanol, the Raman bands of aliphatic hydrocarbons, hereafter called "coke seeds", were detected between 2800 and 3000 cm^{-1}. However, when spectra were measured continuously throughout the experiment, the bands of polyaromatic coke appeared at 1350-1600 cm^{-1} after one hour of irradiation. The bands of coke seeds then disappeared. Thus, under continuous irradiation, the cyclization of aliphatic coke seeds into polyaromatic coke occurred. Simultaneous thermal emission indicates that this transformation was caused by laser-induced heating of the sample. *Ex situ* FT-IR spectroscopy after re-homogenization of the spent catalyst powder did not show any polyaromatic coke. The latter had thus indeed not been formed in the entire catalyst bed but exclusively in the irradiated area. In a reference test during which $H_3PW_{12}O_{40}$ has been irradiated under pure nitrogen, thermal emission was never observed. This suggests that laser-induced heating occurs only when $H_3PW_{12}O_{40}$ is covered with coke seeds. Indeed, it is known that hydrocarbons strongly absorb laser beams due to their darkness [3] and that strongly absorbing materials are subject to laser-induced heating [4].

Conclusions

Monitoring coke seeds on $H_3PW_{12}O_{40}$ with continuous laser irradiation leads them to grow up to polyaromatic coke. This is attributed to the fact that coke seeds render $H_3PW_{12}O_{40}$ sensitive to laser-induced heating due to their strong laser absorption ability. The present study so represents an example of situation in which *operando* Raman spectroscopy may be misleading as not representing the entire operating catalyst bed, as/or inducing an abnormal behavior.

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Preferred form of presentation: poster – Scientific session: Innovative techniques and tools (3)

Using the ν(P-O) vibration frequency of $H_3PW_{12}O_{40}$ as a probe of laser-induced sample heating during *operando* Raman spectroscopy

J. Schnee*, E.M. Gaigneaux
Institute of Condensed Matter and Nanosciences (IMCN) – MOlecules Solids and reactiviTy (MOST) – Université catholique de Louvain. Croix du Sud 2, box L7.05.17 1348 Louvain-la-Neuve, Belgium
*josefine.schnee@uclouvain.be

Introduction and Objectives

$H_3PW_{12}O_{40}$, in short HPW12, is the strongest Keggin-type heteropolyacid. It is commonly studied as acid catalyst [1]. In our work, we investigate HPW12 as catalyst for the gas phase dehydration of methanol. *Operando* Raman spectroscopy allows us to monitor HPW12's structural changes as well as the formation of carbonaceous deposits, the so-called "coke". The latter is an important issue as it is the main cause of heteropolyacid deactivation [1]. In Raman, HPW12's ν(P-O) vibration frequency is reported to be a function of temperature. Indeed, with increasing temperature, the P-O bonds in HPW12 are progressively compressed due to a change in the equilibrium $H_5O_2^+$*(hydrated protons)* $H_3O^+ + H_2O$ $H^+ + 2H_2O$, which brings about the partial reduction of W^{6+} to W^{5+} anions. This P-O bond compression results in an increase of the ν(P-O) vibration frequency [2]. Herein, we investigate the pertinence of using HPW12's ν(P-O) vibration frequency to estimate the extent of laser-induced sample heating that occurs while monitoring *operando* the "coke seeds" formation.

Results and Discussion

During the *operando* monitoring of HPW12's coking behavior under a flow of methanol (10 vol% in N_2) at 50°C, laser-induced heating occurs in the case of continuous sample irradiation. It causes thermal emission and the cyclization of aliphatic hydrocarbons ("coke seeds") into polyaromatic coke. In these conditions, HPW12's ν(P-O) vibration frequency is shifted from initially 1006 cm^{-1} to 1009.5 cm^{-1} after a while, suggesting a laser-induced heating of the sample. In order to determine the corresponding temperature rise, HPW12's ν(P-O) vibration frequency has been measured *in situ* from 25°C to 200°C (furnace setpoints). Under pure nitrogen, it increases continuously from 90°C, reaching 1009.5 cm^{-1} at 125°C and finishing at 1022 cm^{-1} at 200°C. Under a flow of methanol (10 vol% in N_2), it reaches 1009.5 cm^{-1} at 125°C as well. However, it stagnates then until 175°C. At 175°C, it increases again and finally reaches 1013 cm^{-1} at 200°C. Our explanation for the stagnation is the covering by coke of HPW12 units having a shifted ν(P-O) vibration frequency. Indeed, such units possess dehydrated protons which are much more acidic than hydrated ones [1], and which get rapidly coked. This coke formed in high amounts leads to a loss of signal of the dehydrated units [3]. Thus, the small remaining signal of HPW12, on basis of which the ν(P-O) frequency has been measured, is associated to non-covered, less dehydrated, HPW12 units.

Conclusions

Although coke influences the temperature dependence of HPW12's ν(P-O) vibration frequency and renders the frequency-temperature calibration complex, our work demonstrates that the laser irradiation induces a warm-up of the sample: whereas the furnace setpoint is at 50°C, HPW12's ν(P-O) vibration frequency tells us that the irradiated sample is at minimum 125°C.

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P 39

Concentration-Modulation Excitation DRIFT Spectroscopy Study of Carbonaceous Intermediates of the WGS Reaction on Pt/ceria

Julia Vecchietti[1], Adrian Bonivardi[1], Mónica Calatayud[2], Sebastian Collins[1]
[1] INTEC; Universidad Nacional del Litoral and CONICET, Santa Fe, Argentina.
[2] Université Pierre et Marie Curie and CNRS, IUF, Paris, France
scollins@santafe-conicet.gov.ar

Reducible oxides have been shown to greatly improve the activity of water gas shift (WGS) catalysts. The precise mechanism for this effect is a matter of intense debate. We investigate the relationship between the catalytic activity and the reducibility of the support (oxygen vacancies) using well characterized platinum catalysts supported on pure and gallium-doped ceria [1-4]. Pt/CeO_2 and Pt/$CeGaO_x$ catalysts present a remarkable reducibility, enhanced by the incorporation of Ga^{3+} cations [1,3] and a very stable metal dispersion. An inverse correlation was found between the catalytic activity to WGS and the amount of oxygen vacancies. Combining in situ time resolved X-ray diffraction, mass spectrometry and diffuse reflectance infrared spectroscopy (DRIFT) it was found that the oxygen vacancy filling by water is always fast either in Pt/CeO_2 or Pt/CeGa, suggesting that the activation of water molecule in the WGS mechanism is not the rate limiting step in these systems.

Concentration-modulation spectroscopy (c-MES) in DRIFT mode under WGS reaction conditions allows the selective detection of key reaction intermediates: monodentate formate (m-HCOO) and carboxylate ($CO_2^{\delta-}$) species (Fig. 1). Conversely, carbonate, bicarbonate and bridged formate groups behave like spectators. The carbonaceous reactive intermediates are formed by the reaction of CO adsorbed on Pt sites with adjacent Ce^{3+}-OH. It is proposed that m-HCOO/$CO_2^{\delta-}$ species are stabilized in the metal/support(vacancy) interface, which indicates the prevalence of a carboxyl (HOCO) mechanism. DFT calculation provides molecular insights to understand the pathway of the WGS reaction at the metal–oxide interface sites.

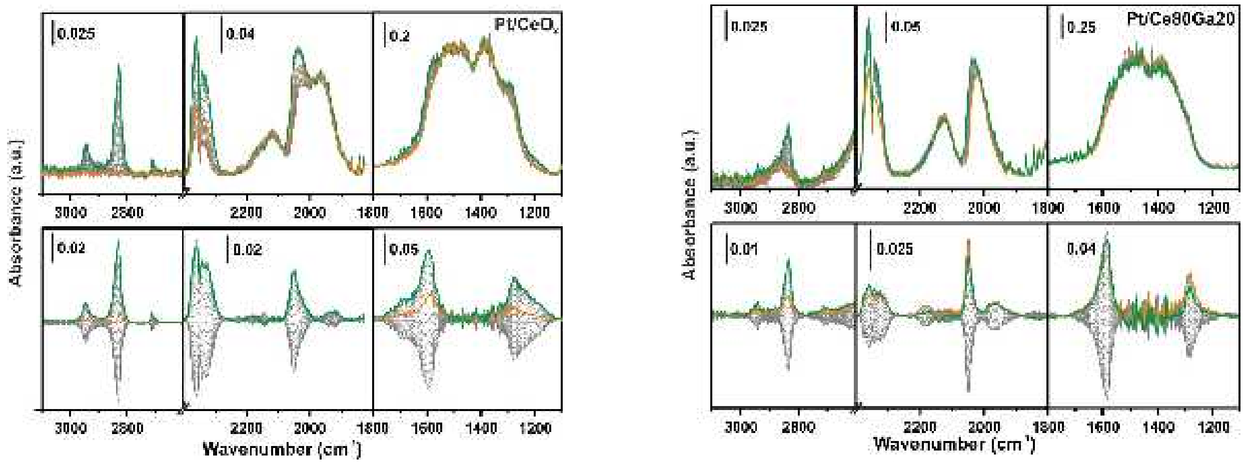

Figure 1. Time domain DRIFT spectra during a c-MES cycle (CO+H_2O)-He (100cm^3/min, 523 K, ω=4.2 mHz), over Pt/CeO_2 and Pt/Ce80Ga20 (top panel) and phase domain spectra after PSD demodulation (bottom panel).

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In situ Characterization of Supported Ni/Al_2O_3 Catalysts for Propane Oxidative Dehydrogenation

João Francisco Sobreira de Oliveira, Lucas Santos Assunção, Patrícia Moreira Lima, Adriana P. Ferreira
Universidade Federal de São Carlos, São Carlos, Brasil e 13565-905 Corresponding author: (apf@ufscar.br)

An alternative route for olefins production is based on dehydrogenation of light alkanes from natural gas. Oxidative dehydrogenation using molecular oxygen is an exothermic reaction ($C_3H_{8\,(g)} + ½\, O_{2(g)} \rightarrow C_3H_{6(g)} + H_2O_{(g)}$; $\Delta H^0 = -118 kJ/mol$), so demands lower temperatures, lower costs and easier products separations. On the other hand, the inflammability limits of hydrocarbons in oxygen implies in a low yield and products from total combustion are favored, which implies selectivity of the catalyst be critical [1]. Oxidative dehydrogenation proceeds according with reactional mechanism *Mars-van-Krevelen* [2]: alkane is dehydrogenated on the catalyst surface (metallic oxide) and the oxidant regenerates the catalyst. Olefins and carbon products are both primary products and they come from reactions that occur in the same Ni sites. However, the oxygen used to convert alkanes to the olefins is from catalyst network, while carbon products are formed by oxygen from oxidant [1]. In order to understand the dynamic modifications on the active Ni sites in the catalytic performances in the propane oxidative dehydrogenation (ODP) promoted by different reaction conditions (residence time and temperature) and vanadium addition, catalysts with 7.5 and 15 wt.% of Ni content supported on commercial Al_2O_3 were prepared by wet impregnation and promoted with 2.5 wt.% of vanadium. Calcined samples 7.5NiAl (125 m^2/g and 6.1 at/nm^2) and 15NiAl (105 m^2/g and 14.6 at/nm^2) were tested in the ODP under 3 residence times (τ: 1.25, 2.5 and 5.0 g.min/L) and 3 temperatures (450, 550 and 650ºC). Increasing temperature from 450 to 650ºC, ODP ($\tau = 2.5$) over 7.5 and 15NiAl show propane conversion increases from 25 to 57% and from 20 and 53%, respectively. Similarly propylene selectivity increases from 13 to 28% and from 14 to 29%, respectively; propylene yield increases from 3 to 16% and from 3 and 15%, respectively, and reaction speed rate increases from 1.2 to 4.5 $(mol/min*m^2)x10^6$ and from 1.2 and 5.1 $(mol/min*m^2)x10^6$, respectively. These results indicate ODP prevails over parallel reactions with the increase of temperature. Moreover, at 650ºC, 7.5NiAl is more active than 15NiAl because its surface density is much lower. TPR-H_2 and EXAFS show predominance of Ni nanoparticles in $Ni_2Al_2O_4$ structure for 7.5NiAl, while 15NiAl also presents NiO structure (crystallites around 12.7 nm). In situ DRX and EXAFS ($\tau = 2.5$) reveal Ni nanoparticles in both structures (NiO and $Ni_2Al_2O_4$) subtly tend to decrease in size when temperature increases and thus interact more strongly with the support (making them slightly more electron deficient), which seem to affect the propane adsorption sites and desorption of propylene. Increasing residence time to 5.0 g.min/L (at 550ºC) propane conversion and yield decrease significantly, follow by higher formation of coke and carbon products. In order to identify the characteristics of Ni sites according to Ni structure, 15NiAl was treated in hydrogen before ODP (at $\tau = 2.5$). In situ EXAFS reveals predominance of Ni nanoparticles in $Ni_2Al_2O_4$ structure after reduction. With the increase of temperature during ODP, nickel tends to reoxidize to NiO structure, presenting similar propylene selectivity to the 15NiAl without previous reduction. However, at 650ºC, in situ EXAFS spectra of reduced 15NiAl show it returns to $Ni_2Al_2O_4$ structure and its propylene selectivity is lower than not reduced sample. Therefore, it could be notice that Ni species in NiO structure seem to be most suitable sites for higher propylene selectivity than Ni species in $Ni_2Al_2O_4$ structure. Finally, vanadium addition to 15NiAl reduces the size and the amount of NiO crystallites. In situ EXAFS reveals Ni nanoparticles in V-15NiAl are smaller than in 15NiAl and the temperature increase causes higher decrease in size of them. In situ DRX of V-15NiAl (at $\tau = 2.5$) reveals higher Ni metallic nanoparticles arise with increase of temperature during reaction than unpromoted sample, while reaction speed rate is two times higher at 650ºC. Curiously, propane conversion and yield V-15NiAl also duplicate when residence time is increased to 5.0 g.min/L, at 550ºC, indicating vanadium make this sample more active. These results reinforce the interaction of vanadium with alumina causes a decrease of the stronger Lewis acid sites (propane adsorption) and an addition of Brönsted acid sites (desorption propylene) [3].

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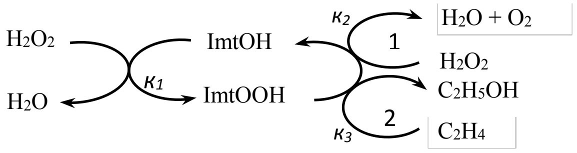
Kinetics and mechanism of coherent synchronized oxidation reactions of alkenes by hydrogen peroxide on biomimetic catalyst.

U.Nasirova[1], I.Nagieva[2], L.Gasanova[1], T.Nagiev[1,2]

[1]*Nagiev Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan*
[2]*Baku State University, Azerbaijani Republic*
tnagiev@azeurotel.com

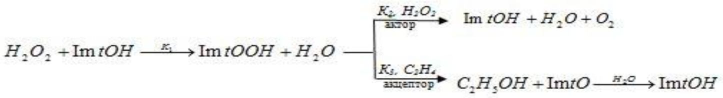
We had possibility to carry out the process of monooxidation of one of the representatives of low alkenes, ethylene, in gas phase due tu use of active stable ironporphyrin bioimitator-per-FTPhPFe^{3+}OH/Al$_2$O$_3$, as well use of hydrogen peroxide as an oxidant. Under condition of 120^{0}C, H_2O_2 concentration = 30%, as ratio C_2H_4:H_2O_2 =1:1,7 yield of ethyle alcohol in 15.4 mas %, (of acetaldehyde -12 mas%) and under condition of 200°C , the concentration of aqueous solution of hydrogen peroxide -30%, mole ratio C_2H_4:H_2O_2 =1:1,7 yield of asetaldehyde in 34,6 mas % (ethanol-4,6 mas%). As each monooxygenase reaction products is the end one, the process selectivity in conditions of maximum yield of ethyle alcohol and minimum yield of acetaldehyde made up practically 100% with account for monooxygenase products. Selectivity in case of maximum yield of acetaldehyde is somewhat lower (87%) owing to formation of CO_2 as by product. Hence it follows that conversion of ethylene to monooxigenase product proceeds in the following succession: $C_2H_4 \rightarrow C_2H_5OH \rightarrow CH_3CHO$. Each of these conversions is a complex reaction and consists of two coherent-synchronized reactions: primary (catalase) and secondary (monooxsigenase or peroxidase).

According [1], monooxygenase processes proceeding with hydrogen peroxide take place in the scale of chemical interference and consists of two coherent-synchronized reactions: catalase and monooxygenase which mechanism describes by following common form:



where ImtOH-bioimitator, ImtOH-intermediate, 1-catalase (primary), 2- monmooxygenase (secondary) reaction.

Such a chemical interaction of the reactions results in chemical interference in the dynamic mode. The effectiveness of chemical interference in this reaction system is measured by its quantitative characteristic determined by the determinant equation; $D = \nu\left({}^{r_{A1}}\!/_{r_{ACC}} + {}^{r_{A2}}\!/_{r_{ACC}}\right)^{-1}$, where r_{A_1} and r_{A_2} are the rates of actor (H_2O_2) consumption for the production of final products in the primary (catalase) and secondary (monooxigenase) reactions, respectively; r_{Acc} is the rate of acceptor (C_2H_4) consumption; and ν is the stoichiometric coefficient of actor (in our case, ν=1).
The rates of both reactions (primary catalase and secondary monooxigenase) can thus be calculated:



For kinetic simulation of ethylene oxidation using the three different methods: Michaelis-Menten equation, method of stationary concentrations and on the bases of the determinant equation. Kinetic model constructed on the basis of the determinant equation and coherence ratio of coherent synchronized catalase and monooxigenase reactions adequately describes the experimental data.
The question of the hydrogen peroxide consumption rate in catalase reaction:

$$r_{2,H_2O_2} = k_2\frac{k_1}{k_3}\frac{D[H_2O_2]^2[\mathrm{Im}tOH]}{[C_2H_4]} \quad \text{or} \quad r_{2,H_2O_2} = k^{кат}_{эфф}\frac{D[H_2O_2]^2}{[C_2H_4]}$$

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P 42

Mechanisms of methanol photooxidation on TiO_2: operando FTIR coupled to Steady State Isotopic Transient Kinetic Analysis (SSITKA)

Mohamad El-Roz, Philippe Bazin, Marco Daturi, Frederic Thibault-Starzyk

Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6, boulevard du Maréchal juin, 14050 Caen, France

Photocatalysis has always been considered as an important and promising approach for green chemistry and energy sustainable solutions. Among various photocatalytic applications, the photo-conversion of methanol is of particular interest. Methanol represents a model for many organic compounds and is an appropriate molecular probe to explore oxide surface properties. Several groups have conducted fundamental studies of methanol photochemistry on the TiO_2 surface in order to provide insight into the molecular detail of such reactions. Nevertheless, further investigations are required to better understand and elucidate the reaction mechanism.

