Welcome to Brookhaven National Laboratory

On behalf of Brookhaven National Laboratory, I welcome you to Operando-IV, Recent Developments and Future Perspectives in Spectroscopy of Working Catalysts. While this is the 4th in this series of international conferences, it is the first to be held in the US, and I am pleased that Brookhaven was chosen to host this meeting.

Established in 1947 on Long Island, Upton, New York, Brookhaven is a multi-program national laboratory operated by Brookhaven Science Associates for the U.S. Department of Energy (DOE). Seven Nobel Prizes have been awarded for discoveries made at the Lab.

Brookhaven has a staff of approximately 3,000 scientists, engineers, technicians and support staff and over 4,000 guest researchers annually.

Brookhaven National Laboratory's role for the DOE is to produce excellent science and advanced technology with the cooperation, support, and appropriate involvement of our scientific and local communities. The fundamental elements of the Laboratory's role in support of the four DOE strategic missions are the following:

• To conceive, design, construct, and operate complex, leading edge, user-oriented facilities in response to the needs of the DOE and the international community of users.

• To carry out basic and applied research in long-term, high-risk programs at the frontier of science.

• To develop advanced technologies that address national needs and to transfer them to other organizations and to the commercial sector.

• To disseminate technical knowledge, to educate new generations of scientists and engineers, to maintain technical capabilities in the nation's workforce, and to encourage scientific awareness in the general public.

Thank you for participating in the meeting. I hope that you enjoy your stay at Brookhaven and get to enjoy some of what Long Island, NY has to offer.

Sam Aronson
Laboratory Director
Welcome to the 4th International Congress on Operando Spectroscopy
Recent Developments and Future Perspectives in Spectroscopy of Working Catalysts

This is the fourth in a series of triennial conferences that began in 2003 in Lunteren, and the first to be held in the United States. We sincerely hope that you enjoy the conference at Brookhaven National Laboratory, and your stay on Long Island, NY.

The field of Operando spectroscopy has developed greatly since the first conference, and the science that is presented at this meeting reflects that. The pursuit is always to try to watch the catalyst in action, as it is turning over and producing the desired product. In this methodology the behavior of working catalysts is probed using physico-chemical methods while simultaneously measuring the catalytic activity and selectivity. The operando approach is an excellent one to assess structure-activity relationships at the molecular level since structural and catalytic parameters are determined together. This conference covers all aspects of operando spectroscopy of catalysts: both heterogeneous and homogeneous catalysis, application of theory, new experimental approaches and techniques, time and spatial resolution, and combination of techniques.

The ultimate success of the conference rests in the scientific presentations and discussions. We believe that we have assembled a fascinating and interesting series of talks and posters, and that these represent the state-of-the-art in operando spectroscopy in the world today. In keeping with the format of the prior Operando meetings, we have a single oral session together with poster sessions to allow all contributors a chance to present their research. We are trying something new in holding a “poster slam.” This will give all poster presenters a chance to highlight the scientific impact of their work in a special oral session. We hope that you will support these special sessions.

We thank our many generous sponsors and vendors.

Our sponsors are: Bruker, ExxonMobil, Shell, UOP LLC, a Honeywell Company, ACS Catalysis, BaySpec, Inc., FEI Company, Harrick Scientific, SPECS Surface Nano Analysis, Inc., Elsevier, PerkinElmer and Physical Chemistry Chemical Physics (PCCP)


We thank ACS Catalysis and PCCP for sponsoring the student/postdoc poster competition.

We thank DOE Basic Energy Sciences for a grant to offset the local accommodation for young faculty, students and postdocs.

The conference would not have been possible without their generous support. We encourage you to visit with the vendors during the conference.

We thank the International Committee for their support and encouragement in the planning of this meeting. I also personally give a special thanks to the local organizing committee for their long hours and dedication and dealing with the myriad of details. It has been amazing to work with them, and it is their efforts that have made this conference possible.

Enjoy the conference, and please send any feedback to me. Thanks!

Simon R. Bare, on behalf of The Organizing Committee
simon.bare@honeywell.com
Committees

International Operando IV Committee
Prof. Miguel A. Bañares, ICP-CSIC, Madrid, Spain
Dr. Simon R. Bare, UOP, LLC, a Honeywell Company, Des Plaines, USA
Prof. Dr. Angelika Brückner, LIKAT, Germany
Prof. Eric Gaigneaux, Université Catholique de Louvain, Louvain-la-Neuve, Belgium
Dr. Frédéric Thibault-Starzyk, CNRS, Caen, France
Prof. Israel Wachs, Lehigh University, Lehigh, USA
Prof. Bert Weckhuysen, Utrecht University, Utrecht, The Netherlands

Operando IV Organizing Committee
Dr. Simon R. Bare (Chair), UOP, LLC, a Honeywell Company
Ms. Gretchen Cisco, Brookhaven National Laboratory
Prof. Anatoly Frenkel, Yeshiva University
Dr. Chris Marshall, Argonne National Laboratory
Ms. Kathleen Nasta, Brookhaven National Laboratory
Prof. Carsten Sievers, Georgia Institute of Technology
Dr. David Starr, Brookhaven National Laboratory
Dr. Eli Stavitski, Brookhaven National Laboratory
Prof. Israel Wachs, Lehigh University
Prof. Chris Williams, University of South Carolina
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Sponsors

Thank you for your support!

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*Thank you for your support!*

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U.S. Department of Energy Office of
Basic Energy Sciences
Photon Sciences Directorate, Brookhaven
National Laboratory
Session Topics

Orals O1 - O5; Posters MP27 - MP33:
New Advances in Reaction Cells Including Improved Time and Spatial Resolution
This session will be focused on the instrumentation that has been developed that allows the operando spectroscopy data to be obtained. Particular focus will be on advances that have allowed improved time and spatial resolution.

Orals O6 - O10; Posters MP1 - MP14:
Bridging the Gap Between Model and Technical Conditions
This session will highlight those studies where an attempt has been made to bridge the gap between studies under well-controlled conditions and those under more technical conditions. Included in this session will also be those studies only on model catalysts or under model conditions (e.g. UHV).

Orals O11 - O13; Posters MP15 - MP21:
Catalytic Bio-conversion Technologies
The rapid growth area of catalytic bio-conversion technologies will be highlighted in this session. These studies could be either gas or liquid phase, and encompass a wide range of spectroscopic probes.

Orals O14 - O27; Posters TP15 - TP34:
Multi-technique Approach to Operando Spectroscopy
This session will highlight the complementary information and understanding that is obtained by probing the active catalyst using at least two probes in the same reaction cell, either simultaneously or sequentially. Examples include XAFS/FTIR, XAFS/UV-vis, UV-vis/NIR/Raman, XAFS/XRD.

Oral O28; Posters TP1 - TP8:
Combining Operando Spectroscopy and Theoretical Studies
This session will encompass studies where theoretical understanding (at any level) is added to the experimental operando spectroscopic studies and thus provides additional insight.

Orals O29 - O31; Posters MP22 - MP26:
Homogeneous/Liquid Phase Catalysis
This session will focus on research performed in the liquid phase or on homogeneous catalysts using any appropriate operando spectroscopy.

Orals O32 - O34; Posters TP9 - TP14:
Electrocatalysis: Fuel Cells and Related Technologies
This session will focus on all aspects of operando studies related to photo/electrocatalysis, from PEM fuel cells to water splitting.
## Agenda

**Sunday, April 29, 2012**

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<th>Starts</th>
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<tbody>
<tr>
<td>9:30 a.m.</td>
<td>5:30 p.m.</td>
<td>Outing to New York City</td>
<td>Berkner Hall Lobby</td>
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<tr>
<td>12:00 p.m.</td>
<td>4:00 p.m.</td>
<td>Exhibitor Setup</td>
<td>Berkner Hall Lobby</td>
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<tr>
<td>12:00 p.m.</td>
<td>5:00 p.m.</td>
<td>Registration Office Opens</td>
<td>Berkner Hall Room D</td>
</tr>
<tr>
<td>5:30 p.m.</td>
<td>7:00 p.m.</td>
<td>Welcome Reception</td>
<td>Berkner Hall</td>
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## Agenda

**Monday, April 30, 2012**

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<tr>
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<tbody>
<tr>
<td>8:00 a.m.</td>
<td>8:30 a.m.</td>
<td>Breakfast</td>
<td>Berkner Hall</td>
</tr>
<tr>
<td>8:30 a.m.</td>
<td>8:45 a.m.</td>
<td>Opening Remarks: Sam Aronson, Director, Brookhaven National Laboratory</td>
<td>Berkner Hall Auditorium</td>
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## Plenary Session I

Frederic Thibault-Starzyk, Session Chair

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<th>Starts</th>
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<tbody>
<tr>
<td>8:45 a.m.</td>
<td>9:30 a.m.</td>
<td><strong>P1: In-situ Spectroscopy of Catalytic Solids at the Single-Particle Level</strong>, Bert Weckhuysen, Professor, Utrecht University</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:30 a.m.</td>
<td>9:50 a.m.</td>
<td><strong>O1: Operando Raman Spectroscopy Applying Novel Fluidized Bed Micro-reactor Technology</strong>, Pablo Beato, Haldor Topsøe A/S</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:50 a.m.</td>
<td>10:10 a.m.</td>
<td><strong>O2: Relating the Effects of Water Partial Pressure to Crystallite Size in Co/Al2O3 Fischer-Tropsch Catalysts Using a Novel In-situ XRD Cell</strong>, Michael Claeys, Director, Centre for Catalysis Research and c*change, University of Capetown</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>Time</td>
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<td>Session</td>
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<tr>
<td>10:10 a.m.</td>
<td>10:30 a.m.</td>
<td>Coffee Break (Group Photo)</td>
<td>Berkner Hall Lobby</td>
</tr>
<tr>
<td>10:30 a.m.</td>
<td>10:50 a.m.</td>
<td><strong>O3</strong>: Application of Operando XAS and FTIR in Gaining Fundamental Understanding of Catalyst Kinetics and Active Sites for NH3-SCR and WGS, Vincent Kispersky, Purdue University</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>10:50 a.m.</td>
<td>11:10 a.m.</td>
<td><strong>O4</strong>: Direct Observation of Surface Ethyl Growth Kinetics Upon Hydrogenation of C₂H₄ on Rh/Al₂O₃ by Step-scan FT-IR Spectroscopy, Miao Zhang, Lawrence Berkeley National Laboratory</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>11:10 a.m.</td>
<td>11:30 a.m.</td>
<td><strong>O5</strong>: Unique Operando Quick-EXAFS Characterization of Bimetallic Heterogeneous Catalysts used for Hydrodesulfurization, Amelie Rochet, Synchrotron SOLEIL</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>11:30 a.m.</td>
<td>11:50 a.m.</td>
<td><strong>O6</strong>: Effect of Pd Addition on the Efficiency of a NOₓ-trap Catalyst: a FTIR Operando Study, Luis F. Bobadilla, ENSICAEN, Université de Caen, CNRS</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>11:50 a.m.</td>
<td>1:15 p.m.</td>
<td>Lunch</td>
<td>Berkner Hall Lobby</td>
</tr>
<tr>
<td>1:15 p.m.</td>
<td>2:00 p.m.</td>
<td><strong>P2</strong>: Single-molecule Sub-diffraction Imaging of Nanocatalysis, Peng Chen, Associate Professor, Cornell University</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>2:00 p.m.</td>
<td>2:20 p.m.</td>
<td><strong>O7</strong>: From Model Systems to Technical Catalysts: Nanostructured Catalysts in Activation of Propane Studied by Electron Spectroscopies and Theory, Michael Hävecker, Helmholtz-Zentrum Berlin / BESSY II</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>2:20 p.m.</td>
<td>2:40 p.m.</td>
<td><strong>O8</strong>: Operando X-ray Absorption Spectroscopy for Understanding the Origin of Phosphorous Induced Chemical Aging of Pd-based Three-way Catalysts, Santhosh Kumar Matama, Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Solid State Chemistry and Catalysis</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>2:40 p.m.</td>
<td>3:00 p.m.</td>
<td><strong>O9</strong>: Operando FTIR-MS Study of Ammonia-ammonium Interplay in a Ge-nuine Monolithic V₂O₅/TiO₂/Sepiolite Catalyst During Selective Catalytic Reduction of NO with NH₃, Søren B. Rasmussen, Institute of Catalysis &amp; Petrol Chemistry</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>3:00 p.m.</td>
<td>3:20 p.m.</td>
<td>Coffee Break</td>
<td>Berkner Hall Lobby</td>
</tr>
<tr>
<td>3:20 p.m.</td>
<td>3:40 p.m.</td>
<td><strong>O10</strong>: The Ag-O System in Catalysis: New Insights by Ambient Pressure XPS, Tulio Rocha, Fritz Haber Institute</td>
<td>Berkner Hall Auditorium</td>
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**Plenary Session II**

Bert Weckhuysen, Session Chair
### Agenda

**Monday, April 30, 2012**

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<tbody>
<tr>
<td>3:40 p.m.</td>
<td>4:00 p.m.</td>
<td><strong>O11: ATR-IR Study on the Kinetics of Aqueous Phase Conversion of Bio-mass over Supported Metal Catalysts</strong>, John Copeland, Gerogia Institute of Technology</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>4:00 p.m.</td>
<td>4:20 p.m.</td>
<td><strong>O12: Understanding the Effect of Sm$_2$O$_3$ and CeO$_2$ Promoters on the Structure and Activity of Rh/Al$_2$O$_3$ Catalysts for Methane Steam Reforming</strong>, Renata Bessa Duarte, ETH Zürich</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>4:30 p.m.</td>
<td>5:30 p.m.</td>
<td><strong>Poster Slam</strong>: Eli Stavitski, Session Chair poster presenters highlight the scientific impact of their work in a special oral session.</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>5:30 p.m.</td>
<td>7:00 p.m.</td>
<td>Poster Session 1</td>
<td>Berkner Hall Conf. Rms. A B and C</td>
</tr>
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</table>
|          |        | **MP1 –MP14**  
Bridging the Gap Between Model and Technical Conditions |                               |
|          |        | **MP15 – MP21**  
Catalytic Bio-conversion Technologies |                               |
|          |        | **MP22 – MP26**  
Homogeneous/Liquid Phase Catalysis |                               |
|          |        | **MP27 – MP33**  
New Advances in Reaction Cells Including Improved Time and Spatial Resolution |                               |
|          |        | **MP34 – MP39**  
Post Deadline Poster |                               |
| 7:00 p.m.| 9:00 p.m.| Dinner                                                                                           | Berkner Hall Cafeteria        |
**Agenda**
Tuesday, May 1, 2012

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### Plenary Session III
Angelika Brückner, Session Chair

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<tr>
<td>8:00 a.m.</td>
<td>8:45 a.m.</td>
<td>Breakfast</td>
<td>Berkner Hall</td>
</tr>
<tr>
<td>8:45 a.m.</td>
<td>9:30 a.m.</td>
<td><strong>P3: From Static Model Systems to Dynamical High Performance Catalysts</strong>, Robert Schlögl, Professor, Fritz Haber Institute of the Max Planck Society</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:30 a.m.</td>
<td>9:50 a.m.</td>
<td><strong>O13: H2 Production by Aqueous Phase Reforming of Biologics: Correlating Catalytic Activity and Selectivity to the Local Coordination and Electronic Structure of Pt and PtNi</strong>, Ayman Karim, Pacific Northwest National Laboratory</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:50 a.m.</td>
<td>10:10 a.m.</td>
<td><strong>O14: Operando X-ray Diffraction Tomography for Revealing Insight into Active Phase Evolution in Catalyst Bodies</strong>, Andrew Beale, Utrecht University</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>10:10 a.m.</td>
<td>10:30 a.m.</td>
<td>Coffee Break (Group Photo)</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>10:30 a.m.</td>
<td>10:50 a.m.</td>
<td><strong>O15: Elucidating the Mechanism of Dimethyl Carbonate Formation by Oxidative Carbonylation of Methanol Over CuY zeolite: An Operando SSITKA/DRIFTS/MS Study</strong>, Ursula Bentrup, Leibniz-Institut für Katalyse e. V. an der Universität Rostock (LIKAT)</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>10:50 a.m.</td>
<td>11:10 a.m.</td>
<td><strong>O16: Modulation Excitation Hard X-ray Diffraction to Capture Red-ox Dynamics of Supported Pd Catalysts</strong>, Davide Ferri, Empa</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>11:10 a.m.</td>
<td>11:30 a.m.</td>
<td><strong>O17: Advantages of Syngas for the Regeneration of NOx Trap System Investigated with Operando IR Measurements</strong>, Anita Kouakou, UCCS UMR 8181, Université de Lille1</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>11:30 a.m.</td>
<td>11:50 a.m.</td>
<td><strong>O18: Operando Synchronous DRIFTS/MS/XAS as a Powerful Tool for Guiding the Design of Heterogeneous Catalysts</strong>, Adam Lee, Cardiff University</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>11:50 a.m.</td>
<td>1:15 p.m.</td>
<td>Lunch</td>
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### Plenary Session IV
Israel Wachs, Session Chair