In this work, *operando* FTIR spectroscopy coupled to gas phase analysis technique (MS and gas-FTIR)[1] is used to reveal the mechanism of total and partial methanol photooxidation reactions. Different methanol concentrations and labeled methanol molecules $^{12}CH_3{}^{16}OH$, $^{12}CH_3{}^{18}OH$, $^{12}CD_3{}^{16}OH$ and $^{13}CH_3{}^{16}OH$ are also used. Coupling *operando* FTIR technique to steady state isotopic exchange kinetic analysis experiments (Figure 1) allows revealing the mechanism of methylformate formation. We demonstrate that methoxy and formate/formyl species play a key role in the reaction: A high coverage of the photocatalyst surface by methoxy species, formed from thermal and photochemical dissociations of methanol, promotes the formation of methylformate. We also show that surface oxygen atoms (adatom (O_a) and/or bridged (O_{br})) exhibit an interesting role in methanol photooxidation. Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments confirm that the conversion of chemisorbed formyl/formate species is the limiting step in methanol photooxidation and that methylformate is produced from a cross coupling reaction between methoxy and neighbor formyl species. These results highlight the effect of different reaction parameters, such as methanol concentration, on the selectivity of photooxidation.

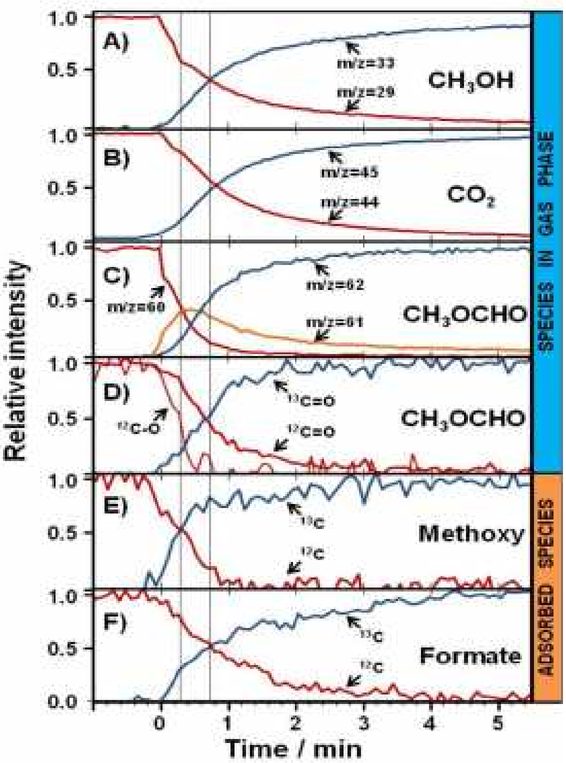

Figure 1. Evolution of adsorbed species on TiO_2 surface and in gas phase during methanol photooxidation versus time of the $^{12}CH_3OH/^{13}CH_3OH$ SSITKA experiment (t = 0 min correspond to the $^{13}CH_3OH/CH_3OH$ exchange).[1] TiO_2 thin film was deposited on a KBr window ($m_{TiO2}\approx 3$mg; diameter = 16 mm; <10 µm of thickness; methanol concentration = 100 ppm; T=301 K; flow=20 cm^3/min; λ=365 nm; I0=15 mW/cm^2).

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P 43

An *operando* FT-IR study of the NOx SCR over Co-HFER using acetylene as reducing agent

Ingrit Castellanos[a] and Olivier Marie[a]

[a] *Laboratoire Catalyse et Spectrochimie, ENSICAEN, 6 Bd. Maréchal Juin, 14000, Caen, France*

The ‘road transport’ is recognized as the main source for NOx pollution: according to the EEA, 40,5% [1] of the NOx total emission is caused by this sector. Therefore, the abatement of this pollutant has been considered mostly in the diesel powered engines whose growth in the automotive market in Europe is important. Furthermore, when compared with gasoline engines, higher amount of NO_x are produced due the operating conditions. Indeed, in these air excess conditions, the catalytic removal of NOx is also challenging. In the ammonia based SCR, zeolitic catalysts play a significant role in the NOx removal thanks to their efficiency in a wide temperature range but also for their easy formulation and economical elaboration. On another hand, in 1989 Iwamoto et al. [2] reported the first works on the elimination of NO_x by hydrocarbons (HC-SCR) in oxygen-rich atmosphere while Wang [3] et al. focused later on C_2H_2.

The first approach in our work was to identify the nature of the adsorbed species formed upon interaction at room temperature between our 1 wt% Co HFER catalyst and either NO or C_2H_2 separately. Regarding NO, two different kinds of species, i.e mononitrosyls and dinitrosyls bonded only to Co^{2+} were observed. Concerning acetylene, typical ν(C-H) and ν(C C) vibrations were found not only for interaction with Co^{2+} but also with the acidic hydroxyls.

The next step of this work consisted in the evaluation of the catalyst performance under flow conditions (400 ppm of NOx, 200 ppm C_2H_2, 2.5% O_2 in Ar) using the ‘*operando*’ methodology.

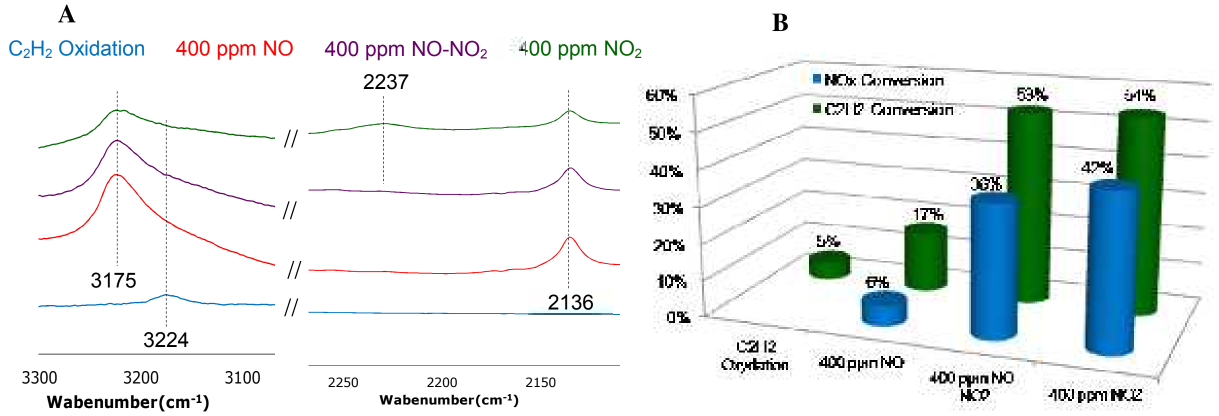

Figure 1. A) IR spectra of species formed at the catalyst surface between 220°C and 240°C **B)** NO_X and C_2H_2 Conversion at 240 °C

Focusing on the catalyst surface at 240°C (**Figure 1A**), the IR spectra show 2 distinct bands in the ν(CH) region. Thanks to the preliminary experiments, the band observed at 3175 cm^{-1} is assigned to acetylene adsorbed onto Co^{2+}. At 240°C, for the acetylene oxidation experiment, this is the only ν(CH) vibration that is observed: C_2H_2 thus no more interact with acidic hydroxyls. As soon as NOx was introduced in the reaction flow, another ν(CH) band appeared at 3224 cm^{-1}. The appearance of this latest band is concomitant with that at 2136 cm^{-1} typical for a ν(C≡N) vibration. Given the fact that at 240°C, the NO_X conversion is established at 6, 36 and 42% under NO, NO-NO_2 mix and NO_2 tests respectively (**Figure 1B**), we propose the formation of hydrocyanic acid as a reaction intermediate for NOx removal. The band observed at 2237 cm^{-1} is assigned to adsorbed N_2O as confirmed by the detection of nitrogen protoxide in the outlet gas.

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Mass spectrometry and *operando* XAS to study the Steam Reforming of Ethanol reaction over CoTiAl catalyst.

Arthur E. Pastore de Lima[1,2], Daniela C. de Oliveira[1*]
[1]Brazilian Synchrotron Light Laboratory, LNLS, Campinas-SP, Brazil, *doliveira@lnls.br
[2] Universidade Estadual de Campinas, UNICAMP, Campinas-SP, Brazil

Introduction

Hydrogen has being studied as a clean energy source since water and CO_2 are the by-products in its combustion reaction [1]. Therefore, steam reforming of ethanol (SRE) shows up as a reasonable CO_2 balanced path for hydrogen production [2,3]. Cobalt catalysts is currently used in SRE reactions due to its capacity to break C-C bonds, its contribution to remove coke deposits from the reaction bed and its economic advantages compared to noble metals. Since the support can have an active role in removing coke deposits from catalysts' surface [4], the aim of this work is to study the effect of TiO_2 on the Co-alumina structure and activity, performing *in-situ* and *operando* X-ray Absorption Spectroscopy (XAS), in order to understand the Co-support interactions.

Results and Discussion

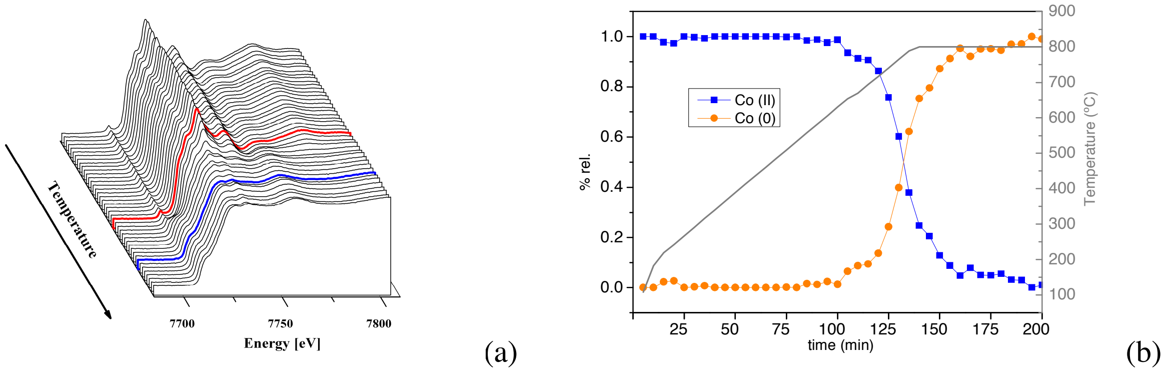

Figure 1. (a) XANES Co-K edge spectra of Co5Ti10Al during reduction step. (b) Relative composition of Co (II) and Co (0) during activation process.

The XANES spectra of fresh Co5Ti10Al catalyst showed similar features to the $CoAl_2O_4$, presenting only Co(II) in its composition. $CoAl_2O_4$ can decrease the catalytic activity because its structure is very stable, but the presence of TiO_2 can change this stability. From *in situ* XANES analysis during reduction (activation in 5%H_2/He), we observed that Co reduction occurred from 680 to 800 ºC, and the Co atoms appear to be fully reduced (Figure 1a, b). By mass spectrometry analysis during SRE reaction, we determined each reaction step due to the similarity of ions pattern with reaction mechanism proposed in literature [3]. The preferred way is ethanol dehydrogenation forming acetaldehyde, followed by acetaldehyde reforming producing H_2 and CO, then CO consumption by water-gas shift (WGS) reaction, producing more H_2 and CO_2. The SRE starts significantly only after 400 ºC by ethanol dehydrogenation. This reaction can be confirmed due to acetaldehyde presence, resulting from the dehydrogenation step. After that we observe the acetaldehyde partial decomposition in methane (CH_4, not desirable). Due to H_2 and CO_2 presence, possibly acetaldehyde reforming may occur as well, followed by WGS.

Conclusions

Co supported on mixed TiO_2-Al_2O_3 catalyst presented a good potential to produce hydrogen from Steam Reforming of Ethanol. The fresh catalyst presented $CoAl_2O_4$-as structure, but still was fully reduced to Co(0). The preliminary reaction showed that SRE reaction starts as ethanol dehydrogenation and we can avoid ethanol decomposition. We still observed some CH_4 formation, which is not desirable due to the higher temperatures to convert CH_4 to H_2, but the increase on H_2 and CO_2 production in higher temperatures showed that we can reach the final reaction steps, as the water gas shift (WGS) reaction, to increase the H_2 production.

References.

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In situ XAS study of Cobalt in Co-Ce-Al catalyst applied to Steam Reforming of Ethanol reaction.

Arthur E. Pastore de Lima[1,2], *Daniela C. de Oliveira*[1*]
[1]*Brazilian Synchrotron Light Laboratory, LNLS, Campinas-SP, Brazil, *doliveira@lnls.br*
[2]*Universidade Estadual de Campinas, UNICAMP, Campinas-SP, Brazil*

Introduction

The growing need of a more rational utilization of natural resources has contributed to increase the interest in hydrogen production, especially from renewable sources. The Steam Reforming of Ethanol (SRE) is a very simple catalytic process applied to obtain hydrogen from ethanol which can be obtained from renewable biomass. Many transition metals have been studied as catalyst active phase as Ni, Co, Cu, Fe [1]. The interest in cobalt catalyst has been reinforced because its low cost, high activity and selectivity to hydrogen [1]. Here we show that the presence of Ce affects the catalyst structure allowing hydrogen production in our preliminary results.

Results and discussion

The catalyst was prepared by wet impregnation of Al_2O_3 by Ce and Co salts with a molar ratio of 5% Co, 10%Ce and 85%Al. The sample named Co5Ce10Al was calcined in air at 800ºC during 6 hours. EXAFS and *in situ* XANES Co K-edge experiments were performed at XAFS1 beamline (LNLS, Brazil) during catalyst activation in 5% H2 atmosphere and during SRE reaction. The XANES profile and edge position showed that the initial sample has a spinel $CoAl_2O_4$ structure (Figure 1a).

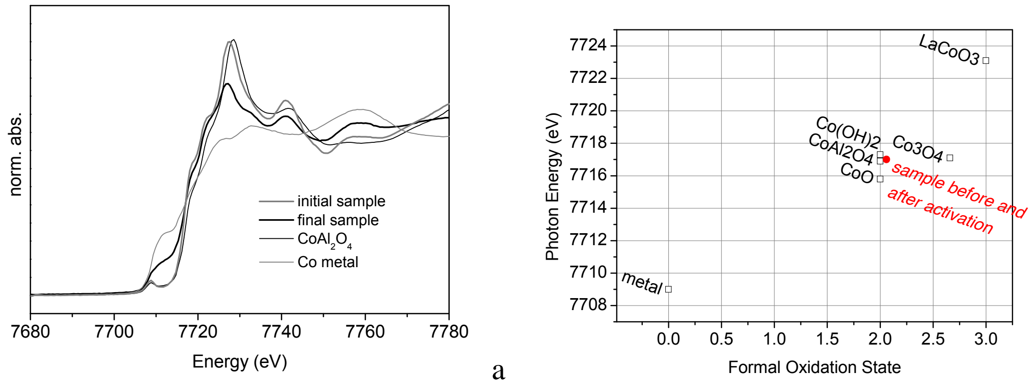

Figure 1: *(a) Co K-edge XANES of reference compounds and sample before and after activation; (b) formal oxidation state of reference compounds and sample from fig. 1a.*

This structure is not favorable to catalytic processes because it removes the active phase (Co) from the surface to form an inactive or a very few active compound. After heating in H2 atmosphere, the Co ion was not completely reduced as shown in Figure 1b. Interestingly, we detected hydrogen production by mass spectrometry (MS) at higher temperatures of 500ºC. Although the fresh sample has formed $CoAl_2O_4$ structure, we obtained an active sample with a mixture of compounds, estimated by non linear fitting curves of XANES spectra. The active phase of this catalyst is formed by 50% of metallic Co, 20% of $CoAl_2O_4$ and 30% of CoO. We attributed the catalytic activity and the structural changes after activation to the Ce presence, which can decrease the thermal stability of $CoAl_2O_4$ and favored the atomic diffusion of Co in the catalyst, with the activation process.

Conclusions

We studied the influence of Ce on Co/Al_2O_3 catalyst. The Ce presence contributed to activate the catalyst and even with the initial $CoAl_2O_4$ formation we obtained a sample with a mixture of compounds which presented hydrogen production by SRE reaction.

Reference

[1] J.L.Contreras, J.Salmones, J.A.Colín-Luna *et.al.* Int. J. of Hydrogen Energy **39** (2014) 18835-18853

Operando Studies of Palladium on Cobalt Oxide and Iron Oxide Catalysts during CO Oxidation

Liliana Lukashuk[a], *Elisabeth Kolar*[a], *Michael Stöger-Pollach*[b], *Günther Rupprechter*[a], *Karin Föttinger*[a]

[a]*Institute of Materials Chemistry, Vienna University of Technology, 1060 Vienna, Austria*
[b]*University Service Centre for Transmission Electron Microscopy, Vienna University of Technology, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria*
liliana.lukashuk@tuwien.ac.at

Controlling automotive emissions during the cold start of a car has remained an unsolved issue because of the strong CO adsorption on the noble metals at low temperatures (<200°C). The search for catalysts that are able to lower the temperature of CO oxidation is still ongoing. In this respect, noble metals supported on reducible oxides have gained considerable attention. The combination of certain reducible oxides as "active supports" with the noble metals has been found to enhance largely the catalytic activity in CO oxidation in comparison to "inert" non-reducible supports such as alumina and silica [1,2]. However, the origin of this enhancement as well as the nature of the active sites, reaction mechanisms is not fully understood and based mainly on the pre- and postcatalyst characterization [1,3]. But under catalytic conditions the structure of the noble metal supported catalysts might be very dynamic adjusting to the reaction environment very fast. Thus, comprehensive operando studies on the electronic and structural changes on the noble metal Pd and the reducible oxide, i.e. structurally similar Co_3O_4 and γ-Fe_2O_3, are of great importance.

In this contribution, we focus on studying the nature of active sites of PdO/Co_3O_4 and PdO/γ-Fe_2O_3 catalysts and the reaction pathways for CO oxidation. Furthermore, the influence of the pretreatment conditions on the CO oxidation catalytic is also investigated. For this purpose, PdO/Co_3O_4 and PdO/γ-Fe_2O_3 have been prepared and characterized. The PdO average particle size on Co_3O_4 was in the range of subnanometer to 2 nm, whereas larger PdO particles between 5-10 nm were detected for PdO/γ-Fe_2O_3. Kinetic data show that PdO/γ-Fe_2O_3 and Pd/FeO_x exhibit the same catalytic activity, while a strong influence of the pretreatment was observed for Pd supported on Co_3O_4, i.e., PdO/Co_3O_4 is much more active than Pd/CoO_x. Interestingly, these catalysts exhibit differences in the nature and amount of surface species (CO, carbonates) present under CO adsorption and CO oxidation conditions. Our operando FTIR demonstrates that on the PdO/Co_3O_4 a surprisingly small amount of CO was adsorbed to Pd upon CO exposure at RT, whereas no CO peaks at all were observed during the reaction with carbonates being the only surface species present. In contrast, on the oxidized PdO/γ-Fe_2O_3, CO adsorbed on Pd (linear and bridged) was present after introduction of CO as well as the reaction mixture ($CO/O_2=1/2$) at room temperature due to the reduction of PdO to Pd. Moreover, for the reduced catalysts, i.e. Pd/CoO_x and Pd/FeO_x, neither CO adsorption to Pd no formation of surface carbonates was observed. Thus, we assume that PdO/Pd is potentially encapsulated into Co_3O_4, CoO_x and FeO_x, forming "inverse" catalysts and CO oxidation proceeds through different mechanisms for PdO/Co_3O_4 and PdO/γ-Fe_2O_3. In addition, our preliminary in-situ near ambient pressure XPS experiments performed at BESSY II revealed the presence of a Pd^{4+} species beside Pd^{2+} under reaction conditions ($CO/O_2=1/2$, total pressure 0.5 mbar). In the C1s region we observed elementary carbon (284.7 eV) and carbonates (288.2 eV) that indicates CO dissociation during CO oxidation on PdO/Co_3O_4.

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P 47

Activation of Pt-based catalysts under PROX conditions: An operando study

S. Palma[a], L. Oliviero[b], Ph. Bazin[b], F. Romero-Sarria[a], J. A. Odriozola[a]

[a]ICMS, Dpto. Química Inorgánica, Centro mixto Univertity of Sevilla-CSIC

[b]Laboratoire Catalyse et Spectrochimie-ENSICAEN, Université de Caen-CNRS

1. Introduction

Preferential CO oxidation in the presence of hydrogen (PROX) is a crucial clean-up step in the production of pure hydrogen for fuel cells. The catalysts for this reaction must be very active and selective to prevent side reactions resulting in hydrogen consumption. Moreover, taking into account that reforming and clean-up units have to be coupled in these devices, good resistance to CO_2 and water must also be imposed to the PROX catalysts. In the case of mobile applications, the catalysts continuously suffer shut-down/start-up cycles and the activation of the solid between them is not possible. Therefore, for these applications, the activation of the catalyst under the reactive flow outgoing the reforming unit is the most suitable option. According to previous data, Pt-based catalysts accomplish these requirements [1]. The activation of Pt-based catalysts has been studied in a fixed bed reactor and the results show that the catalysts may be efficiently activated under the outgoing flow of a methanol reforming unit. However, the activation conditions have to be carefully chosen because the catalytic behavior of the solid is strongly dependent on the activation temperature, heating rate and time in isothermal conditions. This suggests that several processes are involved in the catalyst activation.

In order to identify such processes that induce surface modifications and the creation of active sites under reactive flow, Pt based solids have been studied by FTIR-operando.

2. Experimental

Monometallic Pt (2 wt.%) and bimetallic Cu-Pt (8 wt. %-2 wt.%) catalysts were prepared by incipient-wetness impregnation of a commercial γ-Al_2O_3 (Sasol) with a solution of platinum nitrosyl nitrate and stabilized with an organic solution. After the incorporation of each one of the metals, the solids were calcined at 300ºC (5ºC/min) for 8 hours.

The catalysts were characterized by conventional techniques (SBET, DRX, TPR, …) and by CO adsorption at room temperature followed by FTIR spectroscopy.

In the operando studies, the catalysts were treated under a methanol reformate gas stream surrogate (CO-0.25 %, O_2-0.38%, H_2-50%, CO_2-17%, H_2O-1% in Ar) and both, surface and gases at the exit of the cell, analyzed by FTIR spectroscopy during the thermal treatment (200ºC, 15ºC/min, 45 min).

3. Results and discussion

As an example, Figure 1 shows the monometallic Pt catalyst surface evolution and the corresponding CO conversion calculated from the area of the CO gas band. In the first 15 minutes (heating), the CO concentration in gas phase remains constant, but during the isothermal period an increasing of CO conversion to 85% is quickly reached. On the surface spectra, during the first 15 minutes, bands due to CO_2, carboxylate and adsorbed water, which decreases with time are observed. Despite the CO presence in the reformate surrogate, any band ascribed to CO adsorbed on Pt sites is observed at room temperature, which suggests that the platinum sites are blocked in the initial state of the catalyst.

As the temperature increases, a band at 2032 cm^{-1} attributed to CO on Pt sites and new bands in the 3000-2800 cm^{-1} region start to appear. Bands in the 3000-2800 cm^{-1} region have been previously observed in Pt-based catalysts and attributed to ethylidine/methylidine species formed by hydrogenation of carbonaceous species on the metal. In our case, the presence of carbonaceous species cannot be discarded given that an organic solution has been used to stabilize the metallic phase [2].

During the 45 min isothermal period at 200ºC, the intensity of the bands in the 3000-2800 cm^{-1} region increases and the band at 2032 cm^{-1} shift to 2028 cm^{-1}, which evidences a modification of the electronic density on the metallic sites.

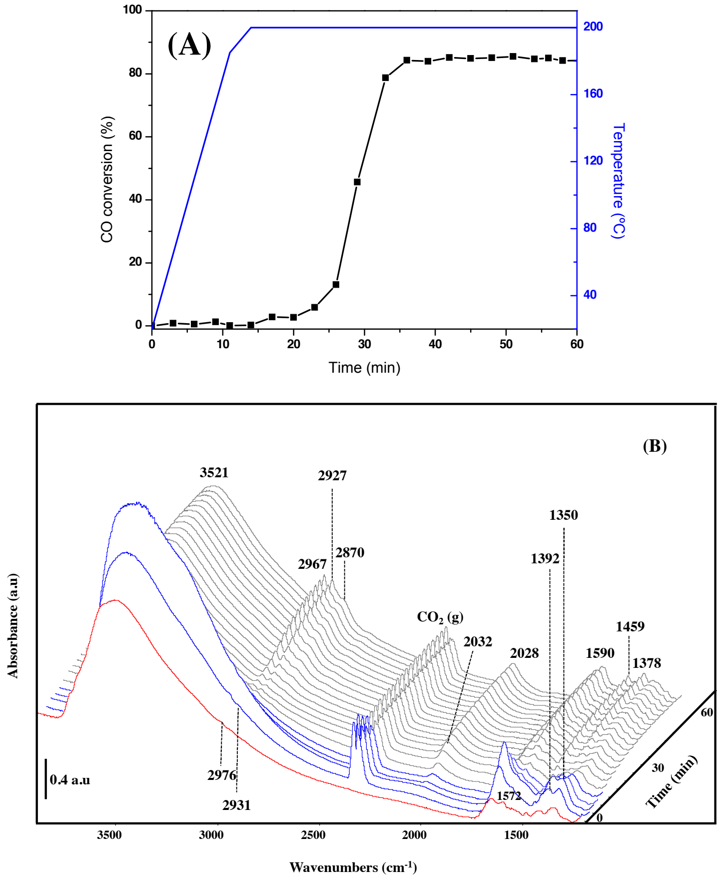

Figure 1: CO conversion (A) and surface evolution (B) during the thermal treatment under PROX flow. Red: Ar flow at room temperature; Blue: reactive flow during the increase of the temperature; Gray: reactive flow at 200ºC

These simultaneous facts suggest that the presence of carbonaceous species controls the accessibility and electron density of the metallic phase during the activation. This study has been completed by XPS of the solid after H_2 treatment and CO adsorption and the results confirm that carbonaceous species strongly influence the state of metallic sites on the surface.

A similar behavior has been observed with the bimetallic catalysts.

4. Conclusions

On Pt based catalysts, the presence of carbonaceous species issued from the preparation stage plays important roles during their activation under methanol reformate gas flow. The hydrogenation of these species may liberate sites initially blocked and control the oxidation state on the metal.

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Propane Oxidative Dehydrogenation: A Combined XAFS/DRIFTS Study

E. K. Gibson[1,2], S. Rogers[1,2], A. Kroner[3], J. Goodall[1,2], J. Callison[1,2], K. Mohammed[1,2], P. P. Wells[1,2], A. M. Beale[1,2], C. R. A. Catlow[1,2],

[1] *UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell Oxon, OX11 0FA.*
[2]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ.*
3. Diamond Light Source Ltd, Harwell Science and Innovation Campus, Chilton, Didcot OX11 0DE.
**corresponding author:emma.gibson@rc-harwell.ac.uk*

Alkane oxidative dehydrogenation (ODH) offers an attractive alternative route to fulfill the growing demand for alkenes than the currently employed energy intensive method of steam cracking. One class of materials which show promise for this reaction are mixed metal oxides with MoO_x. There is a debate on how the ODH reaction proceeds on these systems, one theory is that oxidic Mo^{6+} favours the ODH reaction while others suggest that it is responisble for the unwanted oxidation of the alkene to CO_2.[1,2] Different supports also play a role, with more acidic supports thought to enhance the combustion of propene,[3] a process thought to go via acetate or formate surface species.[4] In this work we have used a combined XAFS/DRIFTS methodology to probe the oxidation state and local structure of Mo whilst assessing the nature of surface intermediates under *operando* conditions.

A DaVinci arm fitted with Praying Mantis optics was used to collect the DRIFTS spectra whilst allowing the transmission of X-rays through the sample, the outlet gas was measured by a mass spectrometer. Measurements were performed at the Mo K-edge on the B18 beamline at the Diamond Light Source on three catalysts with similar MoO_x loadings supported on Al_2O_3, SiO_2 and Fe_2O_3. Each catalyst was subjected to one cycle of propane ODH followed by O_2/He, then propane dehydrogenation and finally a second ODH cycle.

We were able to confirm that under the initial ODH cycle the only form of Mo present was Mo^{6+} the XANES spectra having a characteristic 1s-4d pre-edge peak at 20006 eV and an absorption edge at 20017 eV. However, for the Al_2O_3 and Fe_2O_3 supported samples reduction started almost immediately during propane dehydrogenation, evidenced by the shift in the edge to 20014 eV, an increase in intensity in the 1s-5p transition at 20023 eV, and the Mo becoming more octahedral in character, all consistent with the reduction of Mo^{6+} to Mo^{4+}. During the initial reduction $CO_{2(g)}$ was formed but no evidence of acetate or formate surface species was observed in the DRIFTS spectra. Re-oxidation was almost immediate on introduction of O_2, but the Mo retained some of its octahedral character. This mixed system may be advantageous as an increase in propene production was observed during the 2nd ODH cycle. No reduction or subsequent re-oxidation or change in geometry for the SiO_2 supported catalyst was observed during propane dehydrogenation or ODH which may explain this catalysts lower propene production.

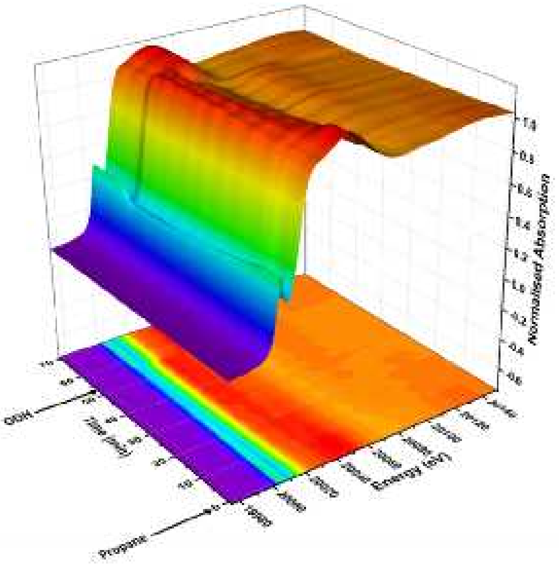

Fig 1. XANES spectra of MoO_x/Al_2O_3 during propane dehydrogenation then ODH.

XAFS is a powerful technique for understanding the local structure of catalysts under reaction conditions, however, being an averaging technique it can sometimes provide limited information about the surface. When used in combination with FTIR, an understanding of both the local structure of the metal as well as the surface species can be achieved. In the case of propane ODH it is a useful *in situ* spectroscopic approach giving added insight into the reaction mechanism.

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Mapping Catalytic Processes at the Nanoscale Using Tip-enhanced Raman Spectroscopy (TERS)

Andrew J. Wain,* Naresh Kumar and Debdulal Roy

National Physical Laboratory, Hampton Road, Teddington, United Kingdom

**andy.wain@npl.co.uk*

The power of *in situ* molecular vibrational spectroscopy for the characterization of heterogeneous catalysts and catalytic processes is undisputed. In particular, analysis of surface adsorbed species under reaction conditions can provide unique molecular insights into process mechanism and kinetics, and is essential to the intelligent design and optimization of catalyst materials. Furthermore, the ability to measure the spatial distribution of activity across a surface is critical to improving our understanding of catalytic performance. Whilst many spectroscopic tools enable chemical mapping of surfaces, the spatial heterogeneity of common catalysts is very often beyond the diffraction-limited resolution of typical far-field optical techniques. It is well-established that near-field approaches such as tip-enhanced Raman spectroscopy (TERS) offer significant potential for high-resolution chemical mapping, but their application to studying catalytic processes has only been demonstrated in a few cases.

In this work we employ TERS to monitor the plasmon-enhanced photocatalytic oxidation of p – mercaptoaniline (pMA) to p, p' – dimercaptoazobenzene (DMAB) on nanostructured silver. We first use Raman mapping to observe this catalytic process occurring at the contact point between a Ag-coated TERS tip and a pMA-covered glass surface. We then demonstrate the application of an ultra-thin alumina coating to suppress the catalytic reaction at the Ag-TERS tip whilst maintaining localized plasmon enhancement. Finally, we show that such innovative alumina-coated probes enable TERS mapping of this plasmon-assisted catalytic reaction at Ag-coated surfaces for the first time with spatial resolution in the tens of nanometers. Our observations indicate that both the catalytic activity and localized Raman signal enhancement are highly sensitive to the morphology of the Ag surface.

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Location and Migration of Cu Species in Cu-SSZ-13 Ammonia-Selective Catalytic Reduction Systems as revealed by in situ X-ray Diffraction

I. Lezcano-Gonzalez,[a,b] W. A. Slawinski,[c] D. S. Wragg[c] and A. M. Beale[a,b,*]
[a] Department of Chemistry, University College London, 21 Gordon Street, WC1H 0AJ, London, UK
[b] UK Catalysis Hub, Rutherford Appleton Laboratory, Research Complex at Harwell, Didcot, OX11 0FA, UK
[c] Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, PO Box 1126, 0315 Oslo, Norway
Presenting author: andrew.beale@ucl.ac.uk

Ammonia-Selective Catalytic Reduction (NH_3-SCR) using zeolites is a well-established technology to remove NO_x compounds from oxygen-rich exhausts, characteristic of diesel engines.[1] Many zeolites of varying topology containing different transition metal ion components have been tested in the NH_3-SCR reaction, with Cu-containing zeolites exhibiting a very high activity and selectivity over a wide temperature window.[1] In particular, the superior activity and enhanced hydrothermal stability of Cu-SSZ-13 zeolite, based on the CHA topology, have lead to its commercialisation for mobile applications, along with a significant research interest over the last few years.[1]

In an attempt to understand its exceptional catalytic performance, much research have been undertaken to determine the nature and location of the Cu ions within the SSZ-13 structure. Nevertheless, despite several studies, a complete understanding of the Cu species present and the cationic positions occupied in the lattice has not been obtained yet. It was initially proposed that Cu^{2+} ions are located in the 6-membered rings (6-R) of the double 6-membered ring (D6R) sub-units however, subsequent works suggested that Cu loading has an effect in Cu location and that at high loadings Cu^{2+} ions occupy positions in both the 6-R and the large cavities.[1] More recently, studies on a high loaded sample showed the majority of Cu to be located at a specific site in the 8-R, assigned to $[Cu^{2+}(OH)^{-}]^{+}$ complexes,[2] while other groups reported the presence of Cu_xO_y species at high loadings, not contributing to standard SCR.[3] On top of that, it has been anticipated the possible movement of Cu ions within the SSZ-13 structure as a result of rehydration or else interaction of adsorbates,[4] complicating even more the overall picture of Cu speciation in SSZ-13.

With the aim to get further insight into the location and movement of Cu species within the SSZ-13 framework, we have performed synchrotron-based in situ XRD measurements during activation treatments in either O_2/He or He flow, as well as during standard SCR. The results obtained during the in situ activation process indicate that at room temperature, fully hydrated Cu species are located in the 8-R windows of the large cavities of the zeolite structure. At 150 °C, the hydration shell is lost and Cu ions migrate to more stable cationic positions in the faces of the D6R sub-units, completing the process at about 300 °C (see Fig. 1). Furthermore, the results obtained show that this process is completely reversible, with Cu species becoming rehydrated upon cooling down to room temperature and returning to the 8-R positions. Similarly, during standard SCR Cu species migrate to the D6R sites at temperatures beginning about 150 °C and continuing with temperature and increased activity for NO conversion.

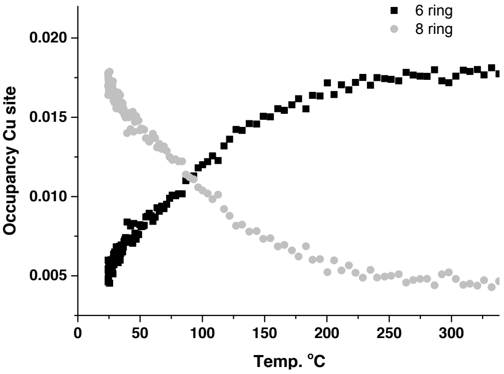

Figure 1. *Cu occupancy in Cu-SSZ-13 during activation in O_2/He flow*

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Influence of oxygen diffusion into nickel on oscillatory regimes of methane oxidation

Valerii V. Ustugov[1]*, Evgenia A. Finkelstein[2], Vasily V. Kaichev[1], Elena A. Lashina, Natalia A. Chumakova[1], Alexander Yu. Gornov[2], Valerii V. Bukhtiyarov[1]
[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
[2]Institute for System Dynamics and Control Theory SB RAS, Irkutsk, Russia
*E-mail: ustugov@catalysis.ru

The study is devoted to a theoretical analysis of self-oscillations in the oxidation of methane over nickel. The model of the reaction was amended with a step of diffusion of oxygen from the nickel surface into its volume, and the influence of this step on the characteristics of the oscillatory regime was studied. A microkinetic scheme of the reaction was suggested, parameters of elementary chemical reactions and diffusion of oxygen in nickel were determined, and a mathematical model of the process was developed.