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<tr>
<td>1:15 p.m.</td>
<td>2:00 p.m.</td>
<td><strong>P4: Coupling of Vibrational and Electronic Spectroscopies: Effective Tools for Exploring Mechanisms of Catalytic Redox Processes</strong>, Angelika Brückner, Prof. Dr., Leibniz Institute for Catalysis at University of Rostock</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Speaker</td>
<td>Location</td>
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<tr>
<td>2:00 p.m.</td>
<td><strong>O19:</strong> Design of In-House Ambient Pressure X-ray Photoelectron Spectrometer and Ambient Pressure High Temperature Scanning Tunnelling Microscope for Operando Studies of Catalysts, Franklin (Feng) Tao, University of Notre Dame</td>
<td>Berkner Hall Auditorium</td>
<td></td>
</tr>
<tr>
<td>2:20 p.m.</td>
<td><strong>O20:</strong> An Operando-IR Study of Photocatalytic Reaction of Methanol on New BEA Supported TiO$_2$ Catalyst, Mohamad El-Roz, Laboratoire Catalyse et Spectrochimie</td>
<td>Berkner Hall Auditorium</td>
<td></td>
</tr>
<tr>
<td>2:40 p.m.</td>
<td><strong>O21:</strong> New Insights into the Water-Gas Shift Reaction over Bulk Cr$_2$O$_3$*Fe$_2$O$_3$ Mixed Oxide Catalysts: A Combined Operando Raman-IR-XAS-MS Investigation, Christopher Keturakis, Lehigh University</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>3:00 p.m.</td>
<td>Coffee Break</td>
<td>Berkner Hall Lobby</td>
<td></td>
</tr>
<tr>
<td>3:20 p.m.</td>
<td><strong>O22:</strong> Combination of X-ray Spectroscopy and Small Angle Scattering with Mass Spectrometry to Observe Catalytic Reactions, Randall Winans, X-ray Science Division, Advanced Photon Source, Argonne National Laboratory</td>
<td>Berkner Hall Auditorium</td>
<td></td>
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<tr>
<td>3:40 p.m.</td>
<td><strong>O23:</strong> Operando Raman-GC Study of Propane Selective Oxidation over Alumina -Supported V$_2$O$_5$ and P$_2$O$_5$ Monolayer Type Catalyst, Ewelina Mikolajska, Instituto de Catálisis y Petroleoquímica, CSIC</td>
<td>Berkner Hall Auditorium</td>
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</tr>
<tr>
<td>4:00 p.m.</td>
<td><strong>Poster Slam:</strong> Carsten Sievers, Session Chair poster presenters highlight the scientific impact of their work in a special oral session.</td>
<td>Berkner Hall Auditorium</td>
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</tr>
<tr>
<td>5:00 p.m.</td>
<td>Poster Session II</td>
<td>Berkner Hall Conf. Rms. A, B and C</td>
<td></td>
</tr>
<tr>
<td>5:00 p.m.</td>
<td><strong>TP1 – TP8</strong> Combining Operando Spectroscopy and Theoretical Studies</td>
<td>Berkner Hall Conf. Rms. A, B and C</td>
<td></td>
</tr>
<tr>
<td>5:00 p.m.</td>
<td><strong>TP9 – TP14</strong> Electrocatalsis: Fuel Cells and Related Technologies</td>
<td>Berkner Hall Conf. Rms. A, B and C</td>
<td></td>
</tr>
<tr>
<td>6:30 p.m.</td>
<td>Dinner - On your own (Transportation will be provided)</td>
<td>Port Jefferson, Long Island, NY</td>
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*4th International Congress on Operando Spectroscopy*

*Recent Developments and Future Perspectives in Spectroscopy of Working Catalysts*

*Brookhaven National Laboratory, Upton, NY, USA*
**Agenda**

**Wednesday, May 2, 2012**

**Plenary Session V**

Miguel A. Bañares, Session Chair

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<tr>
<td>8:00 a.m.</td>
<td>8:45 a.m.</td>
<td>Breakfast</td>
<td>Berkner Hall Cafeteria</td>
</tr>
<tr>
<td>8:45 a.m.</td>
<td>9:30 a.m.</td>
<td><strong>P5: Understanding Real World Catalysts: A Challenge for Spectroscopy and Engineering</strong>, Jan-Dierk Grunwaldt, Prof. Dr., Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT)</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:30 a.m.</td>
<td>9:50 a.m.</td>
<td><strong>O24: DRIFTS and XPS Operando Studies of a CuO-CeO\textsubscript{2} WGS Catalyst</strong>, Arturo Martinez-Arias, ICP-CSIC</td>
<td>Berkner Hall Auditorium</td>
</tr>
<tr>
<td>9:50 a.m.</td>
<td>10:10 a.m.</td>
<td><strong>O25: Role of Pretreatment and of Oxygen Vacancies on the Catalytic Behavior of ZnO Toward Alcohols Conversion: an EPR and DRIFTS Study</strong>, Guylene Costentin, UPMC-CNRS</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>10:10 a.m.</td>
<td>10:30 a.m.</td>
<td>Coffee Break (Group Photo)</td>
<td>Berkner Hall Auditorium</td>
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<td>10:30 a.m.</td>
<td>10:50 a.m.</td>
<td><strong>O26: Active Sites of Gold-Ceria Nanorods for Low-Temperature CO Oxidation Reaction: Operando X-Ray Diffraction and Absorption Studies</strong>, Rui Si, Brookhaven National Laboratory</td>
<td>Berkner Hall Auditorium</td>
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<td>10:50 a.m.</td>
<td>11:10 a.m.</td>
<td><strong>O27: Mechanistic Aspects of CO\textsubscript{2} Hydrogenation at Low Temperature over Rh Catalysts Studied by Operando-DRIFTS</strong>, Alejandro Karelović, Université Catholique de Louvain</td>
<td>Berkner Hall Auditorium</td>
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<td>11:10 a.m.</td>
<td>11:30 a.m.</td>
<td><strong>O28: Towards Using the Reorganization of Heteropoly Compounds: Taking Advantage of Intermediate States in the Frame of the Propylene Oxidation</strong>, Eglantine Arendt, Université Catholique de Louvain</td>
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<td>11:30 a.m.</td>
<td>11:50 a.m.</td>
<td><strong>O29: Catalysis-Induced Fluxionality at the Single Nanoparticle Level with Single Turnover Resolution</strong>, Venkataramanan Ravi, The Pennsylvania State University</td>
<td>Berkner Hall Auditorium</td>
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<td>11:50 a.m.</td>
<td>1:15 p.m.</td>
<td>Lunch</td>
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<td>1:15 p.m.</td>
<td>5:30 p.m.</td>
<td>Excursion - Tour of 2 Long Island Wineries (see page 252)</td>
<td>The Vineyard, Aquebogure, NY</td>
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<tr>
<td>6:00 p.m.</td>
<td>9:30 p.m.</td>
<td>Conference Banquet (see page 252)</td>
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# Agenda

Thursday, May 3, 2012

## Plenary Session VI

Eric Gaigneaux, Session Chair

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<tr>
<td>8:00 a.m.</td>
<td>8:45 a.m.</td>
<td>Breakfast</td>
<td>Berkner Hall Cafeteria</td>
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<td>8:45 a.m.</td>
<td>9:30 a.m.</td>
<td><strong>P6: From the Monitoring of a Real Catalyst to the Catalyst Design</strong>, Marco Daturi, Prof., LCS-ENSICAEN, CNRS, University of Caen</td>
<td>Berkner Hall Auditorium</td>
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<td>9:30 a.m.</td>
<td>9:50 a.m.</td>
<td><strong>O30: Catalysts in Action: Advances in X-ray Spectroscopy Providing New Insights Faster</strong>, Jan Samson, Technische Universität München, Catalyst Characterisation</td>
<td>Berkner Hall Auditorium</td>
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<td>9:50 a.m.</td>
<td>10:10 a.m.</td>
<td><strong>O31: The Effects of Solvent on the Furfuryl Alcohol Polymerization Reaction: Characterizations of Molecular Structure and Thermodynamic Properties</strong>, Taejin Kim, Chemical Sciences and Engineering Division, Argonne National Laboratory</td>
<td>Berkner Hall Auditorium</td>
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<td>10:10 a.m.</td>
<td>10:30 a.m.</td>
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<td>10:30 a.m.</td>
<td>10:50 a.m.</td>
<td><strong>O32: New Insight into the Surface Species During Water Electrolysis by In-Situ AP-XPS</strong>, Rosa Arrigo, FHI der MPG</td>
<td>Berkner Hall Auditorium</td>
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<td>10:50 a.m.</td>
<td>11:10 a.m.</td>
<td><strong>O33: In Situ XAS of Pt Monolayer Model Fuel Cell Catalysts: Balance of Nanostructure and Bimetallic Interactions</strong>, Daniel Friebel, SLAC National Accelerator Laboratory</td>
<td>Berkner Hall Auditorium</td>
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<td>11:10 a.m.</td>
<td>11:30 a.m.</td>
<td><strong>O34: Ambient Pressure Photoemission Investigations on PEM Fuel Cells in Operando Conditions</strong>, Sarp Kaya, SLAC National Accelerator Laboratory</td>
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<td>11:30 a.m.</td>
<td><strong>O35: Operando Characterization of Au/FeOx-CeO2/Al2O3 Catalysts During Water Gas Shift Reaction</strong>, Jose Antonio Odriozola, Director, Departamento de Química Inorgánica e Instituto de Ciencias de Materiales de Sevilla, Universidad de Sevilla-CSIC</td>
<td>Berkner Hall Auditorium</td>
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<tr>
<td>11:50 a.m.</td>
<td>Closing Remarks</td>
<td>Berkner Hall Auditorium</td>
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<td>12:00 p.m.</td>
<td>Lunch</td>
<td>Berkner Hall Cafeteria</td>
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<td>1:30 p.m.</td>
<td>End of Conference</td>
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<tr>
<td>2:00 p.m.</td>
<td>Optional BNL Tour (CFN, NSLS, NSLS II)</td>
<td>Leaving from Berkner Hall and Returning</td>
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The conference proceedings will be published in a special issue of Catalysis Today and will be subject to standard peer review for an Elsevier journal.

The Catalysis Today website is active for this special issue and contributions can be uploaded at any time. An invitation letter will be sent to all presenters (oral and poster) inviting them to submit a manuscript for this special issue. This invitation letter must be uploaded with the manuscript.

The deadline for submission of manuscripts is May 28, 2012.

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To do so, please click on the “Log-in” button and enter your username and password in the required fields. Please ensure that you click on the “Author Log-in” button after entering your information. Once you have accessed your homepage please click on the “Submit New Manuscript” link to begin the submission process of your manuscript.

Remember, you will be submitting to the “Operando IV” Special Issue.

Complete all the necessary steps of the submission process and at the last step “Attach Files”, please upload your Letter of invitation, Manuscript, Figures, and Tables in acceptable format (please refer to Artwork Instructions for reference on accepted file formats).

When you are happy with the files uploaded, you can start the PDF generation process by clicking on ‘Build PDF For My Approval’. While the PDF is created, the submission is moved to ‘Submissions Waiting For Author’s Approval’. The PDF will not open automatically but you will see a ‘View Submission’ link when the PDF is ready. You must click on ‘View Submission’ in order to approve, edit or remove the submission. When you approve your submission, it will now be filed in the ‘Submissions Being Processed’ list in your Author Main Menu.

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In-situ Spectroscopy of Catalytic Solids at the Single-Particle Level

Bert M. Weckhuysen

Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

Introduction and Objectives

The past years have witnessed the introduction of spatiotemporal spectroscopy for the characterization of catalytic solids. These advances allow observation of catalysts at previously unattainable resolution and sensitivity. They reveal that catalytic solids are even more heterogeneous than often anticipated. Dynamic changes in the nature of active sites, active site distribution and accessibility are found to occur at both the intra- and interparticle level. Scientists have now the tools at hand to improve the understanding of catalyst heterogeneities and exploit this knowledge to design new or improved catalysts. This lecture highlights the latest developments of this field of research, with special emphasis on research from our own group. The trends include single particle/molecule detection, super-resolution imaging, 3-D imaging, selective staining, integration of spectroscopy with electron microscopy or scanning probe methods, and measuring under realistic reaction conditions.

Results and Discussion

The dynamic properties of individual catalyst particles will be highlighted by recent literature examples for both structured porous oxides and supported metal nanoparticles.

Significance

Catalysts display heterogeneities in terms of structure, composition and reactivity, all of which change not only as a function of position within a catalyst particle, but also in time. Within individual catalyst particles, even for simple model systems, structural and compositional differences clearly exist and these intraparticle heterogeneities largely impact the overall performance of a catalyst. Within a catalyst batch, interparticle heterogeneities complicate matters even more. Spatiotemporal spectroscopy has opened up new vistas that allow visualization of how catalyst materials work and change during operation.
Operando Raman Spectroscopy
Applying Novel Fluidized Bed Micro-Reactor Technology

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Introduction and Objectives

Due to the usually low Raman cross sections of molecules or solids, high laser powers need to be applied in order to produce a well detectable signal. However, one inherent problem of applying high laser powers is the risk of laser-induced damages in the sample. A critical issue, in particular in the field of heterogeneous catalysis, is that laser induced heating may also lead to significant differences between the measured temperature given by the thermocouple in the reactor and the actual temperature at the measured point. In the case of \textit{in situ} Raman spectroscopy applied to chemical reactions at solid-gas interfaces, such as in the field of heterogeneous catalysis it is of particular interest to know exactly the temperature where chemical transformations occur.

We have recently discovered a new technology to homogeneously fluidize particles inside a micro-reactor and conduct heterogeneous catalytic reactions with it, such that they can be monitored by operando Raman spectroscopy, without the drawback of laser heating/damage\textsuperscript{[1]}. In this contribution we will illustrate the concept presenting results of two relevant case studies that have been performed with the new fluid-bed reactor:

\textit{Case A}. Investigation of the active phase in a commercial sulphuric acid catalyst (VK38, Haldor Topsøe) under realistic operation conditions (1 bar, 300 – 630 °C, 10% SO\textsubscript{2}, 10% O\textsubscript{2}, 80% N\textsubscript{2}).

\textit{Case B}. Follow the formation of hydrocarbon molecules in the micropores of zeolites, during methanol to hydrocarbon reaction (MTH).

Results and Discussion

Raman spectra of a commercial sulphuric acid catalyst were recorded before and after switching the gas in the reactor at 380 °C from air to the reaction mixture (10% SO\textsubscript{2}, 10% O\textsubscript{2}, 80% N\textsubscript{2}) and after a temperature step to 430 °C. Apart from the observed color changes of the catalyst from yellow-brown to dark green at 380 °C, the Raman spectra reveal a structural transformation, which has been interpreted as the transition from a polymeric vanadate to the well defined molecular structure of the (VO)\textsubscript{3}(SO\textsubscript{4})\textsubscript{5}\textsuperscript{4-} ion, implying a reduction of V(V) to V(IV). Upon increasing the temperature to 430 °C further structural changes are occurring, accompanied by an increase in conversion of SO\textsubscript{2}. The main bands in the spectrum of the active catalyst have been assigned according to the literature and correspond to a mixture of mono- and dimeric V(V)-sulphate species which fits well
with the proposed active phases of Lapina et al. [2].

The great advantage of the new experimental set-up is reflected in Figure 1, where Raman spectra of methanol stream at RT on H-ZSM-5 sample with and without particle fluidization are reported. When the sample is fluidized (gray curve), the Raman spectrum of methanol, physisorbed or hydrogen bonded at the surface of the zeolite is easily recognizable, while in the lower energy part (1000-250 cm⁻¹) vibrational fingerprint of the H-ZSM-5 zeolite is visible. When the fluidization is stopped, the high energy laser (λ=244 nm) causes the decomposition of methanol, leading to the appearance of only one broad band centered at 1560 cm⁻¹, assigned to coke-like species deriving from methanol. We have investigated a number of different zeolite topologies and studied the hydrocarbon formation in the pores under MTH reaction conditions (while monitoring reaction products by MS). The structural differences in the hydrocarbon structures will be discussed and related to different zeolite pore geometries.

**Conclusions**

We demonstrate in two examples that fluidization of the catalyst particles is absolutely necessary to obtain the real structure of heterogeneous systems under operando conditions. The molecular structure of the supported molten phase in the sulphuric acid catalyst is very sensitive to changes in reaction conditions and the correlation with the catalytic data provided interesting new insight, enabling us to establish specific structure-activity relationships. The simultaneous monitoring of reaction products and intermediates in the gas phase and inside the micropores of the catalyst during MTH reaction provides unique details on the shape-selectivity of microporous materials. We are currently further developing the experimental set-up to extend the technique for combined operando UV-vis/IR/Raman spectroscopy. Some first results will be presented.

**References**

Relating the Effects of Water Partial Pressure to Crystallite Size in Co/Al₂O₃ Fischer-Tropsch Catalysts using a Novel \textit{in-situ} XRD Cell

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Introduction and Objectives

The paper utilises a newly designed \textit{in situ} cell to help correlate the effects of water partial pressure ($P_{H_2O}$) to cobalt crystallite size whilst monitoring the Fischer-Tropsch Synthesis (FTS) conversion of H$_2$ and CO to hydrocarbons with online gas chromatography (GC). The cell design is such that it can be mounted on any commercial. This \textit{in situ} cell allows for real-time analysis of the catalyst whilst being subjected to harsh conditions. In regards to application for this work, cobalt mediated FTS is reported to be a size-dependent reaction for cobalt crystallite less than 10 nm [1] while increasing $P_{H_2O}$ has been linked to both positive and negative changes in selectivity and activity (based on the system studied), and the deactivation by either oxidisation, sintering and/or surface reconstruction ([2] and citations therein). This experimental approach allows for monitoring all possibilities to link activity, selectivity and phase changes to increasing $P_{H_2O}$ and crystallite size. The phase changes of two industrially-relevant alumina-supported cobalt catalysts (average initial Co$_3$O$_4$ crystallite sizes of 6.7 and 11.1 nm) were analysed throughout reduction ($H_2$ at 1°C/min $\rightarrow$ 450 for 6h) and FTS reaction conditions (220°C, $H_2$:CO = 2, $P_{H_2O}$ = 0-3 bar, and $P_{H_2O}$/$P_{H_2}$ ratios = 0-5).

Results and Discussion

The size-controlled cobalt crystallites were prepared via the microemulsion preparation technique as developed by Fischer et al [2]. The narrow size distribution resulting from this preparation method provided ideal model-like catalysts for this investigation. Catalyst reduction and FTS experiments have been completed using the \textit{in situ} cell, with the catalyst crystallite phase changes having been successfully monitored. Figure 1 gives a representative view of the continuous XRD measurements during the reduction of the 11.1 nm catalyst. The loss of the 43.1°, 70.2° and 77.5° Co$_3$O$_4$ peaks at 350°C give rise to the 49.7° and 72.8° CoO peaks, which disappear during the 450°C holding period to form fcc-Co$^0$ (51.8° and 91.1°). Immediately following reduction, the catalysts were exposed to FTS conditions and continuously monitored as the $P_{H_2O}$ of the system was increased to simulate high conversions (up to 95%). While oxidation has been suggested to occur, these reports are based on indirect techniques [3]. The design of this \textit{in situ} reaction cell provided the ability to observe the rapid structural changes as they happened that led to determining the oxidation threshold of the Co/Al$_2$O$_3$ catalysts.
Conclusions

Factors that were addressed include catalyst activity and product selectivity (by online and offline GC), metal crystallite size effects and water effects. The most significant results revealed the phase changes leading to the catalyst’s oxidation with increasing partial pressure and concluding it is indeed related to the catalyst’s crystallite size.

References

Application of operando XAS and FTIR in gaining fundamental understanding of catalyst kinetics and active sites for NH$_3$-SCR and WGS

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Introduction and Objectives

The application of operando techniques is becoming a more common tool to help unravel catalytic functions. Our group has custom built two operando reactors, one for measurements by X-ray absorption spectroscopy (XAS) the other for transmission FTIR. The objective of this presentation is to show the great advantage and sometimes necessity of performing operando experiments over conventional in situ experiments using the NH$_3$ selective catalytic reduction (SCR) of NO$_x$ and water-gas shift (WGS) reaction.