The microkinetic scheme was based on a mechanism of oxidation of methane over nickel [1, 2]. Parameters of elementary reactions, such as enthalpies and activation energies, were determined using a phenomenological approach suggested by E. Shustorovich [3]. Pre-exponential factors of elementary steps were evaluated in the framework of the transition state theory. Diffusion coefficients of oxygen in nickel were determined on the basis of published experimental data. The mathematical model of the reaction consists of a system of ordinary differential equations and takes into account concentrations of surface intermediates, a concentration of oxygen in subsurface layers, and the heat balance.

In the model with the diffusion of oxygen in nickel, a set of parameters that provide stable oscillation modes were found. A study of stationary regimes and regimes with stable self-oscillations was carried out. Solutions obtained in the models with and without diffusion of oxygen into nickel were compared. In the self-oscillatory regime of the reaction, the concentration of subsurface oxygen was found to oscillate synchronously with concentrations of reaction products. The addition of the oxygen diffusion into the model leads to the appearance of an *induction period*, which is consistent with experimental data.

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Spatially resolved structure-activity relationships on heterogeneous catalysts using QEXAFS and IR-thermography

Andreas Gänzler[1], Alexey Boubnov[1], Henning Lichtenberg[1], Maria Casapu[1], Jan-Dierk Grunwaldt[1*]
[1]Karlsruhe Institute of Technology, Karlsruhe, 76131Germany
*corresponding author:grunwaldt@kit.edu

In the past years operando techniques contributed significantly to the understanding of heterogeneous catalysis under applied working conditions [1,2]. Especially X-ray based techniques proved to be valuable tools: in situ and operando XRD and XAS are established as working horse techniques for the characterization of heterogeneous catalysts. The next step is to correlate structure and catalytic performance in a spatially resolved manner. For catalytic studies often the spaci-MS (e.g. ref. [3]) has been used, for structural studies scanning or full-field X-ray absorption spectroscopy microscopy [2,4] both showing strong gradients in concentration and structure. Here we show that the combination of spatially resolved X-ray absorption spectroscopy and infrared-thermography is very powerful, even under dynamic conditions, e.g., if oscillatory conversion occurs in a catalytic reactor.

Here we focus on the oscillatory oxidation of CO, which has been extensively studied for idealized systems [5]. However, for real powder catalysts in plug flow reactor systems their origin is still controversially debated [6-8]. The combination of operando QEXAFS, IR-thermography and on-line MS analysis (Fig. 1) allowed monitoring the structural dynamics on the macroscopic reactor level (scanning of the X-ray beam and IR-thermography) and the correlation to data obtained on the atomic structural level with XANES and EXAFS [7b].

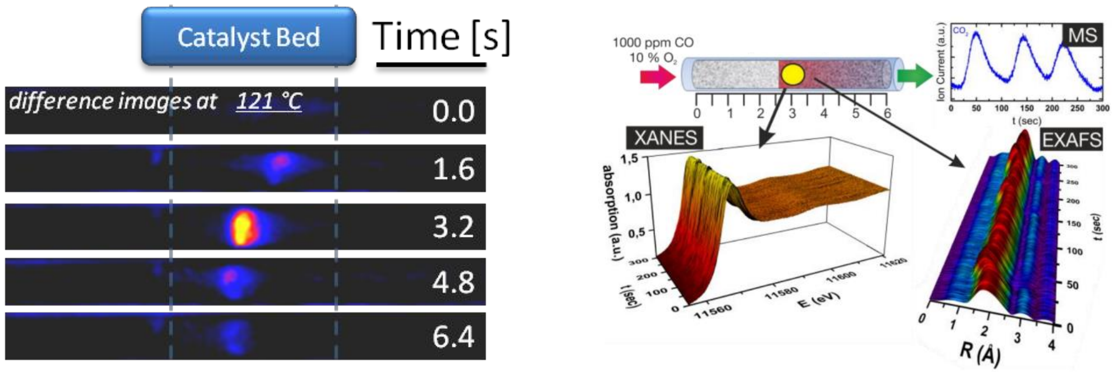

Figure 1. IR-Thermography (left) and XAS (right) during oscillatory CO conditions: Temperature hot spots form at the end of the catalyst bed; Oxidation state of Pt changes periodically (taken from ref. [7b]).

IR-thermography revealed the short periodic appearance of regions in the reactor with high catalytic CO-oxidation activity (temperature hot spots). Those hot spots formed at the end of the catalyst bed and propagated towards the start of the bed until they extinguished (Figure 1, left). Quick-EXAFS provided insight on the microscopic dynamics. The small Pt particles of the catalyst (< 3nm) were oxidized and reduced during oscillatory CO conversion (Figure 1, right). By considering the results obtained with MS (integral activity), IR-thermography (location of the active catalyst as function of time) and XAS (spatially and time resolved dynamics of oxidation state and structure of Pt nanoparticles) the fast oxidation of Pt could be linked to the deactivation of the catalyst, while the reduction could be linked to its reactivation.

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Identification of active species during low-temperature CO oxidation on a ceria-based catalyst.

R. Kopelent[1], J. A. van Bokhoven[1,2], J. Szlachetko[1,3], J.Edebeli[1], C. Paun[1], M. Nachtegaal,[1] O. V. Safonova[1]

[1]Paul Scherrer Institute, 5232 Villigen, Switzerland
[2]Institute for Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland
[3]Institute of Physics, Jan Kochanowski University, 25406 Kielce, Poland
olga.safonova@psi.ch

A rational approach for the improvement of the catalysts' efficiency requires identification of the active species and the rate-determining steps. Various species that may be involved in the catalytic cycle can be observed in situ by spectroscopic methods. However, distinguishing the active species from the inactive spectators can only be done by a quantitative comparison of the kinetic behavior of these species to the global reaction rate[1].
We report on a novel time-resolved in situ X-ray emission spectroscopic (XES) method available at the superXAS beamline at the Swiss Light Source that we used in combination with mass spectroscopy for probing the mechanism of low-temperature carbon monoxide oxidation on a platinum-promoted ceria-based catalyst. By measuring the resonant XES corresponding to the Ce $2p_{3/2}5d_{5/2}$ transition, we detected the kinetics of cerium oxidation state changes under transient conditions with 1 s time resolution. We identified the presence of both active and spectator Ce^{3+} species. We correlated the kinetics of ceria reduction under transient conditions to the steady-state carbon monoxide conversion rate and with that proved that ceria reduction is involved in the rate-determining step of carbon monoxide oxidation.
Based on the results obtained we suggest rational ways for the improvement of the efficiency of ceria-based catalysts for low-temperature CO oxidation. The discussed methodology can be generally applied to identify the solid state kinetics of various catalytic processes involving reducible oxides.

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Combined super-resolution fluorescence and electron microscopy for catalysis research

Jordi Van Loon[1], Kris Janssen[2], Thomas Franklin[1], Johan Hofkens[2], Maarten Roeffaers[1]

[1]Center for surface chemistry and catalysis, Department of Molecular and Microbial Systems, KU Leuven, Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium

[2]Laboratory of Photochemistry and Spectroscopy, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

E-mail: jordi.vanloon@biw.kuleuven.be

Abstract

Recent studies have revealed important inter- and intraparticle heterogeneities within zeolite batches, which are intrinsically introduced during zeolite synthesis and become even more pronounced by post-synthesis treatments. These heterogeneities clearly influence the catalytic performance [1]. Traditional tools for studying heterogeneous catalysts however, either lack the spatial- or temporal resolution necessary to thoroughly correlate this information [2]. Therefore, in recent years there has been increased effort to develop techniques that enable a single particle or even single turnover resolution to establish a well-defined structure-activity relationship.

NASCA or "Nanometer Accuracy by Stochastical Chemical reActions" is one such technique that enables the recording of single turnover maps from single catalyst particles with nanoscale precision, based on wide-field fluorescence microscopy in combination with a fluorogenic reagent [3]. Correlating these highly detailed activity maps with structural information at the relevant nanometer length scale is, however, still challenging. For this purpose we have developed, in collaboration with Delmic, an integrated super-resolution fluorescence and electron microscope. Such a combined wide-field fluorescence and scanning electron microscope enables us to perform SEM and NASCA imaging either consecutively or simultaneously, i.e. correlated or integrated respectively, providing us with a novel tool to study the structure-activity relationship in zeolites with nanoscale resolution.

By using our newly developed iLEM in the correlated fashion, we have demonstrated the influence of intergrowths on the catalytic performance of small-port H-MOR crystals. The fluorogenic probe reaction used is the furfuryl alcohol oligomerization and whereas the dimensions of these reagent molecules prevent them from diffusing deeply into the one dimensional microporous structure, there are catalytic events observed in zones where this was not expected and that were otherwise inaccessible.

Our results clearly show that a powerful correlative technique as described above is necessary in order to get a deeper understanding of the relationship between the inherently large heterogeneity within zeolite batches and their catalytic performance.

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IR study of the protolytic cracking of alkanes over zeolites: tracking the reactant state

Shashikant Kadam[1], Hauguang Li[1], Richard F. Wormsbecher[1,2,3], Arnaud Travert[1]*
[1] Laboratoire Catalyse et Spectrochimie, ENSICAEN – Université de Caen – CNRS, Caen, France.
[2] W.R. Grace & Co Conn. Columbia, MD 21044, USA)
[3] Department of Chemistry and Biochemistry,UMBC, Baltimore, MD 21250, USA

The protolytic cracking of alkanes over zeolites, since its discovery by Dessau and Haag thirty years ago, has been the subject of many fundamental studies and can be considered as archetypical of zeolites acid-catalyzed reactions [1]. Yet, because of the interplay between adsorption and surface kinetics, the interpretations of zeolite/alkane structure-activity /reactivity trends have long been subject to discussion. While the variations of apparent protolytic cracking rates of light n-alkanes over acidic zeolites were initially accounted to changes in the coverage of the active sites by alkane, a new consensus has recently emerged, whereby such differences are primarily due to entropic effects [2-5]. However, strong discrepancies as to the magnitude of adsorption and activation entropies still persist. The aim of the present study was to determine the cracking rates while simultaneously measuring the coverage of active sites at reaction conditions, which is the key for a proper determination of the intrinsic reaction parameters [5].

Here, the surface coverage and protolytic cracking rates of C_3-C_7 alkanes over H-MFI and H-FER zeolites were determined using Operando IR spectroscopy at variable temperatures (400 - 475°C), pressure (0.1-1.0 bar) and contact times. The IR spectra of bridged OH group-alkane complexes were used to assess their concentration prevailing in the zeolite pores, which were found perfectly correlated with the apparent cracking rates r_{app} *(T,P)* and independent of the contact time, hence allowing assessing unambiguously *intrinsic* cracking rate constant k_{int} *(T)* and their parameters (E_a, $\Delta S^{\ddagger}$).

Our results confirm that the activation entropy ($\Delta S^{\ddagger}$) chiefly determines the variations of apparent protolytic cracking rates with the alkane chain length or zeolite structure. The intrinsic activation energies were found similar for all the alkanes investigates in this study (~ 190 kJ mol^{-1}), slightly lower than those generally derived from alkane adsorption heats and apparent activation energies [2,3]. The activation entropies obtained in the present study (-21 to -1 J K^{-1} mol^{-1} for C_3 to C_7 cracking over H-MFI) was also lower than those derived from low temperature adsorption measurements, which probably reflects increase in the entropy and a slight decrease in energy of the adsorbed state with temperature with temperature, as recently proposed by state of the art simulations [4,5], yet at a lower space than predicted. Similarly, the influence of the zeolite structure (H-MFI vs. H-FER) could also be accounted by an increase of activation entropy as the pore size decreased. Overall, our results suggests that the confinement of the reacting state (as defined as alkane size to pore size ratio) primarily governs the activation entropy, and hence the apparent protolytic cracking activities.

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Presenting Author: shashikant.kadam@ensicaen.fr

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In-situ PXRD studies of Pd-promoted Tungsten Carbides Catalysts

Glauco F. Leal [a], *Dean H. Barrett* [b] *and Cristiane B. Rodella* [b,]
[a]*Institute of Chemistry of São Carlos (IQSC)/University of São Paulo (USP)/ C.P. 780, CEP 13560-970, São Carlos, SP, Brazil*
[b]*Brazilian Synchrotron Light Laboratory - LNLS, C.P. 6192, 13083-970, Campinas, São Paulo, Brazil*
cristiane.rodella@lnls.br

The biorefinery concept for residual lignocellulose biomass has opened up a variety of opportunities to investigate and obtain chemicals and biofuels thorough the heterogeneous catalysis. However, the challenge of developing green chemical methods for renewable energy generation based on heterogeneous catalysis relies on a thorough investigation of the physical and chemical properties of the catalyst. Moreover, the catalytic process needs to be viable and profitable. Catalysts based on tungsten carbide supported on activated carbon have great potential for cellulose conversion [4], opening up new possibilities to replace expensive noble metal catalysts for application in residual biomass transformation. The interaction between promoter/tungsten carbide/support and the carburization process is a point that has not been deeply explored. Less attention has been paid to the structural properties of this complex multifunctional catalyst from the preparation to the reaction steps. Thus, this work aimed to investigate the structural evolution of tungsten carbide catalysts during the carburization process using *in-situ* PXRD techniques to determine the influence of the Pd promoter and functionalized carbon with SO_3H groups on the carburization temperature as well as on the formation and stabilization of the carbide phases (W_2C, WC_{1-x} and WC).

The *in-situ* PXRD studies were performed at the I11 beamline at Diamond (UK) and the ex-situ analysis at the XRD beamline at the LNLS-Brazil. A high pressure capillary cell reactor with sapphire capillary, hot air blower and 18 PSD detectors were used in the in-situ experiments. The carburization was be carried out under a total flow of 20 mL/min of H_2/CH_4 gas mixture (18:2 flow ratio). The samples were heated up to 999°C using a heating rate of the 8°C/min, and then held isothermally for one hour. The in situ experiments were performed at 15 keV with 2theta ranging from 3-150°. The XRD patterns collected at the XPD-LNLS were measured at 7.5keV with one Mythen detector installed 1m from the sample. Even after heating to 999ºC, only metallic tungsten was present in the non-promoted sample.The carburization process involves reduction of tungsten oxides to metal ($WO_3 \rightarrow WO_2 \rightarrow W$) and the dissolution of C into the metal lattice [2-3]. The second step starts with the interaction of the carbon source (CH_4 and/or carbon from the support) with H_2 to form CH_x or C^* species which diffuse into the metallic tungsten structure to form the carbide phase. This result show that without the presence of a promoter the temperature was not sufficient for carburisation to take place. XRD and TEM analysis obtained after the carburization process at the LNLS showed that the non-promoted tungsten carbide catalyst produced a mixture of nanosized carbide phases of W_2C, WC_{1-x} and WC. The addition of 2% Pd had the effect of lowering the carburisation temperature. The *in situ* XRD analysis showed that metallic W formation started at ≈561ºC and the carbide W_2C phase formation occurred at 896ºC. Diffraction peaks of the Pd promoter can be seen at 120ºC showing some sintering of the promoter even at low temperatures. A change in the support material whereby a functionalized sulphonated carbon was used resulted in a decrease in the carburisation temperature with respect to the non-promoted sample as well as remarkable decrease in the overall particle sizes of the produced W_2C phase showing broader diffraction peaks. The formation of pure W_2C phase is an important result, as it has a direct correlation with the selectivity property of the tungsten carbide catalyst applied to cellulose conversion. Our catalytic results showed this catalyst was able to produce high ethylene glycol and fructose yields. On the other hand, the non-promoted catalysts, formed by a mixture of carbide phases only produced acetol.

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Hydride formation in Pd Nanoparticles probed by in situ Pd K-edge XAS and XRPD

A.L. Bugaev[1,2], A.A. Guda[1], K.A. Lomachenko[1,2], V.V. Srabionyan[1], A. Lazzarini[2], L.A. Bugaev[1], V.P. Dmitriev[3], J.A. van Bokhoven[4,5], E. Groppo[2], R. Pellegrini[6], A.V. Soldatov[1], C. Lamberti[1,2]

[1] Southern Federal University, Rostov-on-Don, Russia,
[2] Department of Chemistry, University of Torino, Italy,
[3] ESRF, Grenoble, France,
[4] ETH Zurich, Swiss, 5PSI, Villigen, Swiss, 6 Chimet SpA, Arezzo, Italy
carlo.lamberti@unito.it

Temperature and pressure dependent hydride phase formation in the palladium nanoparticles supported on Al_2O_3 and active carbons was studied by X-ray powder diffraction (XRPD), extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) at BM01B. Pressure-composition isotherms for PdH_x nanoparticles shown in Figure 1 were obtained by a single shell Fourier analysis of EXAFS data in a pressure range from 10^{-3} to 10^{4} mbar and in a temperature range from -10 to 110 °C. From the other hand, XANES spectra appeared to be directly influenced by the presence of hydrogen atoms in the Pd lattice [1] which was in a good agreement with theoretical simulations [2] and the performed fitting of these spectra provided quantitative information on the hydrogen concentration in Pd nanoparticles under different (P,T) conditions. The obtained results indicated a non-linear dependence of the Pd-Pd interatomic distances upon the hydrogen concentration during the β-phase formation.