Results and Discussion

Operando XAS for Selective Catalytic Reduction

We have constructed a vitreous carbon based, powder bed, down-flow catalyst reactor to study the active site of Cu/zeolite catalysts for SCR (Figure 1 on right) [1]. Under standard SCR conditions of 300 ppm NO, 300 ppm NH$_3$, 5% O$_2$, 5% H$_2$O and 5% CO$_2$ we found that 15, 45, and 65% of Cu on Cu/SSZ-13, Cu/SAPO-34 and Cu/ZSM-5 was in the reduced Cu(I) state, the remainder maintaining its fully oxidized Cu(II) oxidation state suggesting a redox nature for the SCR reaction. Further evidence of this redox nature comes from unsteady-state experiments where various reactants are systematically cut out of the reaction mixture, thus isolating either the oxidative or reducing portion of the SCR reaction and which leads to the removal or generation of Cu(I). Using a 200 x 200 µm X-ray beam also allowed our group to measure the oxidation state change of Cu over the length of the catalyst bed under non-differential conditions. With a NO$_2$:NO$_x$ ratio of 1:5, for example, there is a marked increase in Cu(I) as the X-ray beam is moved from the top to the bottom of the catalyst bed (i.e more oxidizing to less oxidizing conditions).
Operando FTIR of Au/TiO₂ for the WGS Reaction

Studying the deactivation of a fresh 2.3 wt.% Au/TiO₂ catalyst at 200 °C in our custom built operando transmission FTIR cell (Figure 1 on left), we found that the change in rate directly correlated with the amount of CO adsorbed on Au metal sites (2100 cm⁻¹). A surface regeneration step, which removed nearly all carbonate- and formate-like species while leaving the deactivated catalytic rate unchanged, ruled out accumulation of these surface species as a cause for deactivation. Similarly, CO adsorbed on Au⁶⁺ (2040 cm⁻¹), sites did not correlate with the decrease in rates either. These results, together with TEM measurements, indicate that a loss of surface sites (i.e. particle sintering) caused deactivation and showed metal corner atoms to be the active sites for WGS at these temperatures. More specifically, these metals sites are low coordinated corner atoms on cubo-octahedral particles.

Significance

We describe two new cells that allow us to simultaneously collect high quality spectroscopic (FTIR or XAS) and kinetic data. We have successfully applied each cell to answer fundamental questions about the active site and mechanism of the SCR and WGS reactions.

References

Direct Observation of Surface Ethyl Growth Kinetics Upon Hydrogenation of C_2H_4 on Rh/Al_2O_3 by Step-scan FT-IR Spectroscopy

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Introduction and Objectives

Time resolved FT-IR spectroscopy has recently allowed the detection and kinetic study of reaction intermediates of heterogeneous catalysis under reaction conditions. Specifically, monitoring of transient ethyl and propionyl species upon ethylene hydroformylation over supported Rh nanocatalyst surfaces [1], or of C_2H_5-Pt during ethylene hydrogenation over mesoporous silica supported Pt nanoparticles [2] have provided the first insights into the dynamics of elementary steps by a structure specific, vibrational spectroscopy. The millisecond temporal resolution of the rapid scan method is adequate for observing the kinetics of key reaction steps, yet important elementary processes such as the hydrogenation of surface ethylene (π-C_2H_4) to ethyl are too fast for this method. Here, the step-scan technique which allows time resolution from milliseconds to nanoseconds is required. The goal of the present work is to kinetically resolve the rise of surface ethyl intermediate over supported Rh nanocatalyst and, more generally, expand in-situ FT-IR spectroscopic methods for monitoring heterogeneous catalysis to microsecond regime.

Results and Discussion

A 20 ms ethylene gas pulse (20 psi back pressure) was released into a continuous gas flow of H_2 (300 mL/min) and N_2 (4.5 L/min, 1 atm). The Rh/Al_2O_3 catalyst was held at 295 K. Acquisition of step-scan data was initiated at the end of the 20 ms gas pulse, and 700 time slices at 100 microsecond intervals were collected. The results of up to 60 such experiments were averaged for S/N improvement. Using under-sampling in order to hold the interferogram measurement time in practical limits, spectra were collected in 1400-1100 cm\(^{-1}\) region where the intense wagging mode of surface ethyl species is known to absorb (in rapid scan experiments, a broad band in the range 1240 cm\(^{-1}\)-1160 cm\(^{-1}\) is observed [1]). As shown in the spectral time slices of Figure 1, three peaks, 1223 cm\(^{-1}\), 1187 cm\(^{-1}\) and 1150 cm\(^{-1}\) grow in this region. We attribute these bands to surface ethyl groups, C_2H_5Rh, in different local environments. The growth of the 1223 cm\(^{-1}\) site is shown in Figure 2. A first order fit indicates a rise time of 64 ms. The growth kinetics varies appreciable for the three sites: A rise time of 38 ms was determined for the 1187 cm\(^{-1}\) band, while the 1150 cm\(^{-1}\) peak

![Figure 1. The Step-Scan FTIR spectra in 1300-1100 cm\(^{-1}\) region observed following the initiation of C_2H_4 + H_2 catalysis at 298 K. The bottom trace shows a time slice of a control experiment without C_2H_4 gas pulse.](image-url)
showed a rise time of 58 ms. The spread of the growth kinetics is consistent with the assignment of the sites to different local environments in terms of surface H and ethylene species.

In order to monitor elementary steps of heterogeneous catalysis on the early microsecond time scale, we are developing a method that initiates catalysis with a nanosecond laser pulse for heating of the metal nanoparticle catalyst coupled with step-scan FT-IR monitoring. The laser heating pulse generates hot electrons and lattice vibrations that may activate adsorbed reactants or intermediates. In order to maximize reactant surface coverage prior to arrival of the laser heating pulse, the latter is preceded by a gas pulse from a fast valve for reactant loading (two pulse method). Recent results with this method using hydrogenation of ethylene over supported Rh/Al₂O₃ nanoparticles will be presented.

Summary

In summary, we used step-scan FT-IR spectroscopy to monitor the growth kinetics of the initial elementary step of ethylene hydrogenation over a metal nanoparticle catalyst for the first time. Distinct sites of surface ethyl were observed, each exhibiting different kinetics consistent with variations in the local surface environment. Experiments are in progress to exploit laser pulse heating of metal nanoparticles coupled with step-scan monitoring for resolving heterogeneous catalytic processes on the early microsecond time scale.

References

Unique Operando Quick-EXAFS Characterization of Bimetallic Heterogeneous Catalysts Used For Hydrodesulfurization

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Introduction and Objectives

The catalytic reaction of hydrodesulfurization (HDS) producing fuels with low sulfur content needs to use bimetallic catalysts which consist of Mo and Ni (or Co) dispersed on a high surface area support [1]. Information on the formation of the active phases and their evolution under reaction conditions are crucial for designing catalysts with enhanced performances. Thus the aim of this study is to perform operando X-ray Absorption Spectroscopy (XAS) in order to unravel the sulfidation processes of molybdenum and its promoter. Such characterization still represents a significant challenge and requires the development of analysis cells operating with harsh reaction conditions (temperature, pressure, gas…). A new suitable XAS analysis cell [2] mimicking phenomena that take place in fixed bed reactors under reactive atmosphere at pressure up to 50 bar and temperature up to 500°C is presented.

Results and Discussion

For the first time, Quick-EXAFS technology enabled to characterise, under realistic working conditions, simultaneously molybdenum and nickel (cobalt) K-edges taking advantage of the time resolution and the edge-hopping capabilities available with the Quick-EXAFS monochromator installed at the SAMBA beamline [3].

During the activation phase under H\textsubscript{2}S/H\textsubscript{2} flow, we observed concurrently the sulfidation of nickel (or Co) and molybdenum forming the mixed Ni(Co)MoS active phase. Depending of the catalyst pre-treatments (drying or calcination), we highlighted different mechanisms of sulfidation. In particular we observed for dried catalysts two molybdenum intermediate species: isolated MoO\textsubscript{4}\textsuperscript{2-} and oxysulfide \{MoOS\textsubscript{2}\} (Figure), while for the calcined catalysts only the oxysulfide species are formed during the activation treatment. We also showed that the sulfidation of Ni (or Co) is greatly dependent of molybdenum.
Figure: Simultaneous Quick-EXAFS studies at the Co and Mo K edges of the activation of a CoMo based catalyst under H₂S/H₂ (heating ramp 2°C/min).

Then the latter catalysts were characterized during the first hours of HDS reaction with model molecules (thiophene) using Quick-EXAFS combined to a mass spectrometer on line. Correlations between the evolution of active phases and the catalytic properties of our material are presented.

Conclusions

Simultaneous characterization of two metal species, accessible by the QEXAFS setup installed on the SAMBA beamline, which allowed an accurate description of the activation processes of bimetallic catalysts for hydrodesulfurization. We focused our study on the comparison of catalysts with similar formulations with different pre-treatments (dried/calcined) and two catalysts promoted by different metals: cobalt and nickel.

References

Effect of Pd Addition on the Efficiency of a NO$_x$-trap Catalyst: a FTIR Operando Study

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Introduction and Objectives

In the quest for more energetically and ecologically efficient exhaust control systems, a promising approach called Lean-NO$_x$-trap (LNT) was developed by Toyota in order to remove NO$_x$ from lean burn engines vehicles [1]. The LNT process consists in a first NO oxidation over precious metals (Pt, Pd or Rh) followed by a subsequent trap onto alkaline or alkali earth compounds during rather long lean periods. When the saturation is reached, the catalyst is exposed to a short rich period, during which the storage medium regeneration proceeds through the reduction of the stored NO$_x$ to nitrogen onto noble metals [2]. Due to their high price and incoming shortage, noble metals are the target of numerous studies, in order to limit their concentration and nature. While most of the works focused on Pt as the noble metal, a limited number of investigators also examined the efficiency of Pd, known to be a more active oxidation catalyst for short-chain hydrocarbons [3]. The aim of the present work is thus to study the effect of Pd addition over a commercial Pt/Ba/CeO$_2$/Al$_2$O$_3$ based catalyst, using a gas mixture simulating a real Diesel engine exhaust gas composition. A FTIR Operando study has allowed to further analyze the mechanisms occurring on the catalyst surface and to highlight the most critical points.

Results and Discussion

Two main catalysts were studied: a monometallic Pt (1.3 wt.%) and a bimetallic Pt-Pd (1.3 wt.%, mass ratio Pt/Pd = 27) both supported onto Ba/CeO$_2$/Al$_2$O$_3$. For comparison purpose, the reaction over the metal free support was also performed. A model gas composition which closely mimics a Diesel engine exhaust gas was used, including NO, O$_2$ and CO traces in the lean, decane, CO, H$_2$ and O$_2$ in the rich flows. Water and CO$_2$ were also added for realistic considerations. The nitrification tests were carried out at different temperatures representative of typical engine conditions during vehicle operation. The results relative to the quantification of NO oxidation into NO$_2$ and NO$_x$ storing are presented in Figure 1 (left). At 573 K the highest NO$_x$ storage capacity is observed for all samples and the Pt-Pd catalyst appears to be the most efficient storing system due to its highest NO oxidation capacity. Noble metals are indeed mainly involved in the oxidation of NO under lean conditions, but they can also be involved in other reactions, such as steam reforming or partial oxidation of hydrocarbons, Water Gas Shift and CO oxidation. Our results suggest that CO oxidation could be facilitated by Pd, while Pt would mainly
oxidize NO to NO\textsubscript{2}. \textit{Operando} FTIR enabled to analyze the evolution of adsorbed species upon nitration time on stream (Figure 1 centre). For the bare support, a negative band is observed at 1644 cm\textsuperscript{-1} than can be assigned to acrylates arising from decane decomposition. For monometallic Pt and bimetallic Pt-Pd this band is much less intense, indicating that the presence of noble metals favors the complete decane combustion during the preliminary material stabilization under rich flow. Furthermore, the spectra evolution evidences that carbonate species are substituted by nitrates, being the intensity of nitrate bands higher for the bimetallic Pt-Pd catalyst. This last result is consistent with both the higher NO oxidation capacity and NO\textsubscript{x} storing capacity observed with this catalyst.

**Figure 1.** NO to NO\textsubscript{2} conversion (top left) and NO\textsubscript{x} stored (bottom left) evolution with reaction temperature, difference surface spectra collected during nitration at 573 K (centre), removal efficiency (top right) and NO\textsubscript{x} reduction efficiency (bottom left) during cycles for three samples.

Figure 1 (right) shows the results obtained during lean/rich cycles. Pd addition clearly improved both the removal efficiency and the NO\textsubscript{x} reduction efficiency. A synergistic effect between Pt and Pd is thus evidenced for the LNT process. The progressive loss of efficiency observed upon increasing number of cycles is due to little NO\textsubscript{x} accumulation, being unable the catalyst to fully recover its initial state under rich flow at 553 K.

**Conclusions**

The use of an operando IR/MS approach has allowed evidencing a synergistic effect existing between Pt and Pd to improve the NO to NO\textsubscript{2} oxidation and therefore the NO\textsubscript{x} storage capacity in a LNT catalyst.

**References**

Single-molecule Sub-diffraction Imaging of Nanocatalysis

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Introduction and Objectives

Nanoparticles catalyze a multitude of chemical transformations important for energy conversion, petroleum processing, and pollutant removal. Understanding their structure-activity correlation is paramount for developing better catalysts, but is hampered by their inherent inhomogeneity: individual nanoparticles differ from one to another, and for every nanoparticle, it can change from time to time, especially during catalysis. Furthermore, each nanoparticle presents on its surface various types of sites, which are often unequal in catalytic reactivity. To overcome these challenges, my group has been developing single-molecule fluorescence imaging methods to study the catalytic activity and dynamics of single metal nanoparticles at nanometer spatial resolution, in situ, and with real-time single-turnover resolution.

Results and Discussion

I will present how we interrogate the catalytic activity, mechanism, heterogeneous reaction pathways, selectivity, and surface-restructuring-coupled temporal dynamics of individual Au nanoparticles. I will also present our latest work in imaging and resolving catalytic reactions on a single nanocatalyst at nanometer resolution, which uncovers diverse spatial patterns of reactivity at the nanoscale.

References

**From Model Systems to Technical Catalysts: Nanostructured Catalysts in Activation of Propane Studied by Electron Spectroscopies and Theory**

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**Introduction and Objectives**

The activation of C-H bonds in alkanes is catalyzed by metal surfaces, acid sites or metal oxides implying great diversity in the chemistry of the active species, the type of reaction intermediates and elementary steps. The project presented here is focused on oxidative C-H activation and oxidation of propane for synthesis of olefins or oxygenates over Mo and V oxides. Selectivity in alkane oxidation relies on the nature of oxygen species and the molecular structure of the catalyst in terms of concepts such as “site isolation” and co-operation of H abstraction on O insertion functionalities [1]. Thus, an improved understanding of relations between the reaction network and the catalyst surface structure under working conditions is a key issue. Here, we study both technical catalysts like phase-pure multi-metal oxides (MoVTeNbOx) that are characterized by high crystallinity and purity with respect to undesired amorphous admixtures and, in an effort to model the surface of these complex bulk oxides, mono-dispersed vanadium oxide species anchored on the surface of a host phase (mesoporous silica SBA-15, pristine or modified by Mo, Ti). Both the technical catalysts and the model systems have been investigated under working conditions, i.e. in the presence of reactive gases at a pressure of about 50 Pa at elevated temperatures up to 450 °C using near ambient pressure X-ray photoelectron spectroscopy (XPS) and by applying a recently developed methodology using near ambient pressure soft X-ray absorption spectroscopy near the O K-edge (O K-NEXAFS) [2]. The catalytic performance of the catalysts has been verified by on-line mass spectrometry.

**Results and Discussion**

Fig. 1a shows the evolution of oxygen species of dehydrated VOx/SBA-15 model catalysts with increasing V loading. The O K-NEXAFS was analyzed by comparing the experimental spectra with theoretical spectra of model clusters obtained by simulations using state of the art density functional theory (DFT). Contributions of V-O-V bridges could be identified on the VOx/SBA-15 model catalysts at low V loadings (≤ 8wt%) providing clear evidence of the co-existence of different vanadia species including non-monomeric arrangements (Fig. 1b).
For MoVTeNbO\textsubscript{x} catalysts it was found that the elemental composition of the outer surface responds dynamically on the addition of steam to the O\textsubscript{2}/C\textsubscript{3}H\textsubscript{8} feed. Depletion in Mo content and a significant enrichment with Te and V was observed. An analysis of the V2p\textsubscript{3/2} XP core level spectra reveals the evolution of V\textsuperscript{5+} species that is related to the acrylic acid abundance, i.e. a close relationship between catalytic performance and V\textsuperscript{5+} sites (Fig. 1c). The Te/V abundance ratio remains constant. Thus, it is suggested that a monolayer of Te/V entities on top of the crystalline bulk phase constitutes the active surface of MoVTeNbO\textsubscript{x} during selective propane oxidation to acrylic acid [3].

Figure 1. (a) O K-edge spectra in 50 Pa of O\textsubscript{2} at 420 °C showing the evolution of oxygen species (marked with arrows) with V loading (2wt% - 14wt% as indicated) on SBA-15. (b) Experimental O K-edge spectrum of 8wt%V/SBA-15 is compared with theoretical spectra derived from DFT cluster calculation. The contribution of different bonding configuration to the total spectrum is indicated. (c) Relationship between the acrylic acid abundance and the surface element content of V\textsuperscript{5+} species, V\textsuperscript{4+} species and the Te/V abundance ratio of MoVTeNbO\textsubscript{x} catalyst in the feed of propane, oxygen and water vapor at 420 °C.

Conclusions

Near ambient pressure XPS provided direct detailed insight into the redox chemistry of a complex oxidation catalyst such as MoVTeNb oxide. In the case of model systems like VO\textsubscript{x}/SBA-15 a comparison of experimental O K-NEXAFS spectra with theory allows to differentiate between different bonding configuration of the transition metal oxide species under relevant conditions, i.e. in the dehydrated state at reaction temperature. Thus, near ambient pressure XPS and NEXAFS with their inherent surface sensitivity are a probe than can substantially assist other methods to obtain an in-depth understanding not only of model systems but also materials that are close to a technical catalyst.

References

Operando X-ray Absorption Spectroscopy for Understanding the Origin of Phosphorous Induced Chemical Aging of Pd-based Three-way Catalysts

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Introduction and Objectives

Three-way catalysts (TWC) play an important role in the abatement of hazardous exhaust emissions from spark ignition engines to meet the regulations [1-3]. Although they have proven efficient for this application, new fuel concepts like compressed natural gas (CNG) consisting of mainly methane and new EURO VI legislations post new challenges. One of them is chemical aging caused namely by phosphorous (P) originating from engine oil additives such as zinc dialkyldithiophosphate (ZDDP) which reacts with washcoat and catalyst composition. Commonly observed P compounds are AlPO4 and CePO4 [2-4]. However, the effect of P is not completely understood, especially on noble metals. Therefore, better understanding of the influence of P on TWC may provide a way forward to mitigate P influence on the catalyst efficiency. In this work, model TWC powders namely Pd/Al2O3 and Pd/Al2O3/CeZrO2 were subjected to P aging (1.8 or 7.5 wt.% P poisoned and aged at 700°C for 5h) followed by detailed operando spectroscopic and activity studies.

Results and Discussion

The physisorption data show that both the surface area and pore volume of the catalysts decrease for P aged catalysts as compared to the fresh ones, indicating the presence of P on the surface and within the pores of the supports. Solid state Al27 and P31 MAS NMR spectra suggest the formation (even at 1.8 wt.% P) of AlPO4 and CePO4 like species in the catalysts [4]. The P species mitigate the oxidation and reduction efficiency of the catalysts as evident form the activity data obtained under simulated λ = 1 conditions. The origin of the decreased catalyst efficiency is explored by operando XANES and DRIFTS during the reaction. As an example, operando XANES during methane oxidation are shown in Fig.1. By comparison of the conversion profiles over the fresh and P aged catalysts it is evident that the former is more active than the latter. On the fresh catalyst the conversion starts at around 300°C and completes at around 370°C, while it starts only at 400°C and complete conversion attains only at around 850°C on the P aged one. During cooling from 850°C, the drop in the conversion is observed on both the catalysts but to different extents and at different temperatures. On the fresh catalyst the maximum loss in the conversion is 20% at 550°C, while it is 90% at 650°C on the aged one.
From the corresponding XANES spectra, it is evident that while heating Pd is in an oxidized state up to 800°C and above this temperature it is reduced on both the catalysts. However, during cooling, the reduced Pd reoxidizes (≤435°C) only in the fresh catalyst. This indicates that Pd alters the redox properties of PdO species in the catalysts, which is in line with the H2-TPR followed by XANES data that show the decreased reducibility of PdO species in the catalysts [4]. By correlating the activity and spectroscopic data, it emerges that Pd oxide plays an important role in the methane oxidation at low temperatures (≤675°C) and at high temperatures metallic Pd can also catalyse the reaction as evident from the drop in the methane conversion and from the corresponding XANES spectra. In conclusion, chemical aging caused by P diminishes both the reduction and oxidation efficiency of the catalysts by altering the redox properties of PdO species.

References

Operando FTIR-MS Study of Ammonia-ammonium Interplay in a Genuine Monolithic V$_2$O$_5$/TiO$_2$/Sepiolite Catalyst During Selective Catalytic Reduction of NO with NH$_3$

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Introduction and Objectives

Recently, we have demonstrated the viability of operando spectroscopic analyses of monolithic catalysts using transmission FT-IR coupled with mass spectrometry on real conformed monolithic catalysts.$^1$ During the first decade of development of the operando concept much attention has been on development of sound spectrokinetic cells to ensure proper kinetic measurement during operando spectroscopy.$^{2,3,4}$ Expanding the operando approach from being solely a valuable tool for the catalyst researcher to also providing spatial information is highly valuable for the catalyst engineer.

Almost all industrial implementations of catalysis for environmental applications have been done with the use of monoliths, since they combine excellent gas-solid contact conditions with extremely low-pressure drops. Our work in this area has been concentrated on assessing the water-dependent interplay between NH$_3$ and NH$_4^{+}$ in working monolithic V$_2$O$_5$/TiO$_2$ based NH$_3$-SCR catalysts for the removal of NO$_x$:

$$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$$  \hspace{1cm} (1)

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Figure 1 Operando FTIR-MS study of 1000 ppm NO + 3.5% O$_2$ reaction with pre-adsorbed ammonia over a 5 cm monolithic V$_2$O$_5$/TiO$_2$/sepiolite catalyst at 250°C. The mass spectrometric traces of reactants and products are given at the right.

Both adsorbed ammonia on oxo-vanadia Lewis acid sites and ammonium ions associated with Brønsted acid sites can act as active sites. The relation between Lewis and Brønsted acid V-O sites is not inherent, but dependent on the humidity of the gas phase. This work is performed without added water in the reac-
tion feed; it demonstrates that reaction-generated water, eq. (1), hydrolyzes the surface V=O sites along the channels of a monolith, transforming Lewis acid sites into Brønsted acid sites. Furthermore, during a reaction sequence in the integral monolithic reactor with NO and O₂ titrating the catalyst surface for pre-adsorbed ammonia, it can be seen how adsorbed ammonia is either used for the SCR reaction, or converted into the ammonium ions, which then participates in the SCR reaction. These observations complement more fundamental work performed on kinetically restricted pelletized or powdered catalysts, since it is now possible to achieve direct observation on secondary effects of water produced upstream.

Results and Discussion

Figure 1 illustrates some dynamic variations at 1620 and 1435 cm⁻¹ during reaction. The ammonium ions observed at the latter wavenumber disappear after approx. 200 minutes, which is essentially the time when N₂ traces disappear, as confirmed by online mass spectrometry. However, literature reports that adsorbed ammonia exhibit an IR mode near 1610 cm⁻¹. Alas, that band significantly overlaps with that of molecular water, which increases during reaction time in the experiment. Such rehydroxylation of surface vanadia is due to the SCR reaction-formed water.

The presence of water is unavoidable to genuinely reproduce working reaction conditions of a real industrially used catalyst with binder material, and at the same time operations in the presence of significant amount of water produced during the fuel combustion process. Therefore, these observations motivated us to perform a multi component analysis (MCA) of the 1620 cm⁻¹ peak using commercial indirect hard modeling software (PEAXACT), in order to see if a un-biased hard mathematical model could be able resolve a decreasing band from adsorbed ammonia and an increasing OH band.

Results showed that it was possible to successfully identify the distribution of ammonia and ammonium ions distributed over the catalyst support, which open up new possibilities for FTIR investigations of metal oxide supported V₂O₅ catalysts in wet conditions.

References

The Ag-O System in catalysis: New Insights by Ambient Pressure XPS

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Introduction and Objectives

The oxygen interaction with silver has attracted great attention in the past years because silver based catalysts are used in two important large scale processes in the chemical industry, namely ethylene epoxidation and methanol oxidation[1]. These reactions produce highly valuable feedstock chemicals that are used in many applications. The economic importance of these processes motivated an extensive investigation of the Ag-O system in past years [2-4]. However the mechanisms behind the remarkable selectivity obtained with Ag catalysts for both reactions is still focus of debate in the literature [5]. In this work we applied the ambient pressure XPS technique to investigate the chemical state of the Ag catalyst surface in equilibrium with the gas phase with pure O$_2$ and reaction conditions in the mbar pressure range at industrially relevant temperatures.

Results and Discussion

Initially Ag catalysts under pure O$_2$ atmosphere were investigated in order to identify and characterize the O species formed at different temperatures. In the 150-500 C temperature range, five distinct features in the O 1s XP spectra were identified and assigned to different atomic O species on Ag, as shown in figure 1-a,b. Evidences for the distinct electronic structure of these species were obtained by comparing their binding energies (figure 1-a,b), amount of ionic Ag (figure 1-c), temperature stability, valence band, O-K X-ray absorption near edge and O KVV Auger features [6].

![Figure 1. (a) O1s spectra showing the O species on Ag powder at 180 C. (b) O1s spectra showing the O species on Ag foil at 500 C. (c) Correlation of the abundance of different O species with the amount of Ag $^{+}$](image)

When methanol or ethylene is present together with O$_2$ in the gas phase, drastic changes in the O species distribution are observed, as a result of their different reactivity. Some of the species completely vanish, the abundance of others correlates with the hydrocarbon partial pressure. Simultaneous analysis of the gas phase composition by on-line mass-spectrometry and gas chromatography allows the direct correla-
tion of surface spectroscopy with catalytic performance. For the case of ethylene epoxidation running at steady state conditions, it was observed that the selectivity to the epoxide can be correlated to the ratio of different O species. A model of the role of the different O species in the frame of the oxidation reactions is suggested. Based on the electronic structure and reactivity data, it is proposed that while some species act as nucleophilic centers attacking C-H bonds (O$_{\alpha_1}$ and O$_{\alpha_2}$), which is the first step to total oxidation, other act as an electrophilic agent, attacking the C=C bonds and producing the epoxide (O$_{\alpha_3}$).

**Conclusions**

The surface of unsupported Ag catalysts was characterized by XPS under working conditions for ethylene and methanol oxidation reactions. This analysis indicates that Ag is able to activate molecular oxygen into a number of distinct active forms with different chemical nature, which ultimately lead to different roles in the oxidation reactions. This new insights on the role of different O species can be used to better understand the mechanisms of selective oxidation reactions over silver and in the design of improved catalysts.

**References**


ATR-IR Study on The Kinetics of Aqueous Phase Conversion of Biomass Over Supported Metal Catalysts

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Introduction and Objectives

Due to the growing interest in the development of renewable, carbon neutral chemicals and transportation fuels, there is growing body of research that aims to adapt existing heterogeneous catalysis processes for biomass conversion. Aqueous phase catalytic processes for biomass conversion are promising\textsuperscript{1}, but little is currently known about the reaction pathways of such catalytic systems. The objective of this study is to understand differences in the kinetics and observed surface intermediates formed when flowing aqueous solutions of glycerol and glucose over \( \text{Pt}/\alpha\text{-Al}_2\text{O}_3 \) supported metal catalysts by in-situ attenuated total reflectance infra-red (ATR-IR) spectroscopy. The different molecular structure of these reactants is expected to result in different kinetics for aqueous phase reforming and the formation of carbonaceous deposits. \( \text{Pt}/\alpha\text{-Al}_2\text{O}_3 \) was chosen because it is an active catalyst for the aqueous phase reforming of biomass\textsuperscript{2}, it is stable during the length of these experiments in the conditions used in this study\textsuperscript{3}, and it also has favorable spectroscopic properties.

Results and Discussion

Operando ATR-IR experiments were performed by depositing a layer of Pt/\( \alpha\text{-Al}_2\text{O}_3 \) directly on the internal reflection element and flowing biomass solution over the catalyst. A 300 mM glycerol solution flow resulted in the formation of dissociated hydrogen, linear, and bridging CO species on the Pt particles, Figure 1 a) 1). The development of these modes occurred significantly after the stabilization of bulk glycerol solution signals at 2 min, indicating kinetic control. Returning to degassed flow resulted in the removal of bulk glycerol from the catalyst pores. Introduction of O\textsubscript{2} saturated water resulted in the rapid oxidative removal of all H and CO species, and a small blue-shift of the 1620 carbonyl as well as the growth of the carbonyl species at 1698 cm\textsuperscript{-1}, shown in Figure 1 a) 3). Under these conditions, carbonyls formed from dehydrogenation chemistry are more strongly bound to the Pt than CO. Irreversibly bound carbonyls will poison the Pt and are likely precursors to humin formation.

Conversion of a 300 mM aqueous glucose solution also resulted in the formation of dissociated hydrogen, linear, and bridging CO on the Pt surface, Figure 1 a) 2), all of which are less intense and red shifted when compared to glycerol. A study that used dissolved CO and a Pt/\( \alpha\text{-Al}_2\text{O}_3 \) catalyst suggests the intensity and red shift trends observed here indicate a lower surface concentration\textsuperscript{4}. Also, the observed carbonyl modes are more intense than in the case of glycerol, suggesting a higher concentration of carbonaceous deposits on the surface. Even after exposure to dissolved oxygen, Figure 1 a) 4), the carbonyl peaks remain intense. CO formation kinetics were slower in the case of glucose relative to glycerol, as the time to reach a constant linear CO peak took greater than 30 min, compared to 20 min in the case of glycerol, Figure 1 b). The slower initial rate of CO formation from glucose is likely due to its longer carbon chain length, as carbonyl formation was not seen in the first 5 min.
Figure 1. a) ATR-IR Spectra of catalyst layer during water flow post 30 min glycerol exposure in 1), post 30 min glucose exposure in 2), during dissolved oxygen flow after water flow post glycerol exposure in 3), during dissolved oxygen flow after water flow post glucose exposure in 4). b) Integrated peak areas for linearly bound CO on 5 wt% Pt/γ-Al₂O₃ over time.

Conclusions

At room temperature and pressure, aqueous phase glycerol and glucose are readily activated over Pt/γ-Al₂O₃ forming surface bound hydrogen and CO. These species are removed by O₂ saturated water. The formation of these surface species from glycerol is faster than from glucose. This is likely due to glucose’s being sterically hindered on the Pt surface that cannot be removed by dissolved O₂ in the case of glucose. Glucose also results in more carbonyl species which are resistant to oxidative removal from Pt.

References

Understanding the Effect of Sm$_2$O$_3$ and CeO$_2$ Promoters on the Structure and Activity of Rh/Al$_2$O$_3$ Catalysts for Methane Steam Reforming

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Introduction and Objectives

Conversion of methane into higher value products has been intensively studied because this process is important to reduce our dependence on petroleum. To obtain high methane conversion, an elevated temperature (1033 K or above) is required. The main problems under these conditions are carbon deposition and sintering of active metals, both leading to the catalysts deactivation. This makes development of long-lasting catalysts essential. Recently, it was confirmed that Ru and Rh are the most active metals for methane steam reforming.$^{[1]}$ The most common support for methane reforming catalysts is alumina. Other oxides such as ceria have recently attracted attention mainly due to their oxygen-storage properties and chemical interaction with noble metals. To further enhance the temperature stability of supported ceria it can be promoted with samaria.$^{[2,3]}$ To understand the influence of cerium and samarium oxides on the structure of rhodium nanoparticles and its relation to catalytic performance during methane steam reforming (SR) it is important to study the structure of promoted catalysts under reaction conditions. Giving this, Rh catalysts supported on mixed oxides of Sm$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ were investigated by in situ by X-ray absorption spectroscopy (XAS) in combination with on-line mass-spectrometry.

Results and Discussion

The values of CH$_4$ conversion obtained for the catalysts during methane steam reforming were higher for the samples supported in alumina promoted by ceria and samaria. The samples were heated to 773 K and
in sequence to 1033 K with dwell times of 1 h. All catalysts showed deactivation with time on stream; however Rh/Al showed the strongest decrease in activity. The Figure (A) shows the coordination numbers for Rh-Rh and Rh-O obtained from the EXAFS analysis of all spectra under the various conditions, where we describe temperature/atmosphere in the x-axis for (■) Rh/Al₂O₃, (○) Rh/12CeO₂-Al₂O₃, (△) Rh/12Sm₂O₃-Al₂O₃, (●) Rh/6Sm₂O₃-6CeO₂-Al₂O₃. Initially at room temperature the samples were fully oxidized. Under reductive atmosphere at high temperature the promoted samples got reduced, however Rh/Al showed lower metallic character. The Rh-Rh CN for the reduced samples was around 5, indicative of small particles. Differences were also found between the promoted catalysts and Rh/Al during reaction. Under methane SR atmosphere the samples got partially oxidized. With the increase in temperature up to 773 K, Rh/Al showed a decrease in CN and this could be due re-dispersion of Rh metallic particles owing to CO formation and absorption in the surface, which is an oxidative process. With further increase in temperature up to 1033 K an increase in CN is observed due to the sintering of particles in the unpromoted catalyst. In the samaria-ceria containing samples the Rh-Rh CN remained practically constant with increase in the reaction temperature from 773 K to 1033 K. A possible explanation for the observed behaviour would be the greater metal-support interaction in the presence of promoters. The STEM images for the Rh/Al₂O₃ catalyst after reduction at 873 K (B) and after MSR at 1033 K (C) are depicted in the Figure and they clearly show that sintering of the metallic particles took place during reaction. This process was more pronounced for Rh/Al₂O₃.

Conclusions

The effect of the addition of Sm₂O₃ and CeO₂ on the catalytic behaviour of Rh/Al₂O₃ catalysts was revealed by changes on the structure and electron properties of Rh particles. The higher activity observed for the studied Rh catalysts during methane SR was mainly attributed to the high dispersion of the active phase. The improvement in the activity and stability of promoted catalysts is due to the greater Rh-support interaction, which inhibited Rh oxidation and the sintering of the Rh particles, thus maintaining the high dispersion during the drastic reaction conditions. The EXAFS experiments clearly illustrate the alteration of the topology and therefore the lack of stability of rhodium particles when supported in unpromoted alumina.

References

Introduction and Objectives

Aqueous phase processing of biomass derived products (e.g. sugars, bio-oil) is an important step in the conversion of biomass to fuels [1, 2]. Understanding how to control the catalysts activity for C-C and C-O cleavage is crucial in order to tune the catalyst selectivity to the desired reaction pathway. The effect of the aqueous phase conditions on the electronic structure of the active metal and the physical structure of the alloy is not well understood. In addition, it is not clear whether the metal electronic structure is affected by the solution pH (bio-oil is acidic, pH ~ 2).

In this talk, we will present our recent operando XANES/EXAFS work on understanding the correlation between the local coordination and electronic structure of Pt and PtNi supported catalysts and their catalytic activity/selectivity during aqueous phase reforming (APR) of bio-liquids. In addition, we will discuss density functional theory (DFT) calculations to rationalize the experimental findings.

Results and Discussion

Testing of the catalyst for APR of glycerol was carried out in a microchannel reactor and the catalysts were characterized using an in-house built operando extended x-ray absorption spectroscopy cell (XANES and EXAFS) operating at 225 °C and 30 atm pressure. The catalyst was pre-treated by reduction in H₂, followed by exposure to the feed comprising 10% (wt.) glycerol (or ethylene glycol) in water at 225 °C and 30 atm pressure. Gas samples and liquid products were monitored by MicroGC and HPLC. The operando XANES/EXAFS results revealed a strong dependence of the Pt electron density on the solution pH and this had a strong effect on the Pt activity and selectivity. Addition of Ni resulted in more than twofold increase in reforming turnover frequency when Ni was located in the specific configuration in the bimetallic structure.