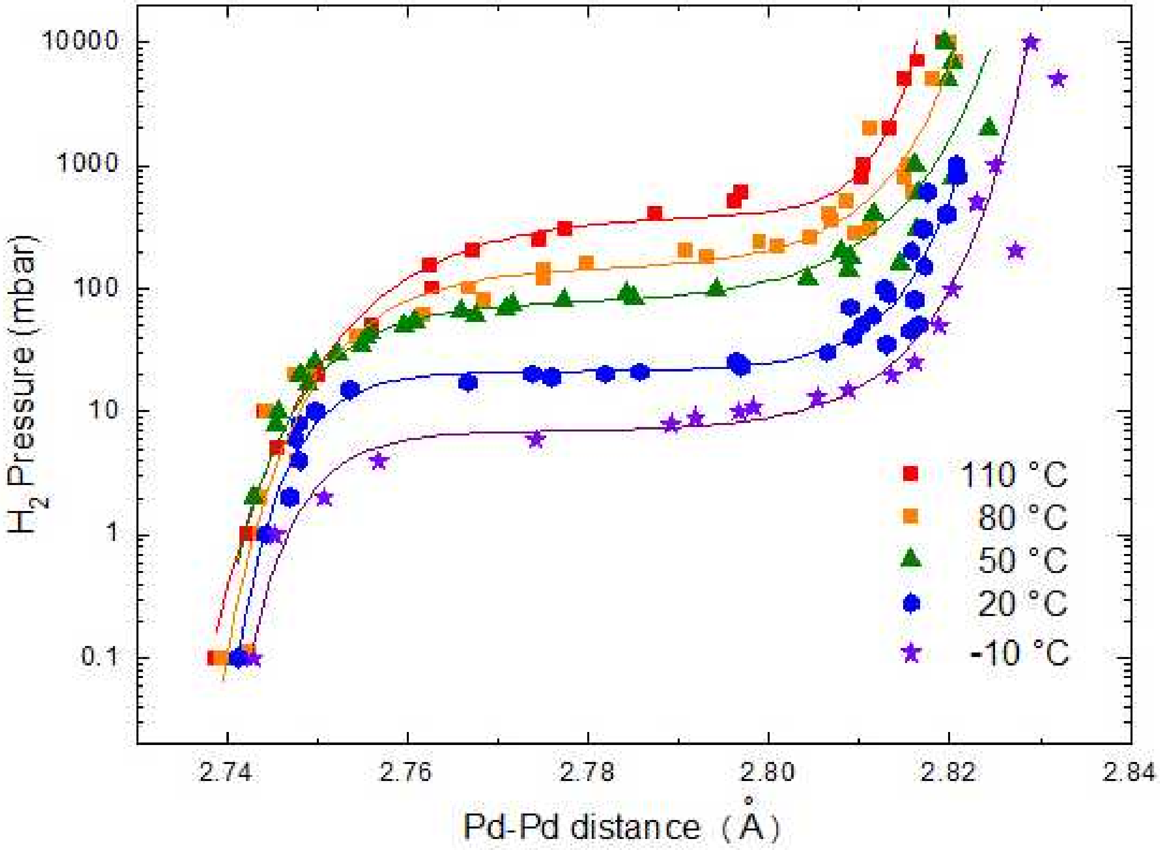

Figure 1: Pressure-composition isotherms for the PdH_x nanoparticles from first shell EXAFS analysis.

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P 58

The Role of Water in the Heterogeneously Catalyzed Oxidation of Acrolein

S. Knoche, T. Petzold, M. Heid, A. Drochner, H. Vogel
Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie,
Alarich-Weiss-Str. 8, D-64287 Darmstadt, E-mail: h.vogel@tc1.tu-darmstadt.de

Introduction

The current production of acrylic acid is about 5,4 million tons per year. The dominant production process today is a two-step oxidation starting from propylene and molecular oxygen. The conversion of acrolein (Acr) to acrylic acid represents the second reaction step, where Mo/V/W oxides are used as catalysts. It is well-known that water enhances the catalysts performance significantly[1,2,3]. Results from DRIFTS and SSITKA as well as their evaluation on computer-based modelling will be presented in order to gain mechanistic details of the effect of water.

Experimental

A hydrothermal prepared mixed oxide with the general formula $Mo_8V_2W_{1.5}O_x$ ($23 \leq x \leq 33.5$) was examined via DRIFTS under several concentrations of water in the gasphase (2-10 vol.%). The same mixed oxide was examined via SSITKA experiments under various feed-compositions (all specifications in vol.%: 5 % Acr, 10 % O_2, 2,5-8.5 % H_2O, balance: He and 2.5-10 % Acr 10 % O_2 7.5 % H_2O, balance: He) and temperatures (100-350 °C). After a pretreatment this technique involved the stepwise exchange of $H_2{}^{16}O$ by its isotopologues $H_2{}^{18}O$ in the gas flow.

Results and Discussion

The DRIFTS studies show a hydroxyl groups formation on the catalyst surface. As expected, the intensity of the hydroxyl bands increases with increasing concentration of gaseous water. The chemisorption of water fits a Langmuir model. In a further equilibrium acrolein adsorbs on hydroxyl groups by the formation of an acetalic surface species. The reversibility of this reaction results in an oxygen exchange between water and acrolein. SSITKA experiments evidence that the oxygen exchange already takes place in a non-reactive temperature range (<200 °C). The kinetics of the oxygen exchange can be described with the help of the aforementioned model, which is consistent with the DRIFTS results (Figure 1).

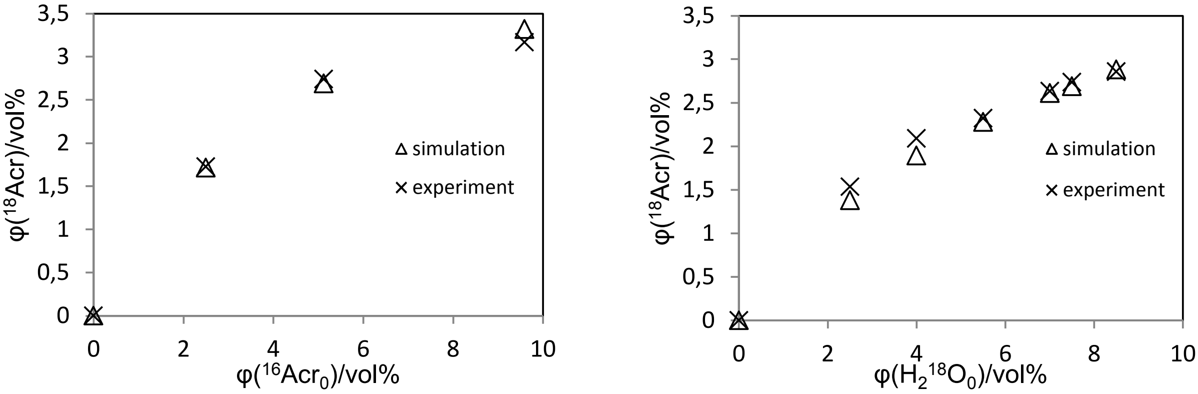

Figure 1: Simulated compared wtih experimental data obtained from $H_2{}^{18}O$-SSITKA experiments. Shown are the stationary ^{18}Acr volume fractions as a function of the fed volume fractions ^{16}Acr (all specifications in vol.%: left: $\phi(O_2)$=10 %, $\phi(H_2O)$=7.5 %, balance: He) or $H_2{}^{18}O$ respevtivly (right: ϕ(ACR)=5 %, $\phi(O_2)$=10 %, balance: He) with 50 mg $Mo_8V_2W_{0,5}O_x$ at T=100 °C.

The reversible adsorption of acrolein on hydroxyl groups is a crucial step in the reaction mechanism of the acrolein oxidation. The first quantification of this step was disclosed by using DRIFTS and SSITKA in combination with a reaction modelling.

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Formation and growth of Pd Nanoparticles on high surface area supports: role of the reducing agent

E. Groppo,[1] G. Agostini,[2] E. Borfecchia,[1] A. Lazzarini,[1] Francesco Giannici,[3] G. Portale,[4] A. Longo,[4,5] C. Lamberti[1,6]

[1] University of Turin, Department of Chemistry, NIS and INSTM Reference Centers, Via P. Giuria 7,10125 Turin, Italy
[2] European Synchroton Radiation Facility (ESRF), 6 Rue Jules Horowitz, Grenoble, BP 156, F-38042, France
[3] Dipartimento di Fisica e Chimica, Università di Palermo, viale delle Scienze, I-90128 Palermo, Italy
[4] Netherlands Organization for Scientific Research at ESRF, BP 220, F-38043 Grenoble Cedex 9, France
[4] Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Via La Malfa, 153, I-90146 Palermo, Italy
[6] Southern Federal University, Internat. research center "Smart materials", Zorge str. 5, 344090 Rostov-on-Don, Russia

carlo.lamberti@unito.it

Simultaneous time-resolved SAXS and XANES techniques were employed to follow in situ the formation of Pd nanoparticles in a porous polymeric and on active carbon supports, using different precursors and gaseous H_2 or CO as reducing agents. These results, in conjunction with data obtained by diffuse reflectance UV−vis and DRIFT spectroscopy and TEM measurements, allowed unraveling of the different roles played by gaseous H_2 and CO in the formation of the Pd nanoparticles. In particular, it was found that the reducing agent affects both the reduction rate and the properties of the hosted nanoparticles, in terms of size, and surface properties. The importance of a multitechnique approach in following the whole process of metal nanoparticles formation clearly emerges [1].

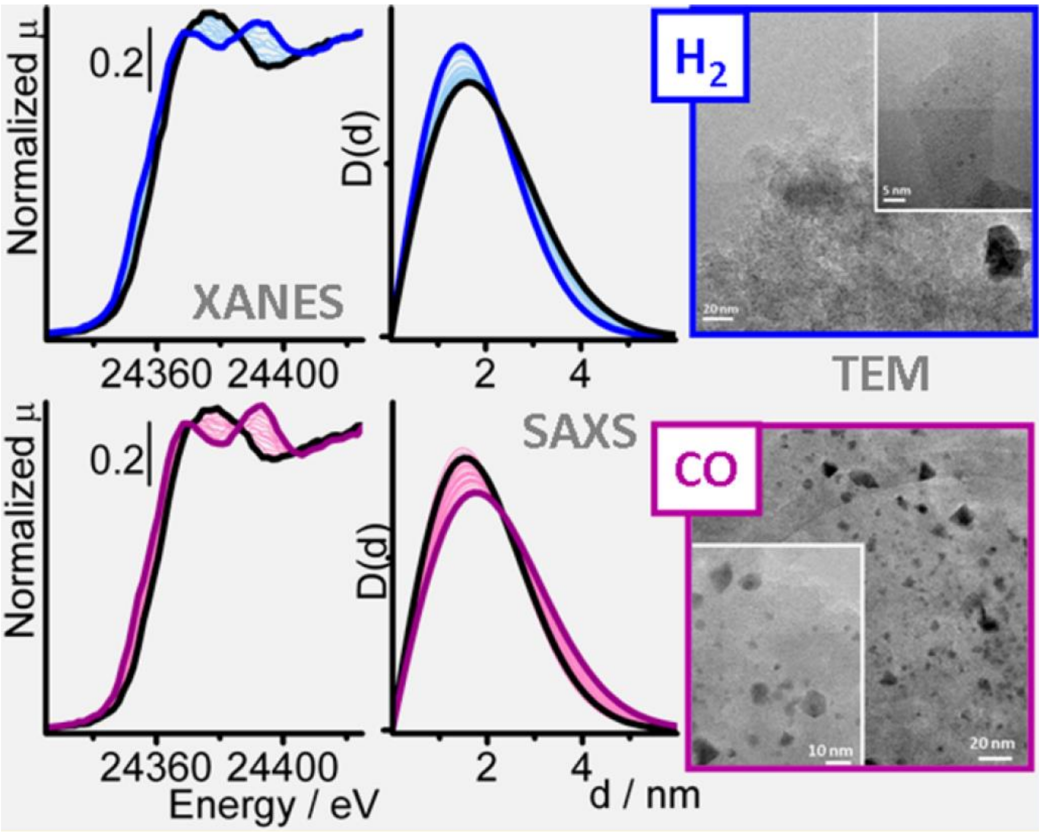

Fig. 01. In situ reduction of Pd nanoparticles on porous polystyrene followed by XANES (left) and SAXS (middle, reporting the nanoparticle distribution in real space). Corresponding TEM micrographs (right). Top (bottom) part refer to H_2 (CO) reduction agent.

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P 60

Active Phase of a NiMoS Catalyst unsupported during In Situ thermo Treatment Raman for Hydrodesulfurization

M.A. Cortés-Jacome, J.A. Toledo-Antonio, M. Pérez Luna, Ma. De L. Mosqueira M., C. Angeles-Chavez, E. López-Salinas
Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas # 152, Col. San Bartolo Atepehuacan, Gustavo A. Madero, 07730 México, D.F. MEXICO.
e-mail: macortes@imp.mx

Hydrodesulphurization of middle distillates is carried out over sulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts [1]. In order to remove the di-substituted sulfur compounds, such as 4.6 dimethyldibenzothiophes, it is necessary to develop hydrogenation active sites in the catalysts [2]. supported catalysts do not fully eliminate such sulphur molecules. To solve this problem, unsupported catalysts are proposed having around three times more active sites than the conventional catalysts [3]. In these case pure nickel molybdate precursor $NiMoO_4$-$nH_2O{\cdot}mNH_3$ is prepared by precipitation method using nickel nitrate, ammonium heptamolybdate and ammonium hydroxide solution at 90 ^{o}C [4], starting from a Mo/Ni 1:1 atomic ratio, this catalyst was prepared and studied by in situ thermo-Raman spectroscopy in nitrogen atmosphere. When the catalyst was annealing at 400 ^{o}C, the Raman spectra (Figure 1) present a main vibrating line at 945 cm^{-1} and a line around 936 cm^{-1}, corresponding to alpha phase, where Mo is tetrahedrally coordinated and Ni in octahedral coordination. Decreasing temperature, the alpha phase transforms into beta phase at 30 ^{o}C, and Mo and Ni are both octahedrally coordinated with principal vibration bands in 953, 942 and 896 cm^{-1} [5], a small amount of MoO_3 (Raman shift at 817 cm^{-1}) is observed. During sulphidation this catalyst generates larger amount of promoted active sites NiMoS in comparison with the supported one, high resolution transmission microscopy image was shown in the Figure 2.

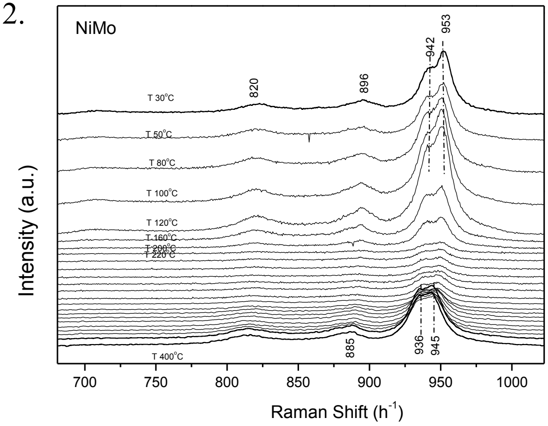

Fig. 1. In Situ Raman spectra of prepared catalyst catalyst

Fig. 2. HREM micrographs of sulfur

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P 61

Effect of an organic additive on the Reducibility and sulfidability of MoOx species on alumina support

J.A. Toledo-Antonio, M.A. Cortés-Jacome,’ P. Guzman-Antonio, C. Angeles-Chavez, E. López-Salinas.
Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas # 152, Col. San Bartolo Atepehuacan,
Gustavo A. Madero, 07730 México, D.F. MEXICO.
e-mail: jtoledo@imp.mx

Molybdenum sulfide supported on alumina is widely used as catalysts for hydrodesulphurization reactions [1]. Properties and catalytic behavior strongly depend on the oxide species dispersion, sulfurability and promotion of MoS_2 layers by a promoter as Ni or Co, which determine the formation of larger amount of active sites in the catalyst [2]. During preparation MoOx species strongly interact with alumina surface delaying its reduction and sulfidation degree during activation [3]. In this work, the influence of the addition of an organic compound which form a metal-ligand charge transfer complex (MLCT) with the MoOx species dispersed on the alumina surface is presented in order to weak the interaction between Mo and alumina and improve its sulfurability during sulfidation process. MoOx species were dispersed on alumina by impregnating molybdenum heptamolybdate and molybdophosphoric acid, and then calcined at 400 °C under dynamic air flow. Thereafter a water solution of thioglycolic acid (TGA) was added with a Mo/TGA molar ratio of 1.0. TGA reacts with MoOx species, reducing partially Mo^{VI} to Mo^{V} Figure 1, weakening the interaction with the alumina surface and increasing its reducibility and sulfidability, which represent an increase in catalytic activity during HDS of DBT.

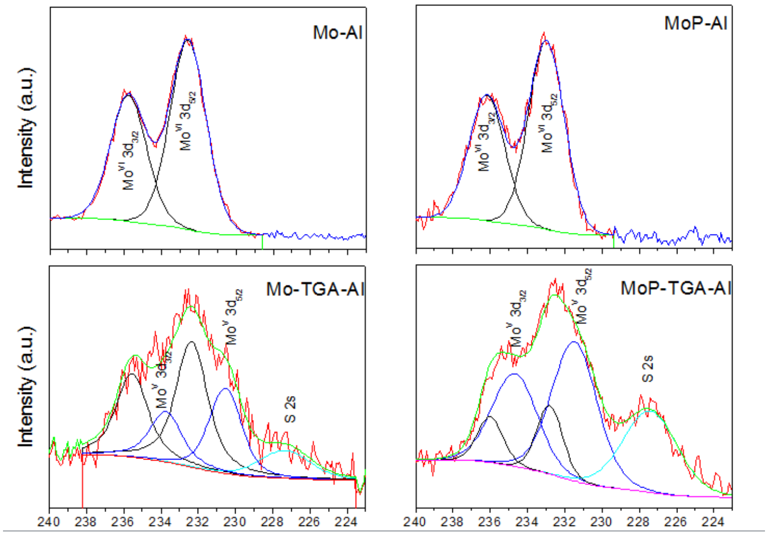

Fig. 1. XPS spectra of a) Mo/Al, b) MoP/Al, c) TGA/Mo/Al y d) TGA/MoP/Al

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Modelling a reactor cell for operando IR studies: from qualitative to fully quantitative investigations

Sébastien THOMAS [a], Olivier MARIE [a], Philippe BAZIN [a], Michele CORBETTA [b], Flavio MANENTI [b], Luca LIETTI [c], Carlo Giorgio VISCONTI [c], Marco DATURI [a]

[a]*Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS 6 Boulevard du Maréchal Juin, 14050 Caen, France*

[b] *Dipartimento di Chimica, Materiali e Ingegneria Chimica ‘‘Giulio Natta’’, Politecnico di Milano Piazza Leonardo da Vinci, 32 – 20133 Milano, Italy*

[c] *Dipartimento di Energia, Politecnico di Milano Piazza Leonardo da Vinci, 32 – 20133 Milano, Italy*

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The determination of reaction mechanism is of great importance in heterogeneous catalysis. The *operando* infrared spectroscopy is a major tool for that purpose, thanks to the observation of a working catalyst surface submitted to relevant operation conditions. In order to perform such investigations, specifically conceived reactor-cells are required whose constraints for the catalyst observation must allow to mimic real conditions [1]. Consequently, the IR reactor cell design is often a compromise between the necessity to obtain useful spectroscopic data and the ability to easily model the flow dynamics. Once a reaction mechanism has been elucidated, a next step consists in a more quantitative approach aiming at determining the intrinsic kinetic parameters. For this goal, the *operando* infrared spectroscopy is again a suitable technique with a possible quantification of intermediate surface species. However this quantification can only be properly applied for kinetic modelling if the flow distribution in the reactor-cell is well known. It is also of paramount importance to know which part of the catalysts is probed by the infrared beam. Nevertheless, this in depth exploitation of the *operando* data is not so common in the literature and relevant kinetic studies based on *operando* infrared spectroscopy data are not so numerous.

In this work, the precise flow modelling of an advanced *operando* infrared “Sandwich” type cell, working in the transmission mode using a wafer shaped as a disk, has been carried out with the use of ANSYS Fluent. It points out that the flow distribution is far from being trivial (Figure 1.a) and consequently the decomposition of the catalytic zone into ideal reactor has been used to perform a kinetic modelling of the methanol adsorption onto ceria when using the SSITKA methodology [2]. Furthermore, the use of masks with hole of 1.2 mm diameter allowed probing specific zones of the wafer by infrared. An acceptable fit was found between modelled and experimental data of both gas and surface concentrations. However, in order to improve the modelling, a new configuration of the reactor cell has to be developed using a square shaped wafer. The resulting flow distribution was found to be close from a perfect plug flow reactor one (Figure 1.b) leading to more simple kinetic modelling which results in a very good fit between experimental and modelled data (Figure 1.c).

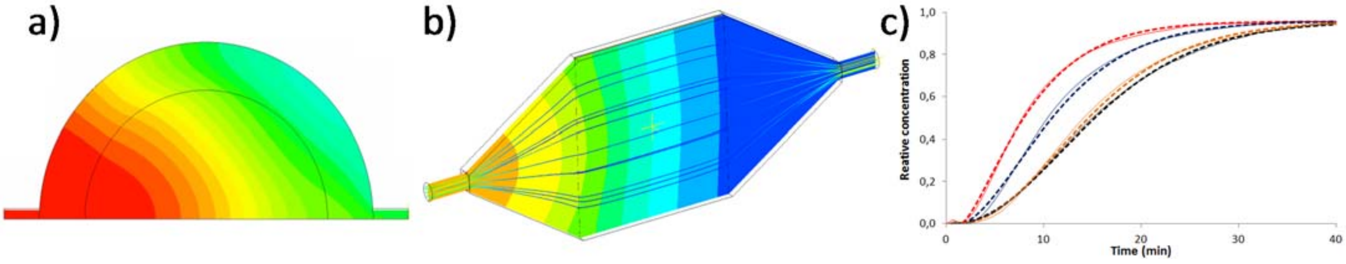

Figure 1: Flow modelling: evolution of the concentration after a concentration step of 10% N_2 in Ar at 30 °C with (a) a disk shaped wafer and (b) a square shaped wafer. (c) Evolution of methoxy relative concentration with ^{13}C labelled carbon during SSITKA exchange at the entry (red) middle (blue) and exit (orange) of a square shaped wafer, evolution of methanol relative concentration with ^{13}C labelled carbon during SSITKA exchange (black); full lines: experimental, dotted lines: simulation.

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P 63

Simultaneous *operando* Raman and infrared monitoring of catalysts

Guillaume Clet[1], Raquel Portela[2], Philippe Bazin[1], Marco Daturi[1], Miguel A. Bañares[2],
[1] Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen Basse-Normandie, CNRS, 6 Bd. du Maréchal Juin, 14050 Caen, France.
2 Instituto de Catalisis y Petroleoquímica, CSIC, Madrid, Spain.
e-mail : guillaume.clet@ensicaen.fr

Extensive characterisation of catalysts at work requires information which is rarely obtained by a single technique. Coupling of techniques is thus often attempted and several successful examples of combinations have been published in the recent years.[1] Among spectroscopic characterization techniques, combination of vibrational spectroscopies is particularly suited but rarely attempted. Raman and infrared spectroscopies bring unique complementary information on the catalyst structure changes and the adsorbed species, respectively, which may in turn be correlated with each other. Such a combination has previously been proposed [2-4] by the use of a specific commercial extension on the Raman microscope allowing the sequential acquisition of Raman and infrared spectra at the same position. These interesting contributions underline the complementarity of both measurements; hurdles remain to be tackled: IR data are not quantitative in reflectance mode and the measurements are not simultaneous. In addition, cells commonly used in microscopy are often designed differently from a usual catalytic reactor (i.e. with large internal volumes). Other approaches relied on the use of DRIFTS or ATR-IR which also complicate a quantitative analysis of the IR data.[5-6]

We propose here a different approach, adapting a home-made *operando* IR reactor[7] to also host a Raman probe. Both transmission FTIR and reflectance Raman spectra can be run on the same catalyst pellet. The cell is placed in the IR spectrometer bench and allows direct acquisition of the transmission IR spectra. For the Raman spectra, the laser excitation (532 nm) is brought in the cell via an optical fibre and focused on the sample with an InPhotonics Raman probe adapted ad hoc. The dual IR-Raman operando reactor can be heated for catalyst activation or reaction, and is placed under a controlled gas flow. Downstream the catalyst wafer, the exhaust gases are directed towards an IR gas cell, a GC and/or a mass spectrometer for simultaneous on line analysis. The current approach has, thus, the advantage of the simultaneous monitoring of Raman and transmission IR spectra while acquiring relevant catalytic data, and easy adaptability on any FTIR and fibre-coupled Raman spectrometers.

Several examples of such combination will be shown here such as the characterisation of supported oxides and their evolution under propane ODH conditions.

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Combined super-resolution fluorescence and electron microscopy for catalysis research

Jordi Van Loon[1], Kris Janssen[2], Thomas Franklin[1], Johan Hofkens[2], Maarten Roeffaers[1]

[1]Center for surface chemistry and catalysis, Department of Molecular and Microbial Systems, KU Leuven, Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium

[2]Laboratory of Photochemistry and Spectroscopy, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

E-mail: jordi.vanloon@biw.kuleuven.be

Abstract

Recent studies have revealed important inter- and intraparticle heterogeneities within zeolite batches, which are intrinsically introduced during zeolite synthesis and become even more pronounced by post-synthesis treatments. These heterogeneities clearly influence the catalytic performance [1]. Traditional tools for studying heterogeneous catalysts however, either lack the spatial- or temporal resolution necessary to thoroughly correlate this information [2]. Therefore, in recent years there has been increased effort to develop techniques that enable a single particle or even single turnover resolution to establish a well-defined structure-activity relationship.

NASCA or “Nanometer Accuracy by Stochastical Chemical reActions” is one such technique that enables the recording of single turnover maps from single catalyst particles with nanoscale precision, based on wide-field fluorescence microscopy in combination with a fluorogenic reagent [3]. Correlating these highly detailed activity maps with structural information at the relevant nanometer length scale is, however, still challenging. For this purpose we have developed, in collaboration with Delmic, an integrated super-resolution fluorescence and electron microscope. Such a combined wide-field fluorescence and scanning electron microscope enables us to perform SEM and NASCA imaging either consecutively or simultaneously, i.e. correlated or integrated respectively, providing us with a novel tool to study the structure-activity relationship in zeolites with nanoscale resolution.

By using our newly developed iLEM in the correlated fashion, we have demonstrated the influence of intergrowths on the catalytic performance of small-port H-MOR crystals. The fluorogenic probe reaction used is the furfuryl alcohol oligomerization and whereas the dimensions of these reagent molecules prevent them from diffusing deeply into the one dimensional microporous structure, there are catalytic events observed in zones where this was not expected and that were otherwise inaccessible.

Our results clearly show that a powerful correlative technique as described above is necessary in order to get a deeper understanding of the relationship between the inherently large heterogeneity within zeolite batches and their catalytic performance.

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P 65

Insights into the relevance of Pt/Ba interaction for the NO_x storage and reduction over Pt-Ba/Al_2O_3 LNT catalyst.

Sara Morandi[1]*, Laura Righini[2], Roberto Matarrese[2], Lidia Castoldi[2], Luca Lietti[2], Pio Forzatti[2]

[1] *Dip. di Chimica and NIS Inter-departmental Center, Università di Torino, Via P. Giuria 7, Torino 10125 (Italy).*

[2] *Dip. di Energia, Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, Via La Masa 34, Milano 20156 (Italy)*

*sara.morandi@unito.it

Pt-Ba/Al_2O_3 Lean NO_x Trap (LNT) catalysts are viable systems for NO_x abatement from lean–burn engine emissions. These systems work under periodic cyclic conditions: during lean conditions NO_x are stored in the form of nitrites and nitrates that are reduced to N_2 and by-products during rich conditions. Formation of nitrites (nitrite route) is based on the oxidative adsorption of NO at Pt/Ba interface, although the role of the Pt-Ba interaction on this pathway is still under debate. Nitrites can be eventually oxidized into nitrates. At variance, nitrate formation also proceeds through NO oxidation to NO_2 over Pt, followed by NO_2 uptake as nitrate (nitrate route).

When H_2 is used as reductant, its activation forms Pt-H species. Then the reductant spills from Pt to Ba, where stored NO_x are converted to N_2 and other by-products. Alternatively, a reverse spillover of stored NO_x from Ba to reduced Pt sites may also occur. In these processes, a major role of the Pt/Ba proximity is expected.

In order to deepen the relevance of the Pt/Ba interaction, the analysis of the storage and reduction of nitrites and nitrates over Pt-Ba/Al_2O_3 and a Pt/Al_2O_3 + Ba/Al_2O_3 physical mixture was carried out. The storage of NO/O_2 mixtures and the reduction of the stored species with H_2 at various temperatures have been investigated with Temperature Programmed Surface Reaction (TPSR) and Transient Response Method (TRM) experiments in a micro-reactor system. TPD measurements have also been run. FT-IR spectroscopy in *operando* conditions have been carried out to elucidate the nature of the surface species involved in the process.

Adsorption data collected at 350 °C over Pt/Al_2O_3 + Ba/Al_2O_3 physical mixture have shown nitrates formation on both Ba and Al sites. Initially nitrites are formed, mainly on Ba phase, and then evolve to nitrates. Similar results have been obtained over Pt-Ba/Al_2O_3, but the nitrites to nitrates transformation proceeds faster if compared to what observed on the physical mixture, underlining the key role of the Pt/Ba interaction on this transformation.

Adsorption data collected at 150 °C over Pt/Al_2O_3 + Ba/Al_2O_3 physical mixture have shown only nitrite formation on both Ba and Al sites. Nitrites on only Ba sites are mainly observed also over Pt-Ba/Al_2O_3 catalyst at 150 °C. After storage at 150 °C TPD measurements up to 500 °C show on one hand the consumption of nitrites with nitrate formation over Pt-Ba/Al_2O_3, on the other hand the erosion of nitrite without nitrate formation over the Pt/Al_2O_3 + Ba/Al_2O_3 physical mixture. Also this result put in evidence the role of Pt-Ba interaction.

When nitrates stored at 350 °C over the Pt/Al_2O_3 + Ba/Al_2O_3 physical mixture are reduced with H_2 under isothermal conditions, the regeneration of the catalyst is inhibited with respect to the Pt-Ba/Al_2O_3 sample. In particular, a fast reduction of the nitrates on Al sites of the Pt/Al_2O_3 particles is observed, while those related to Ba remain stable. This indicates that the NO_x reduction is a Pt-catalyzed reaction implying that stored NO_x have to be adsorbed on the same particle of Pt. To prove if the regeneration process involves spillover of H_{ads} from Pt to the nitrate species and/or of the nitrates from Ba to Pt, the reduction of WO_3 physically mixed with Pt/Al_2O_3 was used as probe reaction. It was observed that H_{ads} is able to migrate from Pt/Al_2O_3 to WO_3, leading to WO_3 reduction. Since on the other hand the reduction of nitrates stored on Ba separate from Pt does not occur (in spite H migrates from Pt/Al_2O_3 to Ba/Al_2O_3), it is concluded that reduction of stored NO_x implies the NO_x migration from the sorption sites to reduced Pt sites.

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Revealing the acid site distribution and molecular transport in mordenite and ZSM-5 zeolites with stimulated Raman microscopy.

Tom De Wit[1], Johan Hofkens[2], Kuan-Lin Liu[2], Maarten Roeffaers[1]

[1]Center for Surface Chemistry and Catalysis, Department of Molecular and Microbial Systems, KU Leuven,
Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium

[2]Laboratory of Photochemistry and Spectroscopy, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001
Heverlee, Belgium

E-mail: tom.dewit@biw.kuleuven.be

Because of the complexity of the heterogeneous catalyzed process at the molecular scale, rational catalyst optimization strongly depends on generating detailed insights into the role of specific catalyst properties like the acid site distribution and accessibility, presence of catalytic sites at the outer surface, etc. - on the final outcome of the process. Since these catalyst properties and their effects are highly interlinked and also because of the significant inter- and intraparticle heterogeneities such information cannot be deduced from ensemble-averaged information. Microscopic characterization such as electron microscopy has revealed that such inter- and intraparticle heterogeneities in physical and chemical properties of zeolites are commonly present; still, they are often neglected or oversimplified when interpreting a catalyst performance.

Traditional vibrational spectroscopy has significantly contributed to the understanding and further development of catalysts. They are however, limited by their spatiotemporal resolution and/or sensitivity. In Stimulated Raman scattering (SRS) the otherwise weak spontaneous Raman signal is stimulated by irradiation with a second laser that provides photons with the same energy as the expected Raman photons(1). This technique is used as a powerful novel physicochemical characterization tool for gaining detailed insight into the catalytic performance at the level of single zeolite particles. This approach allows studying the mass transport and the acid site distribution in zeolite particles in three dimensions and with sub-micrometer resolution.

Mapping the acid site distribution is possible by the change in the fundamental vibrational signatures of molecular probes on their interaction with the local environment. The C-N vibration in acetonitrile, benzonitrile and (substituted) pyridine will be used for this. The recorded stimulated Raman scattering intensities can be converted to local acid site densities by measuring the influence of polarization of the laser light.(2) Real time recording of the uptake of chemicals are also monitored with SRS microscopy. This allows to directly evaluate the uptake by the different zeolites and answer important questions related to the effect of mesoporosity, pore-blockage by extra-framework species, etc.

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Stability of Co and Ni catalysts towards steam reforming of ethanol as function of electronic properties

Adriano H. Braga, João B. O. dos Santos, José M. C. Bueno. Department of Chemical Engineering, Federal University of São Carlos, São Carlos-SP, Brazil. Corresponding author: jmcb@ufscar.br

Temperature resolved XANES (Figure 1) was used to study the NiCo/$MgAl_2O_4$ catalysts during the reduction and in steam reforming of ethanol (SRE) reaction. The catalysts were prepared by impregnation of Ni and Co nitrates onto $MgAl_2O_4$, with 8 wt% metal loading and labeled as 8Ni, 4Co4Ni and 8Co catalysts. The XANES spectra were acquired at Ni and Co K-edges and the products of reaction accompanied by mass spectrometry. Ethanol and water were fed to reactor at room temperature in molar ratio of 3/1, and temperature was ramped and kept for 30 min at 500 and 550°C.

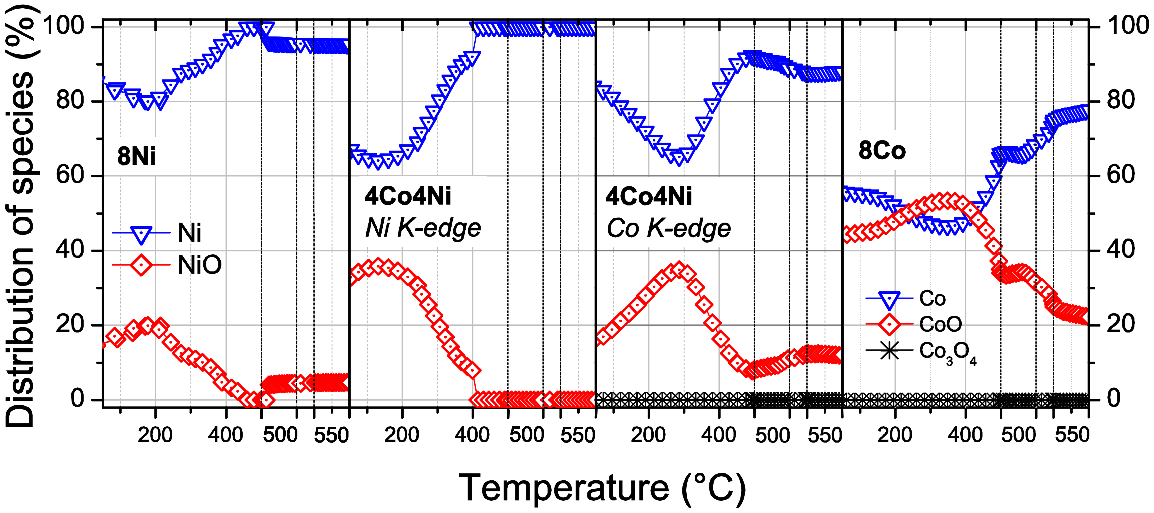

Figure 1: Metallic and oxide species, addressed by XANES, towards SRE as function of temperature.

EXAFS, XPS and TEM-EELS results indicated that after reduction a Co-Ni alloy is formed in 4Co4Ni catalyst. The SRE products as function of temperature showed that the dehydrogenation of ethanol occured at low temperatures where Ni and Co were mostly oxidized. Raising temperature increased the Co and/or Ni reduction's degree due to C-C bond breaking at about 400°C (Fig. 1) with desorption of CH_4 and CO. The CH_4 formation decreased in the order 8Ni>4Co4Ni>8Co. Finally, the reforming of adsorbed CH_x species occurred at temperatures above 400°C, with formation of CO and CO_2. The XANES spectra during SRE evidenced an increase of oxide species in the Co-containing catalysts. Carbon accumulated with time on SRE stream at 550°C was higher on 8Ni (as expected) and surprisingly the 4Co4Ni accumulated carbon as much as 8Co catalyst. In the bimetallic catalyst the Co severe oxidation is prevented (unlike 8Co), and the Ni oxidation, otherwise, enhanced; opposed to 8Ni catalyst which kept well reduced during experiment. Concluding, the formation of CoNi alloy promoted changes in the electronic properties of Ni, and enhances the amount of oxygen available to oxidize the carbon during reaction, being the bimetallic catalyst a more efficient SRE catalyst.