The structure of the bimetallic was found to change under aqueous phase reaction conditions compared with vapor phase reforming and reducing conditions. The correlation between the local coordination, electronic structure and the catalytic activity and selectivity will be presented. The effect of the electronic structure on the reaction pathways and strategies for optimizing the catalyst activity and selectivity will be discussed as guided by DFT calculations and microkinetic model predictions.
Conclusions

The solution pH and PtNi alloy formation affect the electron density on Pt and this has a pronounced effect on the activity and selectivity for bio-liquids reforming. The structure of the PtNi bimetallic is dependent on the reactant atmosphere and the structure/activity relationship is proposed using operando XANES/EXAFS and DFT calculations.

References

Operando X-ray Diffraction Tomography for Revealing Insight into Active Phase Evolution in Catalyst Bodies

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Introduction and Objectives

Industrial catalysis utilizes mm-sized catalyst bodies in fixed bed reactors so as to minimize pressure drops across the reactor vessel. The efficiency of the final catalytic system depends on the nature and distribution of metal/metal oxide ‘active species’ across the catalyst body although this can normally be affected during the multi-step preparation process. The evolution of the active species from an initial precursor complex delivered via liquid phase impregnation is often a highly convoluted process. In recent times several analytical techniques have been utilized in order to obtain real time 2D and 3D spatial information on the nature of chemical species present on the catalyst during preparation, in order to identify the key physicochemical processes occurring that govern both their spatial distribution and final properties. It is envisaged that, armed with such information better control over these properties could be realized leading to improvements in catalyst performance [1]. Recently we employed the novel technique of synchrotron X-ray Diffraction Computed Tomography (XRD-CT) [2] and demonstrated its capability to image a catalyst body as a function of time to follow the preparation process and to study the catalyst as a reaction (CO methanation) takes place.

Results and Discussion

The experiments were performed at stations ID15A and ID15B of the ESRF (Grenoble, France) using a monochromatic (E = 86.88 (ID15B) or 69.95 keV (ID15A), 100 \textmu m square section pencil beam with diffracted X-rays recorded on a Pixium 4700 flat panel detector. Dynamic diffraction imaging was employed to follow the in situ calcination (ambient to 500 °C at 2.5 °C/min with dwell of 2 h) and catalytic reaction of a cylindrical catalyst body (diameter = 3 mm; length = 3 mm) impregnated with Ni catalyst precursor materials ([NiCl\textsubscript{2}(en)(H\textsubscript{2}O)\textsubscript{4}] or [Ni(NO\textsubscript{3})\textsubscript{2}(en)(H\textsubscript{2}O)\textsubscript{4}] where en = ethylenediamine). Calcination was performed under an inert gas atmosphere whereas catalytic methanation was performed in a mixture of CO/H\textsubscript{2} in N\textsubscript{2}.

Catalyst preparation normally involves two or three steps; impregnation of the catalyst body with the active metal in the form of a metal complex, calcination at high temperatures and in some cases ‘activation’ in a pre-conditioning gas. XRD-CT was employed to examine this second step (calcination in N\textsubscript{2}) of a Ni supported γ-Al\textsubscript{2}O\textsubscript{3} catalyst body starting from a NiCl\textsubscript{2} source. Crucially we observed the formation of the cubic (fcc) metallic Ni phases via a number of complex intermediate phases. Importantly 2D XRD-CT scans revealed two different crystalline phases forming located at the periphery and in the centre of the body accordingly. Although both phases yielded fcc Ni, the precursor at the periphery did so in one step, while the phase in the centre did so via a 3-4 step process (Fig. 1). This appeared to affect the particle size of the fcc Ni phase with the fcc Ni particles in the centre of the pellet larger than those seen at the periphery [3]. This will have important implications for the activity/selectivity of these bodies in a catalytic reaction.
In a second recent study, XRD-CT was also combined with absorption-CT to study the phase evolution process in NiNO₃ impregnated Ni/γ-Al₂O₃ catalyst bodies during calcination and activation, but more importantly, under true catalytic conditions. As with NiCl₂ impregnated catalyst bodies two different, inhomogeneously distributed precursors result after the impregnation process although the breakdown of these precursors resulted in the formation of more uniformly-sized fcc Ni nanoparticles. Particles located towards the periphery undergo uncontrolled sintering on exposure to O₂ although this appears to be dependent on both the concentration/distribution of the Ni and its form (where it is expected that Ni is present in the sample in both crystalline and diffraction silent forms). Reduction in H₂ did not induce further sintering but results in an active fcc Ni containing catalyst for CO methanation. Operando catalytic measurements performed during CO methanation, demonstrated the crystalline metallic fcc Ni component to be remarkably stable over the duration of reaction (~ 3 h @ 450 °C), undergoing no change in phase constitution, spatial distribution or average particle size, leading us to conclude that metallic fcc Ni is the active component of the catalyst for CO methanation [4].

Conclusions

By exploiting rapid, time resolved XRD-CT imaging it has been possible to obtain detailed insight into the complex chemistry occurring within catalyst bodies during catalyst preparation and under reaction conditions and how this influences the distribution of these phases and their final properties.

References

Elucidating the Mechanism of Dimethyl Carbonate Formation by Oxidative Carbonylation of Methanol Over CuY Zeolite: An Operando SSITKA/DRIFTS/MS Study

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Introduction and Objectives

Cu-containing zeolites, in particular CuY zeolites, have been found to be appropriate catalysts for the oxidative carbonylation of methanol (MeOH) to dimethyl carbonate (DMC) in the gas phase [1]. Such a process could be an attractive, and environmentally benign, alternative to the traditional synthetic route for DMC using highly hazardous and toxic phosgene as a reagent. However, to improve the catalytic performance of suitable catalysts knowledge about the reaction mechanism and kinetics is needed. Most of the studies published in literature are based upon in situ FTIR observations using Cu-exchanged zeolites [2-4] and higher loaded CuY samples [5]. Up to now, the nature of the catalytically active Cu species and reactive intermediates as well as the role of oxygen within the catalytic cycle is not satisfactorily elucidated.

To get more insight into the reaction mechanism a SSITKA/DRIFTS/MS setup was applied which enables to discriminate between active and spectator species by comparison of the isotopic exchange rate of the surface species, followed by DRIFTS, with the rate of exchange of gas phase species measured by MS. The aim was to elucidate the role of oxygen in the carbonylation reaction and its relevance concerning selective and unselective reaction pathways, and to follow the way of CO insertion. For this purpose the interaction of the catalyst with the different reactants and reactant mixtures (O_{2}, CO, CO/O_{2}, MeOH/O_{2}, MeOH/CO, and MeOH/CO/O_{2}) was studied in detail using ^{16}O_{2}/^{18}O_{2} as well as ^{12}CO/^{13}CO containing gas mixtures. For the experiments a CuY zeolite with a Cu content of 13 wt% Cu was selected which additionally contain CuO_{x} and crystalline CuO.

Results and Discussion

The available information from operando SSITKA/DRIFTS/MS experiments in terms of surface adsorbates and gas phase products are exemplarily displayed in Fig. 1. The Figure shows DRIFT spectra and MS signal intensities obtained after switching from MeOH/^{12}CO/He feed to the respective ^{13}CO-containing feed. Although the feed did not contain oxygen the formation of DMC as well as CO_{2} was observed by MS. As can be seen from the DRIFT spectra besides CO adsorbed on Cu(I) methoxide, formate, monomethyl carbonate (MMC), and DMC species were detected. Separate experiments showed that the formation of formate and CO_{2} is attributed to the oxidation of MeOH and CO by lattice oxygen supplied by CuO_{x} species.
From the observed band shift of νCu(I)−CO (2120 → 2072 cm⁻¹) as well as adsorbed DMC (1735 → 1689 cm⁻¹) after switching from MeOH¹²CO/He to MeOH¹³CO/He follows that CO participates in DMC formation for which obviously no additional oxygen is needed. On the other hand position and intensity of the MMC band at 1639 cm⁻¹ do not change. This suggests that the observed bidentate MMC species can not be an intermediate in DMC formation as discussed earlier. Further experiments showed that DMC is produced via a monodentate monomethyl carbonate (MMC) species as intermediate which is formed by the concerted action of adsorbed methoxide and CO with gas phase MeOH. The MMC formation, which requires an oxidation step, proceeds under participation of lattice oxygen from CuOₓ. Gas phase oxygen is needed to re-oxidize the catalyst (Mars-van-Krevelen mechanism) but favours also the oxidation of CO to CO₂ and unselective oxidation reactions of MeOH to methyl formate, dimethoxymethane, and CO₂. For this reason the appropriate choice of reaction temperature and oxygen content in the reactant gas mixture was found to be indispensable for reaching high DMC selectivities.

Conclusions

The operando DRIFTS/MS measurements under SSITKA conditions provide information on the transient progress of isotopic exchange in educts and products. Only in this manner it is possible to distinguish between active and spectator species which is essential for the elucidation of reaction mechanism especially in complex catalytic reaction systems.

References

Modulation Excitation Hard X-ray Diffraction to Capture Red-ox Dynamics of Supported Pd Catalysts

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Introduction and Objectives

Bulk physical methods such as X-ray diffraction are considered silent with respect to surface dynamics. XRD is limited by crystallite size and therefore supported metal nano-particles of certain size limit are hardly accessible by XRD. However, synchrotron hard-XRD was used to unravel dynamics of metal nano-particles in Pd/Al₂O₃ [1]. Also, it is intrinsic to the bulk nature of XRD that a complete picture of the working catalyst can be obtained in one shot. Here we apply for the first time a concentration modulation excitation approach using phase sensitive detection [2] to observe reduction-oxidation of small Pd nano-particles supported on an otherwise ‘difficult’ oxide, ceria-zirconia (CZ).

Results and Discussion

A concentration modulation experiment consisted in the periodic switch between 1 vol% CO-He (25 sec) and 1 vol% O₂-He (25 sec) at 573 K on 2 wt% Pd/CZ in a homemade cell [3]. A modulation period is the time required to conclude a full CO vs. O₂ sequence. The sets of time-resolved XRD (100 patterns/period, 0.5 sec/pattern) were processed into sets of phase-resolved XRD by phase sensitive detection (PSD) [2,4]. PSD generates diffractograms free from contributions responding with a frequency different from that of the stimulation. Therefore, only the changes biased by the external stimulus, i.e. the concentration variation, are emphasized; all static signals are filtered out and do not appear in the phase-resolved data. The time-resolved hard-XRD data collected during a modulation experiment (100 XRD x 25 periods, Fig. 1) exhibit the reflections of cubic CZ but hardly display any tangible change. No information is available about the state of Pd. This is typically associated with the fine dispersion of PdO particles induced by CZ. The corresponding phase-resolved XRD data exhibit only the very subtle changes associated with the signals responding to the modulation experiment. All signals of the CZ support shift repeatedly to lower and back to higher Q values in response to the CO and the O₂ pulses, respectively. This behaviour qualitatively describes the reduction and the re-oxidation of CZ associated with its oxygen storage capacity. Importantly, the data also exhibit additional broad features (e.g. at ca 2.8 Å⁻¹) that correspond to metallic Pd reflections. The sole intensity change is associated with the relative increase of long range order attributed to PdO reduction. Therefore, the modulation data can capture the dynamic reduction and re-oxidation of PdO and CZ. From the PSD envelopes one can precisely assess the temporal behaviour of the structural changes using the time-resolved XRD patterns and access the detailed structural-dynamic behaviour of the system. Reduction of both PdO and CZ occurs much slower than re-oxidation (Fig. 2). Comparison with Pd/Al₂O₃ reveals that this is the effect of the OSC of CZ.
Modulation excitation spectroscopy and phase sensitive detection demonstrate powerful tools to increase the sensitivity of XRD to capture precious metal nanoparticles at work.

References
Advantages of Syngas for the Regeneration of NOx Trap System Investigated With Operando IR Measurements

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Introduction and Objectives
 Lean NOₓ trap/reduction systems (NSR) for Diesel fuelled engines currently run in sequential conditions with lean and short rich period that ensure the reduction of stored NOₓ to N₂. Subsequent improvement can be achieved by injecting upstream the NSR system a reformate composed of CO + H₂. In the presence of H₂, less attention was paid to the formation of side products during the regeneration process. The production of NH₃ as side product for example can be profitably used to improve the efficiency by coupling the NSR catalyst with a Selective Catalytic Reduction system. Operando in situ infrared spectroscopic investigation was thus performed for the examination of adsorbed species and the simultaneous analysis of N₂, N₂O and NH₃ products particularly for high H₂ and CO concentrations. A specific attention was paid to the influence of time and to the composition of the regeneration between 150 and 350°C.

Materials and Methods
 The catalyst (1%wt Pt-0.5%wt Rh/Al₂O₃-BaO) is grinded and pressed into a self-supported wafer (11.6mg) before being placed in the IR reactor in transmission mode as previously described[1]. Storage is achieved in the presence of 500ppm NO+5%O₂ during 120s-500s whereas regeneration is performed using 2-20%H₂+0-5%CO+He during 1-60s. The switches lean/rich are repeated 20 times with a 4-ways valve for each condition in order to stabilize the activity. The formation of N₂, N₂O and NH₃ is followed using IR spectroscopy (380 Thermo) and mass spectrometry (Pfeiffer). The nature of adsorbed species is recorded on an FTIR 460 Protégé (Thermo) spectrometer fitted with MCT detector and using 64 scans per spectra at 4 cm⁻¹ (1 spectra/13 s).

Results and Discussion
 The regeneration of NOx trap catalyst (Pt-Rh/Al₂O₃-BaO) with high H₂ concentration showed the involvement of nitrite and nitrate in function of temperature and regeneration time. Bridging nitrites were accumulated at 150°C (Fig. 1) and were transformed during long time regeneration (60s) mainly into NH₃. Nitrite and nitrate developed at 250°C. Two processes leading to the formation of products occurred during lean/rich and rich/lean switches, inducing a change in selectivity. In the presence of 5%CO (no H₂), an extensive production of N₂O was observed at 250°C. The addition of H₂ to CO was accompanied by an attenuation of N₂O formation and significant production of NH₃. Spectra of the adsorbed species which accumulate were recorded during the regeneration phase with two different relative concentrations of H₂ and CO (Fig. 2). No signal appears at the end of storage phase in the spectral range 1800-2400 cm⁻¹. After CO/H₂ injection, the carbonyl species over noble metals as well as NCO over alumina [2] developed at 2040, 2080 cm⁻¹ and at 2250 and 2230 cm⁻¹ respectively.
In presence of CO the formation of nitrite and its regeneration was progressively inhibited. This could explain the decrease of NOx trap efficiency at low temperature. The beneficial effect of H$_2$ addition at 250°C which promotes the formation of NH$_3$ could arise from hydrogenolysis of NCO species as well as usual successive hydrogenation of chemisorbed N atoms from NO dissociation.

**Conclusions**

Owing to high H$_2$/CO content in syngas, strong differences in the distribution of adsorbates in function of the relative CO/H$_2$ composition were observed. The changes of selectivity into N$_2$, N$_2$O and NH$_3$ were related to the operating conditions and the nature of adsorbates. The influence of regeneration time gave further information for further coupling of NOx trap catalyst with Selective Catalytic Reduction catalyst. The latter could promote the NOx SCR with ammonia produced from NOx trap catalyst.

**References**

Operando Synchronous DRIFTS/MS/XAS As a Powerful Tool for Guiding the Design of Heterogeneous Catalysts

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Introduction and Objectives

Catalysis is a rich, multidisciplinary field with a global socio-economic impact ranging from improved air quality to the design of new HIV therapies, and creation of bulletproof fabrics. Heterogeneous (solid) catalysis is currently experiencing a global renaissance, with interest soaring in new predictive quantum chemical models and experimental synthetic and analytical methodologies able to deliver tailored catalyst formulations offering precise activities, and selectivities, for diverse chemistries, including artificial photosynthesis. The rational design of new heterogeneous catalysts for sustainable chemical technologies can be accelerated by molecular level insight into surface chemistry [1], and nanoengineering approaches to achieve precise control over the structure and reactivity of novel functional materials [2,3]. Here we highlight how in-situ and time-resolved X-ray spectroscopies can be used to visualise chemistry in action and identify the active catalytic site responsible [4], and thereby help direct the design of tunable nanocrystalline and nanoporous catalysts for clean technologies such as the aerobic selective oxidation (selox) of allylic alcohols [5].

Experimental

Mesoporous silica3 and alumina4 supported Pd catalysts were prepared via surfactant-templating of the parent support and subsequent incipient wetness impregnation. Time-resolved, in-situ synchronous DRIFTS/MS/XAS measurements were recorded during vapour phase crotyl alcohol (CrOH) selox within an fixed-bed reactor upon exposure of catalysts to alternating CrOH or O2 cycles under isothermal conditions. Pd K-edge energy dispersive XAS measurements were collected at beamline ID24 of the ESRF, with activity and selectivity followed by on-line MS, and DRIFTS.

Results and Discussion

Figure 1a shows the set-up for our synchronous DRIFTS/MS/XAS measurements. Below 140 °C, crotonaldehyde is reactively-formed over PdOx nanoparticles upon exposure to CrOH (Figure 1b), but only desorbs during O2 adsorption. Higher reaction temperatures promote reversible nanoparticle surface restructuring, accompanied by a concomitant loss of catalyst selectivity. Analogous liquid phase CrOH selox over Pd/mesoporous silicas reveals significant rate-enhancements associated with the use of 3D interconnected/penetrating support architectures.
Conclusions

Synchronous DRIFTS/MS/XANES measurements have highlighted the importance of stabilising surface PdO, and minimizing catalyst reducibility, in order to achieve high allylic aldehyde yields, guiding the future design of Pd-derived catalysts for aerobic alcohol selox. This methodology is widely applicable to vapour phase organic synthesis.

References

Coupling of Vibrational and Electronic Spectroscopies: Effective Tools for Exploring Mechanisms of Catalytic Redox Processes

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Introduction and Objectives

The majority of catalytic reactions comprise redox steps in which electrons are transferred between substrate molecules and active sites in the catalyst. On the other hand, the molecular structure of reactands, intermediates, products, the local environment of active sites and sometimes even the phase structure of catalysts change during reaction. A comprehensive understanding of all of such processes is essential to derive structure-reactivity relationships as a basis for tailored catalyst optimization. This calls for the combination of spectroscopies monitoring both electronic and structural changes. In the last decade, the use of coupling techniques (e.g. operando EPR/UV-vis/Raman spectroscopy) was widely restricted to thermally activated heterogeneous catalytic gas-phase reactions [1,2]. Very recently, their application potential has been extended to heterogeneous and homogeneous liquid phase reactions as well as to photocatalytic processes. This will be illustrated in this talk by three examples from heterogeneous gas- and liquid-phase catalysis as well as from homogeneous catalysis. Besides the benefits, also limitations such as sensitivity differences of the methods will be discussed.

EPR/Raman combined with FTIR spectroscopy for photocatalytic water reduction

EPR spectroscopy monitors the transformation of the Fe₃(CO)₁₂ catalyst into different low-spin [Fe₄(CO)₆]⁺ radical anions by electron transfer from the sacrificial agent triethylamine (TEA) via a [Ir(ppy)₂(bpy)]PF₆ photosensitizer in homogeneous solution. In contrast, the active [HFe₃(CO)₁₁]⁺ species is diamagnetic and, thus, EPR-silent but visible by Raman and FTIR spectroscopy. For the first time, most of the intermediates in the reaction cycle (Scheme 1) have been visualized by the three in situ spectroscopies. Based on these results, a reliable reaction and deactivation mechanism could be established [3].

Coupled ATR-IR/UV-vis/Raman spectroscopy for imine hydrogenation

The heterogeneous liquid-phase hydrogenation of aromatic imines on a supported Pt/Al₂O₃ catalyst in the presence of a chiral phosphonic acid modifier has been monitored at a H₂ pressure of 20 bar in a special autoclave equipped with fibre optical probes for the three spectroscopies. While the interconversion of substrate and product could be properly seen in ATR and Raman spectra, UV-vis spectroscopy did not provide useful results under the same conditions due to too high concentrations. Nevertheless, useful information on the interaction of substrate, modifier and catalyst surface could be obtained by considering also the results of separate interaction studies using concentrations tailored for the detection range of the methods.
**Scheme 1.** Species detected by different methods during photocatalytic water reduction

EPR, Raman and UV-vis spectroscopy (coupled or separate) for heterogeneous gas-phase reactions

Several binary and ternary vanadium containing VMON (M = Al, Zr, Mo) oxynitrides have been studied during nitridation of the oxide precursors in NH₃ flow as well as during ammoniation of 3-picoline to 3-cyanopyridine. Using the three *in situ* techniques supported by other methods such as XRD and XPS essential features of high catalytic performance as well as the reason for the unexpected detrimental effect of phosphorus could be identified. By combined EPR and UV-vis spectroscopy coupled to mass spectrometry, special Fe³⁺ sites being responsible for the strong acceleration of the selective catalytic reduction of NO/NO₂/O₂ mixtures by NH₃ (fast SCR) in comparison to NO/O₂ (standard SCR) could be discriminated among a variety of Fe³⁺ sites present in Fe-ZSM-5.

**References**

Design of In-House Ambient Pressure X-ray Photoelectron Spectrometer and Ambient Pressure High Temperature Scanning Tunnelling Microscope for Operando Studies of Catalysts

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Introduction and Objectives

In reactive environments (reactive gases or liquids), the surfaces of most materials are likely to restructure their geometrical and electronic structure. Such changes have profound effects on the functions and properties of materials. In these cases, the structures and compositions of the material surfaces in a reactive environment in which they function are different largely from those characterized in high vacuum (HV) or ultrahigh vacuum (UHV), the operational environment of most of conventional electron-based surface analytical techniques. The difference between the HV or UHV condition of samples during characterization and the ambient or high pressure conditions of catalysts during catalytic reactions results in a gap in the studies of heterogeneous catalysis, typically called a pressure gap. This difference was revealed in recent years by using in-situ spectroscopy and microscopy[1, 2]. One of the spectroscopy techniques is the synchrotron-based ambient pressure XPS. A few synchrotron-based ambient pressure XPS systems have been installed in recent years. To increase the availability of this technique, we proposed to design an ambient pressure XPS using monochromated Al Kα in 2010. One objective is to make the AP-XPS technique available in research groups. In addition, to visualize surface structure of the model catalysts under reaction conditions an ambient pressure high temperature scanning tunneling microscope (APHT-STM) was proposed to design.

Results and Discussion

I will present a successful design of a new ambient pressure XPS which we have finished recently. As it uses in-house X-ray source, monochromated Al Kα, we termed it in-house ambient pressure XPS (AP-XPS). The success of this design has made this technique available for any individual research groups.

Fig. 1a shows configuration of this in-house AP-XPS system. Another feature of this AP-XPS is the inte-
Integration of a flowing reaction cell into the setup of X-ray sources and pre-lens, which allows collecting photoelectrons from catalyst surfaces when catalysis is performed in a reactor working in a flow mode. Such a feature makes it offer surface chemistry of catalysts under catalysis conditions compatible to these micro flowing reactors of by catalysis groups. Fig. 1b schematically presents the concept of a flowing reactor. This system can examine surfaces of catalysts up to a condition of 550°C of a sample in a gaseous environment of 25 Torr. I will discuss the evolution of oxidation state of oxide and bimetallic catalysts under reaction conditions including methane oxidation and CO₂ reduction we have performed.

Another technique we developed for operando studies of catalyst surfaces under reaction condition and during catalysis is the ambient pressure high temperature scanning tunneling microscopy (APHT-STM). The feature of this new design is the separation of STM room from the reaction cell by using a dome. This design allows minimizing thermal drift and remaining the temperature of the STM scanning tube and coarse approaching motor at room temperature when catalysis is performed on a model catalyst at high temperature at ambient pressure in reaction cell. I will present the observed structural evolution of model catalysts under reaction conditions.

Reference

An Operando-IR Study of Photocatalytic Reaction of Methanol on New BEA Supported TiO\textsubscript{2} Catalyst

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The growing concern in the general public as well as the increased severity of air control regulations give special interest to the removal of Volatile Organic Compounds (VOC). One of the key features for such removal is the use of heterogeneous catalysts, largely used for the control and treatment of exhaust gases in the chemical and car industries. The reaction on the catalyst can be induced by heating, or by UV light when using a photocatalyst, with advantages such as low cost, excellent efficiency at room temperature and low environmental impact.

In order to study and improve the catalyst efficiency, it is important to have quantitative and mechanistic information of the catalytic reaction. The parameters of the reaction (reactive compositions, temperature, flux rate...) could be play a crucial role on the catalyst reactivity and must be controlled in order to prove the effective role of these parameters. For these reasons, operando techniques could be ideal candidates to study a catalytic reaction; it allows monitoring events taking place on and inside the catalyst in real time. Infrared spectroscopy (IR) is for that purpose very appropriate since it is fast and sensitive.

In this work, a new operando setup was used to study the photocatalytic oxidation of methanol in gas phase using a new BEA zeolite supported TiO\textsubscript{2} (BEA-Ti) photocatalyst. Following the photocatalytic reaction with time resolved IR spectroscopy coupled to mass spectrometry allowed a quantitative and mechanistic study. Two types of photocatalyst have been investigated TiO\textsubscript{2} (P25-Degussa) and BEA supported TiO\textsubscript{2} (BEA-Ti). It highlights the interesting reactivity of BEA-Ti compound. With only \( \sim 10 \) wt.% of incorporated TiO\textsubscript{2}, BEA-Ti showed a relatively high efficiency (50%) compared to TiO\textsubscript{2}. By considering the mass weight of TiO\textsubscript{2}, the reactivity of BEA-Ti was 5 times higher than that of TiO\textsubscript{2}–P25. For comparison, BEA zeolite has been also investigated as photocatalyst. It did not show any photooxidation activity. The selectivity of TiO\textsubscript{2} and BEA-Ti photocatalysts was found to be different. While the major reaction observed in the case of TiO\textsubscript{2} was the photocombustion, the formation of methyl formate species in case of BEA-Ti contributed to \( \sim 50\% \) of the photoxidation (vs \( \sim 50\% \) of photocombustion reaction). The temperature has a direct impact on the reactivity (and selectivity) of the photooxidation especially for BEA-Ti. Indeed, for TiO\textsubscript{2} photocatalysts high temperatures (\( > 443 \) K) favour the chemisorption and lead to a decrease in the reactivity. In contrary, for BEA-Ti, the increase of the temperature increases the conversion of methanol and the reactivity.
Scheme 1 The sandwich IR-reactor cell modified for UV catalysis study.
New Insights into the Water-Gas Shift Reaction over Bulk Cr$_2$O$_3$*Fe$_2$O$_3$ Mixed Oxide Catalysts: A Combined Operando Raman-IR-XAS-MS Investigation

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Introduction and Objectives

The bulk chromia-iron mixed oxide catalyst is the primary catalyst for the high temperature (310-450°C) water-gas shift (WGS) reaction for the production of hydrogen and carbon dioxide from steam and carbon monoxide. Although few in situ characterization studies have been reported in the literature, the magnetite (Fe$_3$O$_4$) phase is present in activated and reduced catalysts recovered from WGS reactors. The commercial lifetime of pure magnetite catalysts is limited because of thermal sintering and chromium oxide addition, 8-12% Cr$_2$O$_3$, has been found to stabilize the surface area and extend the catalyst life to 2-5 years. Despite numerous characterization studies, the role of the chromia promoter is still not completely understood. Edwards et al. have found, from XRD and STEM-EDX studies that Cr$^{3+}$ exists in solid solution within the Fe$_3$O$_4$ phase as an inverse spinel lattice and that discrete Cr$_2$O$_3$ grains are not detected. Similar conclusions were reached from by Robbins et al., Newsome et al. and Pereira et al. from XRD and Mössbauer spectroscopy characterization. Both STEM-EDX and XPS surface characterization by Edwards et al. and bulk and XPS surface characterization by Pereira et al. revealed that the surface of the Fe$_3$O$_4$ catalyst was highly enriched in chromium oxide concentration, but the nature of chromium oxide at the surface could not be determined with these bulk characterization methods. Furthermore, regardless of preparation method, all Cr-doped catalysts were found to be surface enriched in chromium oxide. Recently, in situ EXAFS and Mössbauer studies have confirmed that Cr$^{3+}$ is the active chromium oxidation state and Fe$_3$O$_4$ is the active iron oxide phase, respectively.

![Operando Raman spectroscopy of 3% CrO$_3$/Fe$_2$O$_3$ during Reverse-WGS conditions.](image)

Figure 1. Operando Raman spectroscopy of 3% CrO$_3$/Fe$_2$O$_3$ during Reverse-WGS conditions.
The absence of fundamental *in situ* and *operando* spectroscopic studies of the bulk Cr$_2$O$_3$*Fe$_2$O$_3$ WGS shift catalyst during the WGS reaction in the catalysis literature has hindered the development of molecular level insights about the catalytic active sites, surface reaction intermediates and the reaction mechanism.\(^1\)-\(^{10}\) In order to address the state of the iron oxide catalyst under reaction conditions, the role of the chromia promoter, and the nature of the catalytic active site, *in situ* and *operando* Raman, IR, and XAS spectroscopic studies under reaction conditions were undertaken in the present investigation.

**Results and Conclusions**

The *operando* Raman spectroscopy studies during WGS, given in Figure 1, confirm that crystalline Fe$_3$O$_4$ is the active bulk phase in Cr-doped samples, which forms an amorphous phase for unpromoted Fe$_2$O$_3$, and that crystalline Cr$_2$O$_3$ NPs are not present. The corresponding *operando* IR spectroscopy measurements revealed that dioxo surface (O=)$_2$CrO$_2$ species are also present under oxidizing conditions and become reduced during the WGS reaction. IR measurements also revealed that no surface reaction intermediates are present, even when the reaction is performed at its temperature limit of ~225°C. *Operando* XANES measurements of the Cr K-edge confirm the reduction of Cr$^{6+}$ (dioxo species) to Cr$^{3+}$ at steady-state. The EXAFS Fe K-edge data reveals that the Cr-doped samples stabilize as Fe$_3$O$_4$ under steady-state WGS reaction conditions, while unpromoted Fe$_2$O$_3$ is active as an amorphous phase consisting mostly of Fe metal and some indistinguishable oxidized state (2+ or 3+). Insights into the WGS reaction mechanism and catalytic active site will be discussed on the basis of these observed phenomena.

**References**

Combination of X-ray Spectroscopy and Small Angle Scattering With Mass Spectrometry to Observe Catalytic Reactions

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Introduction and Objectives

In the study of catalytic reactions, grazing incidence SAXS (GISAXS) and grazing incidence X-ray Adsorption Spectroscopy (GIXAS) on flat catalytic support substrates with size-selected metal clusters can provide both ex-situ and in-situ information on cluster size, shape, inter-particle distance, and oxidation state (APS beamline 12-ID-B&C). GISAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data, and it is possible to obtain the interfacial energy. GISAXS is ideal for in-situ studies since it is very sensitive to surface species and there is less parasitic scattering resulting from the substrate compared to a conventional direct-transmission SAXS experiment.

Results and Discussion

The size selected metal particles are prepared by laser vaporization followed by separation in a quadrupole mass spectrometer prior to deposition on the surface. The GISAXS experiments were performed in a vacuum chamber equipped with a heated sample holder mounted on a goniometer at APS beamline 12-ID-C. The design and description of the operation of the cell has been published.1 During heat treatment, scattering data can be collected as a function of time and temperature. The beam is scattered off the surface of the sample at and near the critical angle of the substrate and the scattered X-rays are detected by an area detector. The data is analyzed by taking cuts in the $q_{xy}$ direction for horizontal information and in the $q_z$ direction for vertical information. GISAXS is being used to study the thermal stability and reactivity of Pt, Au, and Ag clusters (6 – 12 atoms) deposited on a variety of surfaces with insightful results.2 One example is the partial oxidation of olefins to alkyl oxides where it has been found that the size and shape of catalytic size-selected nanoparticles is important.3-5 ASAXS refers to the extension of standard SAXS experiments in which the energy of the probing X-rays is tuned near the absorption edge of an element in the sample. This method overcomes the problem of separating the scattering of clusters from that of the support. For the first time anomalous GISAXS has been obtained on metal clusters on surfaces and has provided significant insight into the structure of very small metal clusters on surfaces.6 An example of using all three techniques is shown in Figure 1 where the changes in the Co catalysis in the oxidative dehydrogenation of cyclohexene as a function of reaction temperature are followed. The reactivity starts increasing at 250 °C, from MS analysis, with the initiation of assembly of the nanoparticles and is most active at 300 °C.
**Figure 1.** Left – dynamic oxidation change by XANES, Right – SAXS size analysis

**Conclusions**

The combinations of GISAXS and GIXAS along with MS have been demonstrated as a powerful tool for studying the changes in metal nanoparticles on flat surfaces under realistic reaction conditions. This same approach works with transmission SAXS and spectroscopy for small flow reactors.

**Acknowledgements**

Work performed at Argonne and use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This material (R.E.W., S.L.) is based in part upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

**References**

Operando Raman-GC Study of Propane Selective Oxidation over Alumina-supported V\textsubscript{2}O\textsubscript{5} and P\textsubscript{2}O\textsubscript{5} Monolayer Type Catalyst

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Introduction and Objectives

Much attention has recently been devoted to the surface of bulk catalysts. Most critical phenomena in catalysis occur at the surface, which features differ significantly from those of the bulk. VPO materials are efficient catalysts for acrylonitrile production by propane ammoxidation reaction\textsuperscript{[1,2]}. In order to understand the structure-activity relationship and the nature of the active site, operando Raman–GC analyses were employed to follow the states of vanadium and phosphorous species on alumina support during ammoxidation. V\textsubscript{2}O\textsubscript{5} and P\textsubscript{2}O\textsubscript{5} were supported on “Raman silent” γ-alumina by incipient wetness impregnation at a total V+P loading of two monolayers, which under reaction conditions lead to incipient formation of VPO crystallites possessing a high surface-to-volume ratio. The presence of VPO nanocrystals supported on alumina facilitates investigating the interaction between alumina-dispersed vanadia (V\textsuperscript{5+}) and VPO-lattice vanadium ions (V\textsuperscript{4+}). Thus it becomes possible to study surface species phase transformations near the surface, and relate changes in activity and selectivity to variations in composition and structure.

Results and Discussion

Vanadium and phosphorous supported γ-alumina catalysts were prepared by incipient wetness impregnation. Previous characterization by TPR, UV-Vis and XPS analyses confirm the predominance of V\textsuperscript{5+} in a fresh catalyst while a vanadyl pyrophosphate phase forms under reaction conditions. Operando Raman spectra of the VP/Al catalyst show that V\textsuperscript{5+} reduces to V\textsuperscript{4+} at 500 °C and the V\textsuperscript{5+}=O feature at 1022 cm\textsuperscript{-1} decreases in intensity, while a band due to (VO)\textsubscript{2}P\textsubscript{2}O\textsubscript{7} (V\textsuperscript{4+}) appears at 923 cm\textsuperscript{-1} (see Fig. 1). This suggest a combination of dispersed vanadium oxide and phosphorous into such VPO phase during reaction. The selectivity to acrylonitrile increases with increasing reaction temperature, and it shifts from acetonitrile to acrylonitrile just before the Raman band characteristic of (VO)\textsubscript{2}P\textsubscript{2}O\textsubscript{7} appears.
The highest amount of the acrylonitrile is obtained in the presence of a slightly reduced catalyst, with high V$^{4+}$ content, while a specific V$^{5+}$/V$^{4+}$/V$^{3+}$ equilibrium is probably reached under reaction conditions (seen by the bands at 1023, 927, 875 cm$^{-1}$). The oxidized sample (after exposure to air at 500 °C for 30 min) containing dispersed V$^{5+}$ surface species is significantly more reactive towards propane, but acetonitrile becomes the main reaction product.

**Conclusions**

Dispersed V$^{5+}$ species are stabilized on alumina support; subsequently, vanadyl pyrophosphate phase forms during ammoxidation reaction. The stabilization of V$^{4+}$ as (VO)$_2$P$_2$O$_7$ shifts the selectivity to acrylonitrile but an equilibrium between V$^{5+}$/V$^{4+}$/V$^{3+}$ rules during ammoxidation reaction. Catalysts containing higher amount of dispersed vanadium surface species (V$^{5+}$) is more active, but also more selective to acetonitrile.

**References**


Understanding Real World Catalysts: A Challenge for Spectroscopy and Engineering

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Introduction and Objectives

Detailed understanding of the structure of catalysts is required for a rational design of new or improved catalysts. Thereby the establishment of structure-performance relationships gained by studying catalysts at work is considered one of the key steps [1]. Furthermore, the development of appropriate in situ cells is decisive. The spectroscopic setup should resemble as much as possible the catalytic experiment [2,3]. Nevertheless, in most cases it is a compromise between the spectroscopic experiment and the real working conditions and engineering issues. Preferentially, for each study both the spectroscopic side and the engineering solution should optimised to finally find the best compromise.