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Fischer-Tropsch SSITKA experiments over hcp and fcc Co/Al_2O_3

E. Rebmann[1,2], P. Fongarland[1], V. Lecocq[2], F. Diehl[2], Y. Schuurman[1]
[1] *IRCELYON, Université Lyon 1, CNRS, UMR5256, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
[2] *IFP Energies nouvelles, Etablissement de Lyon*
Rond point de l'échangeur de Solaize, BP3, 69360 Solaize, France
* yves.schuurman@ircelyon.univ-lyon1.fr

Introduction

With the need for energy resource diversification, there is an increasing interest in Fischer-Tropsch (FT) synthesis. This process allows syngas ($CO+H_2$) conversion issued from natural gas, coal or biomass into long-chain paraffins that can be upgraded into excellent diesel/kerosene fractions. Catalytic properties of cobalt-based FT catalysts strongly depend on their morphological and structural properties [1-2]. Previous in-situ XRD and magnetic studies during the activation showed the possibility to selectively orient the cobalt crystal phase to either mainly face centered cubic (fcc) or mainly hexagonal closed packed (hcp) according to the operating conditions during activation [3]. These catalysts have been tested in Fischer-Tropsch synthesis in order to differentiate activity, selectivity and potential mechanism specificities regarding to each crystal phase orientation as well as the particle size distribution. In order to get a fine description of the catalyst systems, high resolution chromatographic analysis combined with multi-product isotopic transient kinetic experiments have been carried out. In addition to classical data analysis, micro-kinetic modeling using different reaction mechanisms is used to correlate the key kinetic parameters to the catalyst structure.

Experimental

Catalyst testing for FT synthesis was carried out in a quartz plug flow reactor at 1.6 bars, 215-235°C with a H_2/CO ratio of 2 and about 300 hours of time on stream (TOS) to account for catalyst ageing. Catalyst preparation and activation (via carbidization/decarbidization) affording mainly hcp and mainly fcc Co° crystal phase orientation have already been described elsewhere. Note that in both cases a mixture of hcp and fcc phases are obtained, but we refer to them as fcc or hcp Co°. The online analysis system for catalyst testing was composed of a cryogenic GC, a GC/MS with 16 storage loops and a MS gas analyzer. The combination of these techniques allowed monitoring product distribution (paraffins, α- and β-olefins and isomers) and determining the isotopic composition of a large range of products during SSITKA experiments (replacement of ^{12}CO by ^{13}CO).

A large product's isotopic diversity is transiently induced the SSITKA switch of the feed. To face this complexity in the modeling work, an algorithm has been developed to automatically explore all possible paths of the reaction network. It starts from a flexible reaction network based on elementary steps. The code then generates all species involved before and after the $^{12}CO/^{13}CO$ switch. The fully coupled ordinary differential equation system governed by the considered network is integrated by DVODE while ODRPACK is used for the multi-response adjustment of the kinetic parameters.

Results and Discussion

The hcp Co° oriented catalyst is less active than the fcc Co° oriented catalyst. The methane selectivity is slightly higher for hcp Co° than fcc Co° at low temperature (205°C) whereas hardly any difference between the two samples is exhibited at higher temperature. Analysis of the product distributions reveals that the olefin to paraffin ratio for hcp Co° is lower than fcc Co° at the same time on stream (100h) indicating that hcp Co° have a weaker hydrogenation power. SSITKA experiments were performed over both catalysts. Selected SSITKA responses of 1-hexene are reported in figure 1. After the $^{12}CO/^{13}CO$ switch, the response curves for fcc Co° are faster than for hcp Co°. This is, the replacement of ^{12}C by ^{13}C in the final products is faster for fcc Co° catalyst. Based on SSITKA principles [4], it can be deduced that intermediates surface residence times are longer on hcp Co° particles for all intermediates leading to the product distribution than for fcc Co°. This delay over the hcp Co° could be explained by a slow-down of the intrinsic kinetics and/or by the existence of a larger intermediate reservoir taking more time to be replenished.

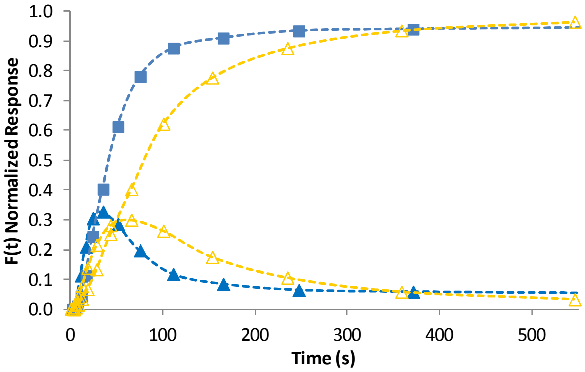

Figure 1: SSITKA responses of 1-hexene at 220°C, H2/CO ratio of 2 (,■ $^{13}C_6H_{12}$ & Δ, $^{13}C_5{}^{12}CH_{12}$) after a $^{12}CO/^{13}CO$. Open and full symbols refer respectively to hcp and fcc Co^0).

SSITKA experiments over fcc and hcp Co° with increasing time on stream show an increase of the surface residence time of intermediate species during the first hundreds hours on stream which could be linked to catalyst ageing.

Since many products share the same intermediates and can be reinserted in the polymerization process, the direct quantification of the reaction rates and reservoirs sizes is not obvious. Micro-kinetic modeling work is in progress in order to shed light on these results.

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Speciation of adsorbed species on heterogeneous surfaces by a new 2-dimensional approach: 2D infrared inversion spectroscopy (2D IRIS)

Pawel Stelmachowski, Sergey Sirotin, Philippe Bazin, Françoise Maugé, Arnaud Travert
Laboratoire Catalyse et Spectrochimie, ENSICAEN – Université de Caen – CNRS, Caen, France.

A new methodology based on the inversion of adsorption isotherms obtained using infrared spectroscopy has been developed. It provides a description of coexisting surface species in terms of their individual IR spectra and surface affinities in a new two dimensional, 2D IR spectroscopic technique. When implemented with simultaneous gravimetric analysis, it further provides the quantification of adsorbed species.

The adsorption of CO_2 on monoclinic ZrO_2 was investigated using this technique with temperature and pressure ranges of 353–673 K and 10^{-4} – 0.4 bar, respectively. The sets of spectra obtained at constant temperature and variable pressures (spectroscopic isotherms) were inverted assuming they obey a generalized Langmuir isotherm. This procedure yields a 2D map in which the IR spectra of the prominent surface species formed upon CO_2 adsorption are resolved in one dimension – hydrogen carbonates, bidentate carbonates and polydentate carbonates – while these species are resolved according to their surface adsorption affinities (logarithm of adsorption equilibrium constants, ln K) on the other dimension. This technique also allows for the unambiguous determination of the thermodynamic stabilities of the various adsorbed species. The inversion of the gravimetric isotherms recorded simultaneously with the infrared spectra leads to quantitative distribution function of CO_2 adsorption sites whose components match those of the 2D infrared map and allows for a straightforward quantification of the corresponding sites, namely (i) weakly basic sites leading to bridged carbonates, hydrogen carbonates and bidentate carbonates), (ii) mild basic sites leading to a second type of bidentate carbonates and (iii) strong basic sites leading to polydentate carbonate species.

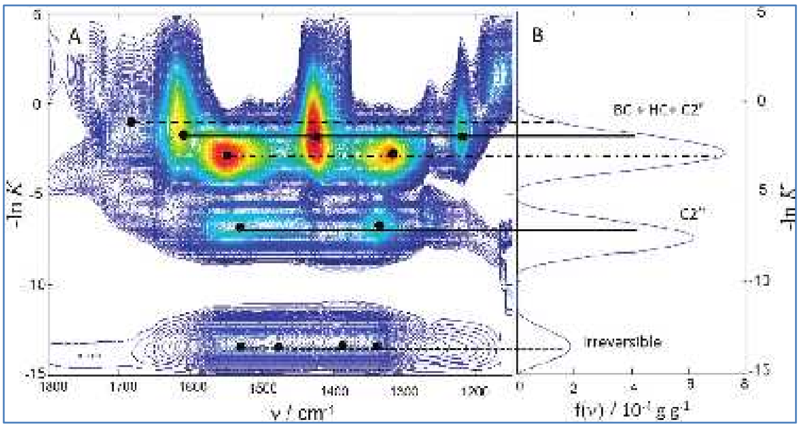

Figure 1: Comparison of distribution functions obtained from inversion of the IR spectroscopic isotherm (A) and of the gravimetric isotherm (B) at 573 K.

The method presented here provides a new technique for characterizing surface heterogeneity in terms of nature, number and strength of adsorption sites, in a more complete way than conventional adsorption studies. Finally, despite some inherent limitations, limited to the choice of the adsorption equilibrium model, the present method is not restricted to a particular spectroscopy or physical process and should find other applications in the field of spectroscopic characterization of surfaces.

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Presenting author :

P 70

In situ EPR study on redox properties of CuO−CeO$_2$

Feng Ryan Wang[1], Robert Büchel[2], Anton Savitsky[3], Michal Zalibera[3], Daniel Widmann[4], Sotiris E. Pratsinis[2], Wolfgang Lubitz[3], Ferdi Schüth[1*]

[1]Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim an der Ruhr, Germany, [2]Department of Mechanical and Process Engineering, ETH Zürich, 8092 Zürich, Switzerland, [3]Max-Planck-Institut für Chemische Energiekonversion, Stiftstrasse 34–36, 45470 Mülheim an der Ruhr, Germany
[4]University Ulm, Institute of Surface Chemistry & Catalysis, D-89069 Ulm, Germany
*E-mail: schueth@kofo.mpg.de, Tel: +49(0)208/306-2373

Understanding of the redox properties of metal oxides is a major task in catalysis research. *In situ* study provides with direct observation of change of valences and formation of active sites during redox or reaction conditions, and thus helps unveil the ongoing redox pathways. Here *in situ* electron paramagnetic resonance, combined with online gas analysis, mass spectrometry, x-ray photoelectron spectroscopy, x-ray diffraction and temporal analysis of products reactor, has been utilized to study the thermodynamic and kinetic redox behaviors of CuO−CeO$_2$. A synergetic mechanism that involves the redox pair of Ce^{4+}/Ce^{3+} is observed via studying the sample under subsequent CO/N$_2$/O$_2$ flow at *in situ* conditions (Figure 1). In addition, a direct mechanism that bypasses Ce^{4+}/Ce^{3+} has also been identified using isotopic $^{17}O_2$ labelling. Both two mechanisms suggest that strong interactions between Cu and Ce lead to better catalytic performance. With such guideline, CuO-CeO$_2$ is optimized and shows 11 K of operation window ranging from 377 K to 388 K, with 99% conversion and selectivity, in preferential oxidation of CO in excess of H$_2$ feed gas.

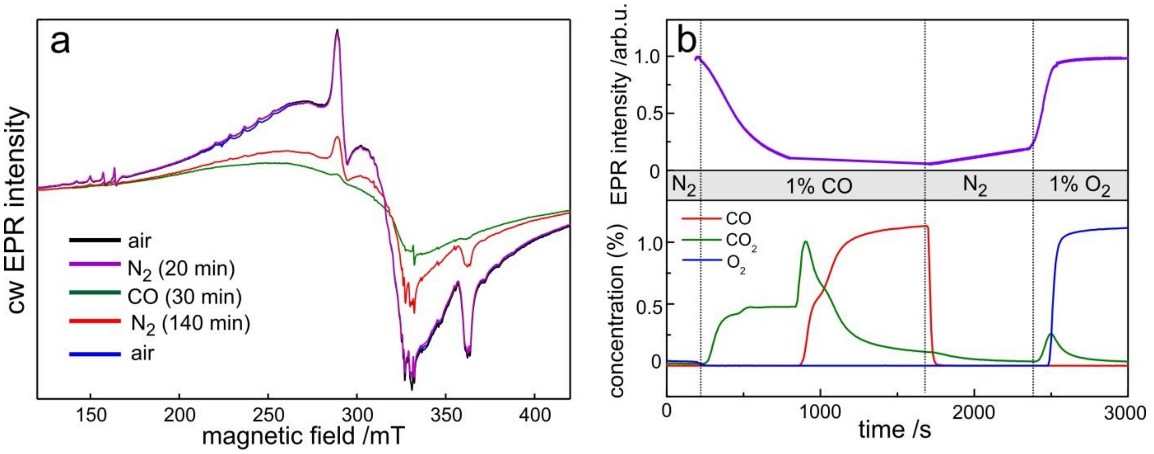

Figure 1. (a) X-band cw EPR spectra of 20wt% CuO-CeO$_2$ recorded at 453 K during the treatment with air/N$_2$/CO/N$_2$/air cycle. The times of the particular gas treatment are indicated. (b) Upper trace: Time dependence of Cu^{2+} dimer EPR intensity at 289 mT during N$_2$/CO/N$_2$/air cycle at 453 K. Lower traces: Corresponding CO, CO$_2$ and O$_2$ concentration simultaneously recorded by gas analytic system.

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In situ spectroscopic investigation of the active intermediates during catalytic combustion of methane over structured cobalt based catalysts

Przemysław J. Jodłowski[1*], Roman J. Jędrzejczyk[2,3], Damian Chlebda[3], Ewelina Piwowarczyk[4], Magdalena Chrzan[4], Joanna Łojewska[3]

[1] *Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland*

[2] *Malopolska Centre of Biotechnology, Gronostajowa 7A, 30-387 Kraków*

[3] *Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland*

[4] *Technical University of Lodz, Faculty of Process and Environmental Engineering, Wólczańska 213, 90-924 Łódź, Poland*

(*Corresponding Author's E-mail: jodlowski@chemia.pk.edu.pl)

The catalytic combustion of methane over transition metal catalysts is one of the most attractive alternative for the gas exhaust abatement. Methane appears as a main component of biogas, an renewable energy source that can be used to produce electricity at local levels [1]. The current exhaust gas abatement technology for biogas engines or turbines is based mainly on supported noble metal catalysts [2], out of which the most efficient in catalytic combustion are platinum and palladium catalysts [3]. Due to their superior activity total methane combustion is possible at relatively low temperatures, however, due to their high price and low stability at higher temperatures, the non-noble metal oxides are considered as an alternative for noble metals catalysts.

Over the years non-noble metals has attracted much attention in terms of their application as catalysts for methane combustion, although without a great success [4–7]. What is known is that, deposition of transitional metals over various metal oxide supports enhances their activity in catalytic combustion. However, the mechanism of catalytic combustion of methane remains still unresolved [2]. Notwithstanding the fact that in the literature the general agreement is that the rate determining step in the combustion mechanism is due to hydrogen abstraction from methane molecule resulting in the formation of methyl radicals at the catalyst surface, the mechanism of C-H bond braking step is still unexplained. Also, the combustion intermediates may vary coming from one catalyst to another [8]. The aim of this study is to provide some more information on the reaction intermediates and composition of active centres in cobalt palladium doped alumina supported catalysts which demonstrated higher activity than pure palladium supported catalyst in methane combustion.

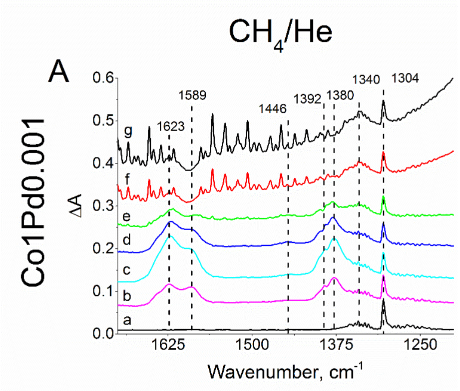

Figure 1. In situ DRIFT dynamic experiments; 1.6% CH_4/He 25 cm^3/min over cobalt palladium doped catalyst

In this study methane catalytic combustion over structured catalysts is examined by in situ DRIFT spectroscopy. The structured reactor internals made of kanthal steel that had been precalcined at high temperature and then wachcoated with γ-Al_2O_3, were used here as the catalysts supports. The catalytic activity was examined using CSTR reactor. The in situ UV/VIS, FTIR and Raman experiments were performed to study the composition in active sites and the reactive intermediates. The depth profiling experiments revealed that exclusively palladium is present on the surface even though it was provided on the catalyst surface in the very low quantity (2 times lower than in the commercial catalyst). The in-situ experiments performed under methane oxidative and non-oxidative conditions revealed that formates/carbonates are active intermediates in methane catalytic combustion (Figure 1).

Acknowledgments

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P 72

Methanation of CO_2: Structural response of a Ni-based catalyst under fluctuating reaction conditions unraveled by *operando* spectroscopy

*Benjamin Mutz[1,2], Hudson W. P. Carvalho[1], Stefan Mangold[3], Wolfgang Kleist[1,2], Jan-Dierk Grunwaldt[1,2]**

[1]Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany
[2]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
[3]Institute for Photon Science and Synchrotron Radiation (IPS), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

*Corresponding author: Jan-Dierk Grunwaldt Email: grunwaldt@kit.edu

Long term storage of renewable energies is of great importance for future power supply to balance the seasonal availability of wind and sunlight resources. Within the "power to gas" concept (PtG), renewable energy can be stored in the form of chemical energy. According to the Sabatier reaction the greenhouse gas CO_2 is hydrogenated by green H_2 to methane ("synthetic natural gas", SNG), which is a versatile energy carrier [1].

The Sabatier reaction over supported Ni or Ru catalysts is a well-known process under stationary conditions [2-4]. However, not much is known regarding the behavior of the catalyst and its deactivation processes under highly dynamic conditions, e.g. fast load changes that are expected for a fluctuating supply of renewable H_2.

Therefore, in the present work a well-characterized commercial Ni-based catalyst was investigated under dynamic reaction gas atmospheres in methanation reactions using *operando* X-ray absorption spectroscopy [5]. Detailed XANES (X-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure) evaluation demonstrated the importance of *operando* spectroscopy and revealed remarkable structural changes in the Ni particles, e.g. fast bulk oxidation after switching the reaction atmosphere from CO_2/H_2 to pure CO_2 (step 3 in Figure 1). This leads to a deactivation effect after reintroducing H_2 to methanation conditions (step 4 in Figure 1). The CH_4 yield did not reach the previous performance due to the presence of partly oxidized Ni particles. Further *operando* XAS experiments with next generation catalysts showed a steady deactivation of the catalyst with each cycle of changing reaction atmosphere. However, the initial oxidation state of the catalyst was successfully recovered by reactivation in hydrogen atmosphere.

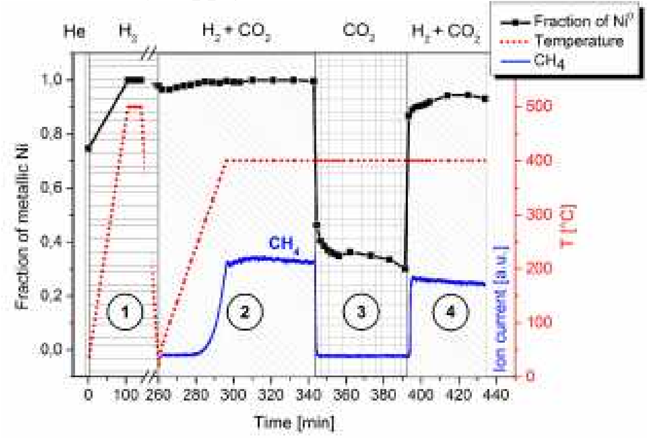

Figure 1: *Operando* XAS experiment during methanation of CO_2 using a commercial Ni-based catalyst (figure taken from ref. [5]). The plot shows the fraction of reduced Ni from linear combination of the XANES spectra, the reaction temperature as well as the MS signal of CH_4.