Since in situ X-ray absorption spectroscopy (XAS) is a well-suited method for the establishment of structure-activity relationships, in this contribution different facets for the understanding of real world catalysts are outlined using XAS and related techniques. Additionally, structure-performance studies on gas sensors are presented to demonstrate that the concepts can also be transferred to related topics. Finally, the potential of time-resolved studies, new photon-in/out techniques and spatially resolved studies is outlined.

Results and Discussion

Structure of noble metals during catalytic partial oxidation of natural gas and total oxidation of methane:

The partial oxidation of methane to hydrogen and carbon monoxide over Pt- and Rh-based catalysts [4] and the total combustion of hydrocarbons over Pd [5] are good examples for the importance of structural identification of catalysts in its working state during. The measurement of the catalytic performance is essential and for studies during the total oxidation of methane XRD, XAS and Raman spectroscopy were combined. In order to study the ignition of the catalytic partial oxidation of methane over Pt and Rh-catalysts as well as chemical oscillations over Pd-based catalysts measurements in the subsecond time scale were recorded in the QEXAFS scanning mode [6].

Hydrothermal synthesis of transition metal oxides and C-C coupling reactions over Pd-catalysts (Heck-reaction):

The hydrothermal synthesis of metal oxides and the study of solid/liquid reactions like Heck reactions require studying both the liquid and the solid phase. For this purpose a specially designed in situ cell was used. During the preparation of transition metal oxide catalysts both the evolvement of liquid species and the transformation of the solids could be monitored; the occurrence of intermediates was detected using the QEXAFS technique [7]. This approach together with special analysis tools also allowed gaining new insight into the Heck reaction starting with solid Pd-catalysts [8].
**Understanding SnO$_2$-based gas sensors:** A new cell and a special sensor device were designed to derive structure-performance relationships during gas sensing and the catalytic action of Pt and Pd promoters in SnO$_2$. Using a high resolution fluorescence detector for acquirement of the XAS data uncovered that the noble metal ions remain – in contradiction to previous studies – mostly in oxidized state under working conditions [9].

**Spatially resolved studies:** Spatially resolved studies become important if gradients occur in catalytic reactors and/or catalyst shaping comes into play [10]. This appears for example important during the catalytic partial oxidation of methane as well as time-resolved studies during the ignition of reactions (ref. [10,11]).

**Significance**

The case studies demonstrate not only the importance of in situ studies and the engineering of appropriate in situ cells. Equally important are the application of better time-resolution, new analysis methods and spatially resolved methods. This allows tracking the catalytic structure from its evolvement (preparation and activation), via its active state (structure-activity relationship) and finally deactivation and regeneration.

**References**

DRIFTS and XPS Operando Studies of a CuO-CeO₂ WGS Catalyst

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Introduction and Objectives

Copper-cerium oxide catalysts constitute an interesting, cheaper alternative to precious metals-based systems for the preferential CO oxidation (CO-PROX) and water gas shift (WGS) processes used in hydrogen production from fossil fuels or biomass feedstocks. It is normally assumed that CO is activated on Cu sites and extract oxygen from the Ce oxide, which is then reoxidized by O₂ or water in a Mars-van Krevelen mechanism; but some aspects of the redox changes and adsorption-desorption steps remain unclari-

Here we study WGS-related reactions on a catalyst having inverse configuration (CeO₂ on CuO), which has shown good performance in previous works of ours [1]. Operando-DRIFTS experiments as well as SSITKA-DRIFTS tests exchanging ¹²CO and ¹³CO were performed under WGS conditions in order to get insights into mechanistic details. In turn, such results were complemented by XPS data taken at the ISIS station of BESSY synchrotron in Berlin, under either vacuum or 0.5 mbar of flowing gas containing 7% CO and/or 20% H₂O (He balance) while monitoring gas composition with MS.

Results and Discussion

DRIFTS results display the formation under WGS reaction conditions of Cu⁺-carbonyl species as well as hydroxyls and various carbonate-type and/or formate species at T < ca 523 K while above such temperature a new carbonyl at ca. 2010 cm⁻¹ (most likely related to a metallic copper carbonyl in a particularly stable geometrical configuration [2]) starts to be formed and grows with the reaction temperature. In turn, SSITKA-DRIFTS experiments show important changes in the region related to carbonate-type and/or formate species although in principle analysis of ¹²CO₂ vs. ¹³CO₂ gas evolutions do not point towards active involvement of such species as reaction intermediates, at least at practical relatively high reaction temperature.

XPS and Cu Auger spectra show that both Cu and Ce are partially reduced to Cu⁺ and Ce³⁺ already upon contact with CO at 295 K; at 473 K, under CO, surface Cu is almost totally Cu⁺ and larger amount of Ce³⁺ is formed (Fig. 1a). Adding H₂O at 473 K (Fig. 1b) starts to form Cu⁰ (Auger peak at 918.6 eV) and increases the amount of Ce³⁺ (XPS peak at 894 eV). Thus the initial effect of H₂O interaction appears not to be a reoxidation one, but maybe it facilitates reduction by H₂, which begins to appear as shown by MS, and the ensuing nucleation of Cu⁰ particles. Other possible effects can be related on the one hand to stabilization of reduced states of cerium in the presence of hydroxyl species (considering the higher thermodynamical stability of Ce³⁺ hydroxide) as well as possible electron transfer processes between copper and cerium oxide. Correlation with bulk results obtained in previous work by XRD and XANES will be also
Fig. 1 Cu Auger and Ce XPS spectra of CuCeOx catalyst a) at 473 K under CO, b) after adding H2O at 473 K and c) raising temperature to 523 K under both gases

used to analyse the possibility of surface-bulk oxygen transport effects under reaction conditions. In turn, at 523 K (Fig. 1c) extensive reduction of Cu to Cu⁰ and increase in the amount of Ce³⁺ occur under WGS reactant mixture.

Conclusions
Mechanistic details for WGS reaction over an inverse CeO₂/CuO (initial form according to previous characterization by XRD, XANES and HRTEM) have been analysed by DRIFTS and SSITKA-DRIFTS as well as XPS. The results suggest the absence of direct involvement of carbonates and/or formate species as reaction intermediates at practical relatively high temperature thus suggesting a redox mechanism could rather be the operative one. Nevertheless, details achieved by XPS suggest redox processes of a complex nature must be taken into account to explain the WGS activity of this type of systems.

Acknowledgements
Thanks are given to M. Hävecker and rest of ISISS station personnel for assistance during measurements at BESSY synchrotron. Financial support by Spanish MICINN Plan Nacional (project CTQ2009-14527) is gratefully acknowledged.

References
Role of Pretreatment and of Oxygen Vacancies on the Catalytic Behavior of ZnO Toward Alcohols Conversion: an EPR and DRIFTS Study

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Introduction and Objectives

Zinc oxide is a common white semiconductor material, used in many applications such as pigments or antiseptics, and also widely studied in optoelectronics and in heterogeneous catalysis [1]. Its catalytic properties are usually assigned either to morphology effects or to the possible influence of oxygen vacancies (VO) [2-3]. Indeed, ZnO becomes a defective material under an oxygen deficient atmosphere. The aim of this work is to study the role of oxygen vacancies in the catalytic conversion of alcohols, exemplified by a model reaction, 2-methylbut-3-yn-2-ol (MBOH) conversion into acetone and acetylene [4] and by the conversion of ethanol. The oxygen vacancies formation depending on the conditions of the pretreatment is followed by \textit{in situ} and \textit{operando} EPR. The influence of the reaction products on the stability of oxygen vacancies and the related impact on catalytic deactivation is discussed thanks to an \textit{operando} DRIFTS study.

Results and Discussion

Two ZnO samples, commercial kadox (9 m\textsuperscript{2}g\textsuperscript{-1}) and ex-carbonate (issued from thermal decomposition of zinc carbonate at 773 K in the air) (22 m\textsuperscript{2}g\textsuperscript{-1}) were systematically pretreated at 773 K (ramp 5 K.min\textsuperscript{-1}) under inert (N\textsubscript{2}) or oxidant (O\textsubscript{2}, air) flows before catalytic tests as well as for \textit{in situ} EPR measurements (spectra recorded at room temperature). The conditions of existence of oxygen vacancies of zinc oxide were studied following the increase or decrease of the EPR signal at g = 1.96 after thermal treatment under inert or oxygenated atmospheres, respectively. For both samples, the related signal was shown to be an indirect probe of oxygen vacancies: its intensity was increased / decreased upon trapping / release of the electron associated to the formation / filling of oxygen vacancy. It is also shown that oxygen vacancies created upon inert thermal treatment at 773 K can be further filled by treatment in an oxygen atmosphere at lower temperature.

For both reactions (MBOH or ethanol conversion performed in gas phase at 403 and 673 K respectively), the conversion level is controlled by oxygen vacancies concentration, as illustrated by the direct correlation between MBOH basic conversion and the EPR signal reported for both samples on Figure 1. Thus, the catalytic properties of ZnO can be tuned by the atmosphere of pretreatment with enhanced activities measured after inert pretreatment compared to oxidative conditions.[5] The reactivity inhibition after oxidative pretreatment is however less pronounced in the case of ethanol conversion. Indeed, from \textit{operando} EPR experiments performed under air flow in the 338-623 K range during the cooling down step of the pretreatment, the filling of oxygen vacancies becomes really efficient below a critical temperature of about 500 K. Thus, it was concluded that the higher reaction temperature of ethanol conversion limits the impact of pretreatment atmosphere on the conversion level under oxidative atmospheres.
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Figure 1: Variation of the MBOH conversion \( (T_{\text{Read}} = 403 \text{ K}) \) for kadox and ex carbonate samples versus the variation of the EPR signal (measured at room temperature) after various pretreatments: - ramp up to 773 K and cooling under air (taken as a reference), \( \text{N}_2 \), or \( \text{O}_2 \) or - ramp up to 773 K and cooling to 403 K under \( \text{N}_2 \) followed by a dwell under \( \text{O}_2 \) at 403K (\( \text{N}_2 + \text{O}_2 \)).

From Operando DRIFTS studies indicated that there was a splitting of the contributions relative to \( \nu_{\equiv\text{C-H}} \) (3325 and 3308 cm\(^{-1}\)) and \( \delta(\text{C-}-(\text{CH}_3)_2) \) (1379 and 1362 cm\(^{-1}\)) of MBOH reactant on kadox sample which evidenced the existence of two different adsorption sites. The former one exists on both samples and its basicity is directly influenced by the enhanced electronic availability resulting from oxygen vacancies formation and the second one, only present on kadox sample, is a weaker basic site which is responsible for the residual activity of kadox sample in the absence of oxygen vacancies (Fig. 1).

Moreover, this operando characterization could also explain the two phases deactivation process observed during MBOH basic conversion that is quite rapid in the first minutes of reaction and then becomes slower. In fact, the just activated surface upon a nitrogen pretreatment exhibits acid base pairs that are efficient toward aldol condensation of the acetone formed (apparition of bands at 1437, 1419 cm\(^{-1}\) associated to diacetone alcohol), leading to the first rapid deactivation step. This polymerization is however quite rapidly inhibited. This can be assigned to the fact that the water issued of this condensation reaction dissociates on oxygen vacancies (apparition of a band at 3528 cm\(^{-1}\)), which could tune the acid-base pairs behaviour. It results in a filling of oxygen vacancies and in weakening of the strength of the sites, stopping the extension of polymerization at the benefit of the enhanced amount of acetone adsorbed on the surface (increase of the 1737 and 1725 cm\(^{-1}\) bands after several minutes of reaction). This second phase is responsible for the slow second deactivation phase observed.

Conclusions

Operando EPR and infra red are very complementary tool to evidence that the oxygen vacancies of ZnO which concentration can be tuned by pretreatment conditions govern not only the conversion level toward alcohols, but also the deactivation process.

References

Active Sites of Gold-Ceria Nanorods for Low-Temperature CO Oxidation Reaction: Operando X-Ray Diffraction and Absorption Studies

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Introduction and Objectives
Since 1990's, gold nanostructures that interact strongly with oxide supports were reported to be extremely active for many redox reactions, such as CO oxidation [1]. Such unique catalytic properties were found to be strongly dependent on the local crystal and electronic structures of active Au centers, i.e. particle size and size-distribution, oxidation states, coordination number with surrounding ions, etc. X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) have been widely used as the structural detectors for the heterogeneous catalysts [2]. Therefore, operando XRD & XAFS (XANES and EXAFS) techniques are especially helpful on the studies of reaction mechanisms, i.e. reaction pathways, and active sites. Here, we will focus on studies of active sites of gold-ceria nanorods for the low-temperature CO oxidation reaction with the aids of operando XRD and XAS measurements.

Results and Discussion
The 1 at.% Au-CeO\textsubscript{2} nanorods were prepared by the deposition-precipitation method reported previously [3]. In-situ XRD patterns were collected during CO oxidation reaction (1%CO/4%O\textsubscript{2}/He) under a “steady-state” mode between -65 and 70 °C (15 °C/step). The fresh Au-CeO\textsubscript{2} catalysts were pre-oxidized (20%O\textsubscript{2}/He, 300 °C) or pre-reduced (5%H\textsubscript{2}/He, 200 °C) before the catalytic tests. The pre-reduced Au-CeO\textsubscript{2} sample showed higher CO conversion below room-temperature than the pre-oxidized one (Figure 1), although their apparent activation energies between -35 and -5 °C were very close (13–15 kJ/mol). To our surprise, the lattice constants of the CeO\textsubscript{2} support for both pre-oxidized and pre-reduced conditions were unchanged (around 5.40 Å, see Figure 1) during the whole reactions, indicating that the creation of oxygen vacancies or Ce\textsuperscript{3+} ion may not be required to activate the gold catalysts. The operando XAFS measurements (Au L-III edge) were carried out under the same reaction conditions, but kept at room-temperature. The EXAFS fittings (not shown) determined that the ionic gold (Au-O, CN = 2.1±0.9) was the main phase in the pre-oxidized sample, while metallic gold (average particle size: 1.3 nm) was dominant in the pre-reduced one. XANES data, together with the linear combination results inserted in Figure 2, display that the Au in pre-oxidized catalyst was gradually reduced even under the room-temperature reaction. This is also consisted with the XRD results in Figure 1a, i.e. the activity was enhanced (400–600 min) after the cool-down and heat-up cycle. The Au oxidation states were kept in metallic form for the pre-reduced sample during the reaction. In summary, metallic gold is more active than the ionic gold in Au-CeO\textsubscript{2} nanorods for the low-temperature oxygen-rich CO oxidation reaction.
Abstracts

Figure 1. CO conversion (blue line) and cell dimension of CeO$_2$ (red line) as a function of reaction time for the Au-CeO$_2$ nanorods: (a) Pre-oxidized; (b) Pre-reduced.

Figure 2. In-situ XANES (Au L-III edge) spectra for the Au-CeO$_2$ nanorods under CO oxidation conditions at room temperature: (a) Pre-oxidized; (b) Pre-reduced.

Conclusions
The operando XRD and XAFS results on gold-ceria nanorods confirmed that metallic (pre-reduced) Au is more active than ionic Au (pre-oxidized) for the low-temperature CO oxidation reaction, while the reduction of the CeO$_2$ support is not necessary to activate the catalysts. The active sites could be well-dispersed gold atoms/clusters (< 1-2 nm) stabilized by the oxide matrix.

References
Mechanistic Aspects of CO₂ Hydrogenation at Low Temperature over Rh Catalysts Studied by Operando-DRIFTS

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Introduction and Objectives

The transformation of CO₂ in high added-value chemicals to be introduced in chemistry and petrochemical industries is a realistic contribution to the protection of the environment. We have shown previously that on Rh-based catalysts, CO₂ methanation occurs with 100% selectivity and at low temperature (< 200°C) [1, 2]. By operando-DRIFTS it was demonstrated that CO₂ is adsorbed dissociatively on Rh, that different CO(ads) species with different reactivity are formed on the surface of the catalyst, that formate species are only spectator during the reaction and that the activation energy of the CO hydrogenation correspond to the same activation energy of the overall CO₂ hydrogenation, supporting the fact that hydrogenation of CO(ads) species could be the rate limiting step of the reaction [3]. In this work we present further results using the same technique which give new insights of the mechanistic aspects of the CO₂ methanation over Rh/TiO₂ and Rh/γ-Al₂O₃ catalysts.

Results and Discussion

Rh/γ-Al₂O₃ and Rh/TiO₂ catalysts with varying Rh cluster size were using different metal contents. Mean Rh particle sizes were between 1.8 and 17 nm. The activity of the catalysts in CO₂ methanation is shown in Table 1. Catalytic activity increases with Rh particle size and is up to 10 times higher for Rh/TiO₂ catalysts. Operando-DRIFTS was used to explain the important differences in activity between catalysts with different particle sizes and supports. XPS complement these results. The interaction of CO₂ + H₂ with the catalyst surface led to the formation of linear CO(ads) species (2040-2050 cm⁻¹) at temperatures as low as 50°C. In the case of large Rh particles, bridge-bonded CO was also detected. In the case of Rh/γ-Al₂O₃ catalysts, CO(ads) is associated to hydrogen as Rh carbonyl hydride [3]. The reactivity of surface species was

Table 1. Activity of different Rh catalysts in CO₂ methanation (CO₂/H₂ = 1/4) at 150°C and 1 atm. SV = 100 ml g⁻¹ min⁻¹.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh particle size (nm)</th>
<th>TOFCH₄ (x10²) s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(0.5 wt.%)/TiO₂</td>
<td>1.8</td>
<td>0.072</td>
</tr>
<tr>
<td>Rh(1 wt.%)/TiO₂</td>
<td>4.5</td>
<td>0.500</td>
</tr>
<tr>
<td>Rh(3 wt.%)/TiO₂</td>
<td>17.3</td>
<td>2.260</td>
</tr>
<tr>
<td>Rh(1 wt.%)/γ-Al₂O₃</td>
<td>3.6</td>
<td>0.092</td>
</tr>
<tr>
<td>Rh(3 wt.%)/γ-Al₂O₃</td>
<td>15.4</td>
<td>0.333</td>
</tr>
</tbody>
</table>
studied by transient experiments. When the gas feed is changed from CO₂ + H₂ to H₂, CO(ads) bands start to disappear due to their hydrogenation to form methane. In Figure 1 the comparison of the two supports is presented. In the case of Rh(3 wt.%)/γ-Al₂O₃, the reactivity of CO(ads) band is lower than Rh(3 wt.%)/TiO₂. This stresses the fact that CO(ads) species are the direct precursors of methane over these catalysts, and that the differences in CO₂ methanation activity are related to the differences in the rate of CO(ads) hydrogenation.