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P 73

A newly developed spatially resolved high pressure analyser

John Åhlund[1]

1. VG Scienta AB, Box 15120, 750 15 Uppsala, Sweden

john.ahlund@vgscienta.com

High-pressure Photoelectron Spectroscopy (HP-PES) is a rapidly developing technique with applications in a wide range of fields ranging from fundamental surface science and catalysis to energy materials, environmental science and biology. Here we present the design and performance of a newly developed high pressure photoelectron spectrometer capable of recording spatially resolved spectra under high pressure

The tests of the new analyser is done using a laboratory based system equipped with an Al Kα X-ray anode and a hemispherical electron energy analyser equipped with a differentially pumped electrostatic lens.

First, the performance of the HP-PES system is demonstrated. The transmission of the analyser is measured using Ag in up to 25 mbar of nitrogen. The instrument is demonstrated to be capable of measuring core level spectra as well as valence band spectra with unprecedented transmission.

Second, the spatial mode of the analyser is tested using a test sample of well-defined gold stripes on a silicon sample. A spatial resolution of better than 5 μm of the Au 4d 5/2 core level line was demonstrated under vacuum conditions as well as for high pressure measurements of 1 mbar.

Effect of sulfidation pressure and chelating agent on the structure and activity of hydrotreatment catalysts

Jian Jun Chen, Françoise Maugé, Laetitia Oliviero
Laboratoire Catalyse et Spectrochimie, ENSICAEN – Université de Caen – CNRS, Caen, France.

The worldwide demand for low sulfur containing fuels keeps increasing while the raw crudes contains higher amount of sulfur. Thus, the interest of academic and industrial partners remains sustained to improve the performance of hydrodesulfurization (HDS) catalysts. Sulfidation is a key step to determine the catalytic performance of the sulfided catalysts. Industrial sulfidation is generally performed under high pressure (3~5MPa), high temperature (573–723 K) while in academic studies, sulfidation is mostly carried out at atmospheric pressure. It is generally accepted that increasing the sulfidation pressure leads to better catalytic performance, even if no consensus exists on the site structure changes.

Infrared spectroscopy (IR-CO) is a powerful technique to characterize the HDS catalyst and recent development of in situ high-pressure sulfidation and characterization apparatus (CellEX) makes it perfectly adapted to address the question of the effect of high sulfidation pressure on the catalyst structure[1]. Hence, the objective of this work is to study the effect of sulfidation pressure on the active phase nature, concentration and activity of last generation-type CoMo/Al_2O_3 catalysts.

The study of a series of (Co)Mo/Al_2O_3 prepared with various amounts of citric acid (CA) shows that both citric acid addition and high pressure sulfidation (in a lower extent) increase the S- over M-edge ratio of MoS_2 slab (Fig. A), the MoS_2 promotion degree by cobalt (Fig B), and the HDS activity. The IR/CO data reveals that addition of citric acid strongly enlarges the CoMoS sites concentration, whereas high pressure sulfidation leads the significantly decrease of CO adsorption on the sulfide phase suggesting a change in the sulfur coverage of the edge sites.

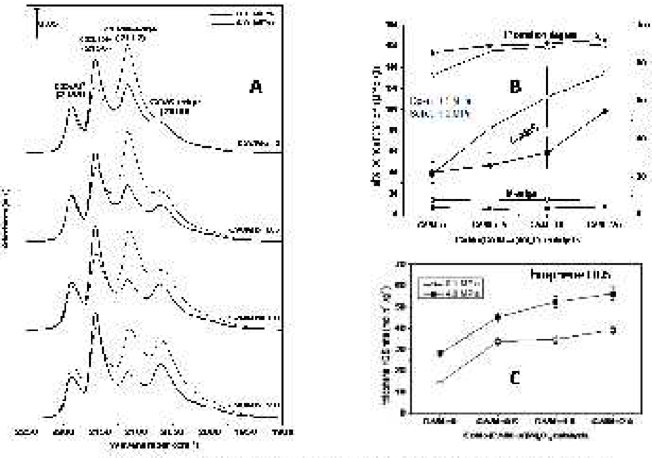

Figure. Effect on sulfidation pressure (0.1 vs 4.0 MPa) on: A: IR CO on Mo(CA/Mo)/Al_2O_3; B: IR-CO on CoMo(CA/Mo)/ Al_2O_3 ; C: thiophene HDS activity on CoMo(CA/Mo)/ Al_2O_3

In conclusion, citric acid addition and high pressure sulfidation facilitate the genesis of MoS_2 slabs with high S- over M-edge ratio and favors CoMoS sites formation. High pressure sulfidation by changing the sulfur coverage structure of edge sites modifies the intrinsic activity of CoMoS sites, and generate a lower amount of accessible sites that present a very high activity.

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Presenting author : Laetitia Oliviero

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The ceria influence on the Cu structure on CeO_2-Cu-Al_2O_3 catalysis under water gas shift reaction

Paula C. P. Caldas, Laís R. Borges, Adriana P. Ferreira. José M. C. Bueno
Universidade Federal de São Carlos, São Carlos-SP, Brasil, 13565-905 Corresponding author: (jmcb@ufscar.br).

Ceria supported Cu catalysts show high activity for the water gas shift reaction (WGSR, $CO+H_2O \rightleftharpoons H_2+CO_2$) however the ceria influence on catalyst activity is not fully understood. The Cu particle size and the density of active sites are dependent upon synthesis method and the nature of support. The catalytic activity is strongly influenced by Cu particle size, which changes superficial Cu^+/Cu^0 ratio [1]. In order to understand the ceria effect on the activity of Cu-catalysis in WGSR, CuO/Al_2O_3 catalysts with different Cu particle size were obtained through changes in Cu loading (5, 10 and 15 wt.% of Cu) and then the Cu-Ceria interface were created by addition of ceria onto the CuO/Al_2O_3 with 12 wt.% of ceria loading. The copper structure and the composition of Cu^+/Cu^0 were investigated by EXAFS and XANES, respectively, at Cu K edge. The Ce^{3+}/Ce^{4+} composition was obtained from XANES analysis at Ce LIII edge. The DRIFTS and XAS spectra were collected throughout the reaction at temperature range of 200 and 350 °C, with a $CO:H_2O$ molar ratio of 1:3, all samples are reduced before reaction. The EXAFS spectra of the reduced Cu/Al_2O_3 catalysts, before the ceria addition, showed the Cu nanoparticles sizes of 0.65, 0.78 and 0.91 nm with increasing of the Cu loading (see Table 1). The increase of $N_{Cu\text{-}Cu}$ is followed by the decrease of N_{CuO}, indicating that the Cu^+/Cu^0 ratio decrease with increase of Cu particle size. The copper structure formed of a Cu-Cu core with Cu-O-Cu species on the surface is proposed. Interestingly, with ceria addition onto CuO/Al_2O_3 catalysts the coordination numbers $N_{Cu\text{-}Cu}$ in reduced catalysts do not show significantly changes as well the reduction degree (Table 1). The $N_{Cu\text{-}Cu}$ in all catalysts slight increases with time on reaction stream. The Ce LIII XANES spectra indicate that the cerium partially reduced, around 50:50 $Ce^{4+}:Ce^{3+}$ for all samples.

Table 1. Results of EXAFS analysis of reduced samples and turnover frequency (TOF) at 300 ^{0}C.

	5Cu/Al	10Cu/Al	15Cu/Al	12Ce/5Cu/Al	12Ce/10Cu/Al	12Ce/15Cu/Al
E_0 (eV)	0.7(±0.6)	1.4(±0.4)	1.1(±0.6)	1.4 (±0.7)	0.9 (±0.4)	0.5 (±0.5)
$N_{Cu\text{-}Cu}$	6.1(±0.6)	6.9 (±0.3)	7.5 (±0.3)	5.5 (±0.7)	6.7 (±0.3)	7.3 (±0.4)
$N_{Cu\text{-}O}$	0.8 (±0.1)	0.5 (±0.1)	0.3(±0.1)	0.8 (±0.3)	0.5 (±0.1)	0.3 (±0.1)
$r_{Cu\text{-}Cu}$ (Å)	2.49(±0.01)	2.49(±0.01)	2.49(±0.01)	2.49(±0.01)	2.49(±0.01)	2.49(±0.01)
$r_{Cu\text{-}o}$ (Å)	1.87(±0.01)	1.89(±0.02)	1.89(±0.02)	1.86(±0.01)	1.88(±0.02)	1.87(±0.03)
D (nm)	0.65	0.77	0.9	0.65	0.78	0.91
Cu^0 (%)	70	78	90	68	76	88
TOF (10^4s^{-1})	1.7	3.6	6.6	2.3	5.5	8.0

The TOF values for Cu/Al_2O_3 catalysts (Table 1) indicate an increase of activity with Cu^+/Cu^0 ratio decrease, as consequence of the particle size increase. Therefore, the copper structure has a direct effect on the catalytic activity. Comparing the TOF results between the Cu/Al_2O_3 and $Ce/Cu/Al_2O_3$ with similar $N_{Cu\text{-}Cu}$, the Ce-containing catalysts show a higher activity. The absence of characteristic bands of formats in FTIR spectra *in situ*, indicate the absence of stable formats for all catalyst. The change on activity could not be explained simply by differences on stability of formats species on ceria surface. Moreover, the Cu-nanoparticles size and Cu^+/Cu^0 ratio are similar between the catalysts with and without Ce with the same Cu loading. These properties could not explain the catalytic activity difference. Therefore, these results indicate that the activity for CO oxidation depends on density of Cu^+ species on surface of Cu^0 core and the Cu-O-Ce interface sites were formed between Cu-nanoparticles and Ce_2O_3. The Cu-O-Ce interface facilitates H_2O activation, which is a limiting step of the WGSR [2], and the O* was transferred to Cu sites for CO oxidation.

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Fourier self-deconvolution of IR spectra as a tool for in-depth studies of Brønsted acid sites in zeolites

Dmitry B. Lukyanov

Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, United Kingdom
D.B.Lukyanov@bath.ac.uk

The unique feature of the zeolite catalysts is the presence of catalytically active acidic hydroxyls, also known as Brønsted acid sites (BAS), in the zeolite micropores of molecular dimensions. The catalytic properties of BAS, including their accessibility, depend on their local chemical and geometrical environment. Thus, the ability to study different BAS is the key for their detailed characterisation. Such studies however are currently very much restrained, since the traditional characterisation techniques, e.g. the most widely used IR spectroscopy, cannot distinguish between acidic hydroxyls in different chemical and geometrical environment. As a result, the observed IR bands normally represent a superposition of the unknown number of individual OH bands. This lack of recognition is the inherent problem in the IR (and FTIR) studies of zeolites, since the IR bands corresponding to distinct acidic OH groups overlap in such a way that they cannot be resolved by the enhancement of the instrument resolution (the distance between the maxima of the single contributing IR bands is not large enough in comparison with the width of these bands). Interestingly, the tool for dealing with exactly the same problem in the FTIR studies of proteins, Fourier self-deconvolution (FSD) of inherently overlapped IR bands of the amide groups, was developed in 1981 [1]. However, until recently [2,3], this technique was not used in the IR studies of functional groups in porous solids (including acidic OH groups in zeolites), in spite of the vast number of publications in this field.

This paper will provide brief introduction to the FSD-IR method followed by a short discussion of the new insights into BAS present in MOR zeolites [2,3]. The paper will be then focused on the discussion of the novel data on BAS in FAU zeolites and will demonstrate for the first time the presence of the four groups of BAS in zeolite Y. The change in the relative amounts of these four distinct BAS (as well as the shift in the positions of the IR bands) with the change in the Al content will be considered leading to possible explanation of the obtained experimental data. A number of interesting observations will be discussed and it will be shown that the acidic hydroxyls located in the large 12-membered ring channels of highly siliceous FAU and MOR zeolites vibrate at the same frequency that is ~3620-5 cm^{-1}. The concluding part of the paper will detail some limitations of the FSD-IR method due to the number of distinct BAS in zeolites. The key experimental details necessary for successful FSD of the IR spectra will be also discussed.

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LNT Rh- and Pt-based catalysts: an *operando*-FTIR study and a spectrokinetic analysis

Lukasz Kubiak[1], Silvia Pompa[1], Lidia Castoldi[1], Carlo Giorgio Visconti[1], Marco Daturi[2], Luca Lietti[1]*
[1]Politecnico di Milano, Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Via La Masa,34
20156 Milano (Italy)
[2]Laboratoire de Catalyse et Spectrochimie, UMR 6506, ISMRA, 6, Bd du Maréchal Juin,
14050 Caen Cedex (France)
*luca.lietti@polimi.it

An interesting solution to reduce emissions from vehicles is represented by the so-called Lean NO_x Trap (LNT) systems, constituted by a NO_x storage component (e.g. K and/or Ba) and by noble metals (Pt, Rh). The catalytic systems operate under transient regime alternating lean and rich phases; during the lean phase the storage of NO_x occurs, whereas during the rich phase stored NO_x are reduced. In our previous works, *in situ* and *operando* FT-IR spectroscopy and reactor experiments have been proved to be very useful techniques to gain complementary information on surface species and gas phase composition, which allowed elucidating the storage pathways from NO/O_2 mixture on $Pt-Ba/Al_2O_3$ catalysts [1]. In this work, these techniques have been used to gain insights on the role of Rh on the nature of the stored species (i.e. to confirm the storage pathway proposed for the Pt-based catalyst) and its role in the reduction with H_2 of both gaseous NO and stored NO_x (at 150 and 350°C). Collected data have been used to develop a spectrokinetic model that is a detailed kinetic model able to describe the evolution of both the gas-phase molecules and the adsorbed species. This allowed to quantitatively prove our hypothesis on the dominant reaction pathway. The study has been performed over homemade Pt- and $Rh-Ba/Al_2O_3$ samples using an optimized reactor cell, specifically designed to enable in situ spectroscopic analysis of the surface under working conditions, while simultaneously monitoring gaseous products leaving the reactor. The gas phase composition and the nature, time evolution and relative amounts of NO_x surface species were investigated upon adsorption of NO in O_2 at 150 and 350 °C. The reducibility of stored species has been tested with H_2 under isothermal conditions and by TPSR experiments while heating the system up to 400°C. The reactivity of gaseous NO and H_2 has also been tested by TPR experiments, where NO is admitted to the reactor cell along with H_2 while the system is heated up to 400°C (4°C/min).

Adsorption data collected at 350°C over Pt- and $Rh-Ba/Al_2O_3$ catalysts have shown that the storage is accomplished through two alternative pathways, with predominance of nitrates at high temperature and nitrites at low temperature. This result has been confirmed through our spectrokinetic model. Comparing Pt- and Rh-based catalysts, it appears that although the storage pathway is the same for the two catalysts, some characteristic features are recognizable. On $Pt-Ba/Al_2O_3$ nitrites (formed mainly on Ba sites, band at 1214 cm^{-1}) are the most abundant species up to 250°C; on $Rh-Ba/Al_2O_3$ they seems to be form also on Al_2O_3 sites (band at 1230 cm^{-1}) and present intense bands at 300°C, too. Also, the nitrates species are slightly different, changing the relative abundance between bidentate and ionic species.

The results of H_2 isothermal reduction (350°C) showed that both catalysts were active in the regeneration, however the Rh based sample was less efficient and more selective towards NO. Similar results have been obtained under temperature programming (TPSR): the Rh-based catalyst showed a lower reactivity if compared to Pt. Since literature reports that the reduction of stored NO_x involves a preliminary NO_x release step, followed by the reduction of the released NO, the reactivity of gaseous NO has been also considered. The results indicate that i) Rh shows a lower activity than Pt in the reduction of NO since the onset of reaction significantly shifted towards higher temperature; ii) the order observed in the product evolution (N_2O, N_2 and NH_3) reflect the oxidation state of the noble metal, with presence of oxidized Pt (and Rh) sites at low temperatures; iii) adsorbed species (e.g. nitrites) may also play a role in the formation of reaction products such as ammonia and nitrogen protoxide; iv) Rh is able to decompose NH_3 at high temperatures.

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Multivariate Component Resolution (MCR) applied on X-ray Absorption spectroscopy. A suitable technique for very large dataset processing analysis to enhance irreducible component resolution and to reveal surface/interface contributions.

Andrea Cognigni[*], Magnus Rønning[*]

[*] Department of Chemical Engineering - Norwegian University of Science and Technology
NO-7491 Trondheim - Norway

XAS technique is a central and more suitable technique to probe the local structure, electronic transition and chemical evolution of nearly all catalytic systems. XAS open the way for the detailed study of the catalytic active site and to follow, through in-situ measures, structural and chemical changes of the catalyst under the operando reaction conditions. The whole collection of these information, contained in different parts of the spectrum XAS at the same time, can be extracted by different kinds of calculations. In particular one can extract, from a qualitative and quantitative point of view, the chemical nature of the species and their relative concentration. This process requires the measurement of the standard of the chemical species a sort of a priori knowledge (not always fully available) and it's time consuming especially for large datasets. Furthermore this system does not allow identifying the new species (adsorbed species and surface/interface phenomena) that appear during the process. Improvements on this domain have already been done in the past by introducing and adapting some classical statistical approach like PCA and EFA especially suitable for analyzing large data sets such as those that come from in-situ measurements and for a sort of "blind" identification of components. Since that the great development of the experimental setup during the last few years has allowed more and more thorough study of the reactions in the operating condition of the catalyst. Such measures make it possible to collect a large amount of data which is very difficult to analyze following the standard procedure and techniques used in EXAFS analysis. Furthermore it is important to uniquely identify the chemical species which evolving during the reaction and that make up the dataset spectra. For these reasons, in order to improve the sensibility of this technique and make it more faster and reliable: MCR (Multivariate Component Resolution) technique have been recently applied to large dataset collected during in-situ XAS (XANES and EXAFS) experiments upon catalytic systems. In a classical configuration for this kind of experiments a catalyst's sample is subjected to a reaction cycle (i.e. Oxidation/reduction) recording at same time XAS spectra continuously. Reaction cycle is repeated many times. Spectra are averaging over a number of cycles to increase S/N. Such final dataset are finally treated by MCR calculation. The MCR algorithm was able to figure out the irreducible spectra of components which are the actors during the reaction process and, at the same time, their corresponding concentration profile. Preliminary experiments have been made on a reversible reduction-oxidation reaction of a rhenium promoted cobalt Fischer-Tropsch catalyst. MCR was successfully applied to extract the pure active components and the proper profile concentration. Validation procedure, based on classical least fitting square approach with standard reference compound, confirmed the correctness of the calculation.