Catalysts with different Rh particle sizes show very different behaviour in transient experiments (Figure 2). In the case of catalysts with larger particle sizes (e.g. Rh(3 wt.%)/TiO₂, dp = 17.3) when CO₂ was switched off, the methane formed showed a steady decrease with time. This is explained by the depletion of CO(ads) species from the surface, which is the primary source of methane. In contrast, the behaviour of Rh/TiO₂ catalysts with smaller cluster size (Rh (0.5 wt.%) and Rh(1 wt.%) with Rh cluster sizes of 1.8 and 4.5 nm respectively) is different: After changing from CO₂ + H₂ to H₂, the decrease in CO(ads) peak is accompanied by an increase in methane signal, that is, the production of methane is favoured when CO(ads) coverage is decreased. It is suggested that the supply of hydrogen is more easily performed in Rh/TiO₂.

**Conclusions**

Operando DRIFTS allowed the study of the effect of support and metallic cluster size on the activity of TiO₂ and γ-Al₂O₃-supported Rh catalysts. It was found that smaller Rh clusters are less reactive due to their saturation with CO(ads) species during reaction. TiO₂ was found to be a more effective support than γ-Al₂O₃ which is related to its promoted CO(ads) hydrogenation over this class of catalysts.

**References**


Towards Using the Reorganization of Heteropoly Compounds: Taking Advantage of Intermediate States in the Frame of the Propylene Oxidation

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Introduction and Objectives

Heteropoly compounds (HPCs) are unstable materials during oxidation reactions. However, by applying adequate treatments, they can act as precursors of active species [1-4]. This work aims at understanding the genesis, evolution and functioning of the catalytic active phases obtained from HPCs. We therefore studied the evolution of their structural rearrangement when being used in the propylene oxidation. Our recent research has shown that Dawson HPC rearranged into a 3D network of Mo oxide, which could easily alternate the formation of corner- and edge-sharing MoO$_6$ octahedra [3]. The present contribution now concerns the influence of the redox strength of the gas feed on the HPCs catalytic performance. The purpose is to gain insight into the formation of catalytic active phases obtained from HPCs as a function of the environment. The strategy is thus to perform operando Raman investigation of Dawson and Keggin HPCs under the atmosphere of propylene oxidation with O$_2$:C$_3$H$_6$ molar ratios varied within the range [0.5-2].

Experimental

The Dawson (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$ and Keggin [(NH$_4$)$_3$PMo$_{12}$O$_{40}$ and H$_3$PMo$_{12}$O$_{40}$] HPCs were synthesized and characterized as explained in [1]. The operando Raman investigation was done in a setup combining a fixed bed reactor, a Raman spectrometer and GC on line analysis. Reactions were run between 250 and 450°C with a stepwise temperature of 50°C. A staying time of 2 h was respected at each step, except for the last step at 450°C at which the samples were kept for 8 h. The concentration of C$_3$H$_6$ was 10 vol.% with He and O$_2$ flows adjusted to have 30 mL min$^{-1}$ in total. The recovered samples were characterized by ex situ XRD and FTIR analyses.

Results and Discussion

Below 350°C, the Dawson HPC was no active whatever the redox condition. With the molar ratio of 2, at 450°C, the conversion increased (with acrolein as main product), reaching 13%. A small decrease in the C-balance (down to 95%) was noted. On the contrary, when Dawson HPC was tested with the ratios of 1 and 0.5 at 450°C, the conversion increased, but only apparently as it was related to a C-balance of only 80%, not linked to any increase in any selectivity. Keggin HPCs were active at a lower temperature than Dawson; e.g., at 350°C, a conversion of 25% (mainly in COx) was observed with (NH$_4$)$_3$PMo$_{12}$O$_{40}$ tested with a ratio of 2. A lower conversion was noted under ratios of 1 and 0.5 (12 and 8 %, respectively). In these 3 cases, there was no deficit in the C-balance.

Based on these catalytic results we hypothesised that propylene was trapped in the working Dawson catalyst whatever the conditions (but mainly with the ratios of 1 and 0.5). This phenomenon was thus facilitated by a more reductive atmosphere: the catalysts released more O atoms and were thus more able to
change their configuration. The Dawson HPCs adapted their structure forming a lattice with channels occupied by propylene. However, differences exist between the structures of the recovered samples. Unlike Dawson samples tested under ratios of 1 and 0.5 which displayed Keggin features, the one tested under a ratio of 2 acquired a MoO₃-looking structure. These differences could be explained as follows: (i) Highly reductive feeds promoted the Dawson rearrangement; more channels were formed making the retention of propylene more effective. The structure formed was then stabilised with no more rearrangement possible. The rearrangement consequently stopped at the Keggin state. (ii) In a less reductive feed (ratio of 2), the Dawson sample rearranged slower and modifications occurred. A Keggin structure was formed (attested by operando Raman) and then decomposed to yield a 3D network of Mo oxide (attested by ex situ characterisations) extremely selective to acrolein. The formation of such peculiar phase did not occur when starting with the Keggin HPCs. Typical Keggin features remained more visible on the tested samples with the molar ratios of 1 or 0.5. It seems that a highly reductive feed stopped the Keggin rearrangement into MoO₃ at an earlier stage than under a molar ratio of 2, as observed for the Dawson HPC. The working Keggin catalyst thus never acquired the very active MoO₃ structure which display good selectivity towards acrolein product.

Conclusions

Working in a moderately reductive feed, it is possible to control the rearrangement of Dawson HPC to a Mo oxide like structure very selective to acrolein. This structure was never acquired with more reductive feeds, or starting from Keggin HPCs. The combined adjustment of the redox strength of the feed and the nature of the starting catalyst dictated the formation of the species generated via the HPCs rearrangement and thus allowed to optimize the HPC catalytic performance.

References

Catalysis-Induced Fluxionality at the Single Nanoparticle Level with Single Turnover Resolution

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Introduction and Objectives

Metal nanoparticles are key components in the advancement of future energy technologies since they are catalytically active for several organic-inorganic syntheses, electron-transfer, and energy conversion reactions. The nanoparticle surface before, during, and after a catalytic turnover event is not static in nature, but dynamic due to the movement of surface atoms. This rearrangement is both intrinsic due to the metastability of nanoparticles or extrinsic. Extrinsic sources leading to fluxional behaviour of nanoparticles include adsorption and reaction of small molecules. This fluxionality cannot be studied by ensemble methods because catalytic turnover and reaction-induced fluxional behaviour is asynchronous among nanoparticles.

In order to probe fluxional behavior at the most fundamental level, we propose to study catalytic turnover events on single nanoparticles with single turnover resolution in a two-state (off-on) reaction using fluorogenic reactants at different temperatures and reactant concentration. We have used a single-molecule fluorescence approach similar to Xu et al. to monitor the real-time catalysis of individual gold nanoparticles (Au NPs) for the reduction of resazurin (non-fluorescent) to resorufin (fluorescent) in the presence of NH₂OH and small molecule adsorbates with single turnover resolution. Coupled with adsorbate-induced restructuring effects and temperature considerations, we aim to fundamentally understand how real-time structural variations influences reactivity and energy transfer in nanoparticle catalysts. Ensemble level reactivity measurements and isothermal titration calorimetry (ITC) complement the body of single nanoparticle reactivity data.

Results and Discussion

We have studied the real-time reduction of resazurin to resorufin by NH₂OH on the surface of 5, 10, and 20 nm Au NPs at the single nanoparticle level using total internal reflection fluorescence (TIRF) microscopy. In order to quantify the adsorbate-induced fluxional behavior of Au nanoparticles, we added a sufficient amount of the adsorbate; 3-mercaptopropionic acid (3-MPA) or β-alanine, to cover 10-100% of Au surface atoms (Auₙ) based on their stoichiometric binding ratio. ITC results obtained for the binding of 3-MPA to Au NPs indicate strong irreversible binding (with a binding ratio of 3 Au to one 3-MPA molecule) with a binding constant of 10⁷ M⁻¹ while the binding of β-alanine is weak and in the order of 10³ M⁻¹. β-alanine and 3-MPA were chosen because of their aqueous solubility, similar structure, but different functional group interacting with Au.

In single molecule TIRF experiments, we recorded trajectories of stochastic fluorescent bursts from localized spots corresponding to Au NPs on a cover slip inside a flow cell. These fluorescent bursts (off-on signals) represent the formation and desorption of resorufin (Figure 1). The consistent heights of these bursts (Figure 1A-F) indicate each fluorescent burst comes from a single resorufin molecule. The fluorescence trajectories with increasing 3-MPA coverage show a clear transition from being stochastic to trajec-
tories that appear more digital in nature. The waiting time for both product formation and desorption increase with increasing 3-MPA coverage (Figure 1A-F) indicating 3-MPA covered Au NP provides increased resistance towards product formation and desorption. The increased coverage of β-alanine on the 5 nm Au NP surface does not cause any significant change in the waiting times and the fluorescence trajectory remains stochastic in nature even with 100% coverage of the Au. A statistical evaluation of the single nanoparticle trajectory has been averaged over at long times to arrive at average properties, <TOF> that can be compared directly with ensemble measurements. The adsorbate-induced fluxional behavior can be quantified by observing the non-uniformity in the off-on waiting times but more importantly by the change in the standard deviation (S.D.) of the waiting times. In the presence of increasing 3-MPA coverage, we observe a significant decrease in the S.D. of <τ_{off}> and <τ_{on}>, while no change in the S.D. was observed even in the presence of 100% β-alanine.

![Figure 1. Schematic representation of a single molecule turnover trajectory displaying the off-on behavior. Image of the fluorescent spot shows the formation of a product molecule and the blank image shows its desorption. A segment of the fluorescent trajectory with increasing 3-MPA coverage on the 5 nm Au nanoparticle surface; (A) 0% (B) 10% (C) 25% (D) 50% (E) 75% (F) 100% Au surface atoms covered by 3-MPA.](image)

### Conclusions

Single molecule experiments with single turnover resolution allow the measurement of intrinsic kinetics of individual nanoparticles which are masked during ensemble measurements. This study provides insight into the structure-activity and the size-activity relationship of a catalyst thereby promoting the development of highly selective catalysts.

### References

From the Monitoring of a Real Catalyst to the Catalyst Design

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Our society is confronted to an epoch-making crisis, bearing contradictory and challenging requests: on one side, raw materials and energy sources are rarefying, on the other, populations call for a better quality of life and easy access to goods, especially in the developing countries. Answers to these demands necessarily go through a more efficient use of the natural and energetic resources, limiting waste and reducing pollutant emissions. Practically, this can be obtained using efficient catalytic processes designed for sustainable energy economy and/or for emission abatement. The time of catalysts formulation by empirical “trial and error” methods is already well behind us, while the use of screening methods have not been able to produce significant advances in catalyst discovery. Both academia and industry are convinced that in order to have an efficient catalyst design, a rational approach is necessary.

Real-time spectroscopy during reaction coupled to simultaneous activity measurements in a kinetically relevant cell (operando methodology) provides the insight for a knowledge-based catalyst design. The use of spectroscopic techniques during reaction monitoring uncover how a catalytic surface behaves and which are the relevant catalytic steps, active sites and reaction intermediates during a given process. IR spectroscopy is a technique particularly adapted for understanding the mechanism of a catalytic reaction, being able to probe the surface mechanisms at the molecular level. Therefore, several examples will be presented to highlight the pertinence of the infrared tool in the characterization of a catalyst at work. The majority of them will deal with environmental relevant reactions, such as the exhaust catalytic control (particularly challenging to be studied, since the catalyst is submitted to extreme conditions, as in NOx-trap or SCR processes), or the VOC abatement (oxidation of oxygenated molecules). To discover the active sites and discriminate the intermediates, transient conditions are known to provide clear added value. To circumvent the problem of maintaining the real reaction conditions of the operando approach while simultaneously using transient parameters, the SSITKA methodology will be discussed, completed by thorough kinetic calculations.

The determination of kinetically relevant data requires that the chemical engineering aspects of operando reactors are fully considered: thermal, mechanical and fluid-dynamic constraints present in the industrial applications must be respected. Once the mechanism and actual working phase are established, the pathway to a successful formulation and improvement of catalytic systems is paved. While there has been significant progress in the assessment of catalysts in powder shape, there are additional constrains for shaped catalysts, notably monoliths, where a large part of the processes are carried out. Therefore, the direct analysis of a monolithic catalyst during reaction is of paramount importance. Up to now, mainly the active phase in powder or pelletized form has been studied, eventually upon removal from the wash-coated device. The results obtained in such a way are certainly informative, but they suffer from the loss of information due to casting removal/alteration and the lack of a truly relevant dynamic regime. Understanding the behaviour of surface species in real conformed catalysts during real catalytic operations is a paradigm shift towards a more rational development of future catalytic systems. When IR
spectroscopy (one of the most advantageous for mechanistic studies) is used, measurements in transmission conditions are essentially necessary to provide quantitative information. Recently, we have demonstrated the feasibility of such an approach showing the possibility to record IR spectra of a cordierite-supported catalyst analysed by transmission and even monitoring a catalytic reaction inside a monolith using a newly conceived operando IR reactor-cell, providing academic and industrial relevant parameters such as intrinsic activity constants, mass transfer constants and efficiencies of the porous system as a function of operating parameters, such as temperature and fluid dynamic conditions.\(^6\)

This methodological approach allows at investigating also other kinds of materials at work besides catalysts. For example, membranes and absorbers can be monitored both under the point of view of the guest molecules interacting with the functional sites and of the dynamic modifications induced in the hosting solid. Again, this is the first step leading to the design and synthesis of new generations of performing devices.

References

**Catalysts in Action: Advances in X-ray Spectroscopy Providing New Insights Faster**

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**Introduction and Objectives**

X-ray Absorption spectroscopy (XAS) is a technique for detailed structural and electronic characterisation of materials. Its strengths include the ability to perform experiments in situ/operando (variable temperature and pressure) and time-resolved. The technique is element specific and it does not require long-range order so amorphous systems and solutions can be studied, which makes it a powerful techniques in catalysis. New technique developments are centred on increased energy resolution and thereby increased information content as well as increased time-resolution. The techniques are developed as tools in single site and homogeneous catalysis, where the use of XAS is still very limited.

**Results and Discussion**

So far, XAS has been mainly used to obtain a structural picture whereas the electronic structure is often poorly understood. Moreover, the major disadvantage of XAS is that it determines an average of all the different structures present, as such complicating the analysis and interpretation. New developments in XAS using new instrumentation and data acquisition methods while selecting specific x-ray energies provide more detailed electronic information as has been feasible so far [1,2]. The charges on and bonding between atoms can now be visualised and their distribution and orientation studied, creating ultimately a 3-dimensional electronic picture or movie of the material. In catalysis insights in the changing electronics of active sites is obtained, which is not available from any other method (see figure 1). Theoretical simulations are currently being developed.

**Figure 1.** $W L_3$ Valence band RIXS on W organometallic systems during metathesis. Whereas only C and N atoms are interchanged, EXAFS provides limited information. UV-Vis is not accessible for these brown solutions.
At the same time, fast moving monochromators and energy dispersive acquisition methodologies have enabled the study of catalytic systems down to the millisecond time scales and reaction mechanisms have been obtained. For example, time-resolved XAFS in combination with UV-Vis has allowed detailed characterization of homogenous reaction intermediates in situ and time-resolved, making it a powerful tool in revealing reaction mechanisms [3,4]. For many catalytic systems, this time resolution is sufficient for the information required. However, an even higher time resolution is required when one wants to investigate photochemical or photocatalytic systems, as well as formation of some catalytic intermediates. The activated or intermediate states in general have lifetimes of picoseconds to nanoseconds. Using new detector developments in combination with an energy dispersive data acquisition approach, XAS spectra down to a time resolution of 10s of picoseconds have been obtained [5] (see figure 2).

**Figure 2.** Differential Cu K edge XANES on photoactivated system (left) and decay activated state in time (right).

### Conclusions
These novel XAS techniques, both theory and instrumentation, are currently being developed and applied to catalytic systems. The properties and catalytic performance of homogeneous (and heterogeneous) catalysts are studied during their synthesis and activity, with a combination of complementary (spectroscopic) techniques. The influences of different ligands and/or supports on the structural and electronic properties of the active site are investigated. Detailed insights in reaction mechanisms are obtained. Ultimately, a combination of fast time-resolved RIXS is pursued.

### References
The Effects of Solvent on the Furfuryl Alcohol Polymerization Reaction: Characterizations of Molecular Structure and Thermodynamic Properties

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Introduction and Objectives

With declining resources and increasing demands for petroleum, there has been a great interest in (1) the production of energy from biomass and (2) the effective utilization of furanose materials, which arising from the acid-catalyzed dehydration of pentose and hexose. Furfuryl alcohol (FA) has been considered as an important furan commodity and is industrially produced via hydrogenation reaction from furfural derived from selective dehydration of xylose. FA can be converted to levulinic acid (LA) via dehydration and polymerized under acidic conditions.[1,2] The polymerized FA is synthesized by the cationic condensation of FA by acid catalysis. To minimize polyfurfuryl alcohol (PFA) and maximize LA product, fundamental understanding of undesired side reaction, such as coke formation, is required. We have been used a combined Raman spectroscopic and density functional study to understand carbonaceous material known as humin development mechanism.[3] The present study focuses on the identification of the intermediate species structure, mechanism, and rate of PFA during the FA polymerization reaction with different FA/solvents (ethanol, butanol, and iso-butanol) molar ratios.

Results and Discussion

As shown in the figure 1, solvents concentrations or FA/solvents molar ratio, and the kinds of solvents were changed for the FA polymerization reaction. Without solvents, the symmetric C=C (1504 and 1597 cm\textsuperscript{-1}) and C-C (1384 cm\textsuperscript{-1}) ring stretching band intensities in FA spectrum decreased quickly with time and new band was observed to grow at 1654 cm\textsuperscript{-1}. By using density functional theory calculations, we have constructed the Raman spectra to analyze the formation of conjugated diene and diketone molecular species. On the basis of the theoretically calculated diene and diketone spectra, we conclude that the strong band measured at 1654 cm\textsuperscript{-1} should be assigned to the acyclic C=C bond. Solvents included samples Raman spectra provided that the intensity of 1654 cm\textsuperscript{-1} band is continuously decreased with increasing solvent concentrations at the similar reaction time. This result indicate that different 1504 cm\textsuperscript{-1} and 1654 cm\textsuperscript{-1} peak intensity patterns reflect the important effect of the solvent on the reactivity of FA polymerization reaction.
Conclusions

The Raman spectra of various intermediates involved in the acid-catalyzed polymerization of furfuryl alcohol (FA) were calculated by using the B3LYP level of theory and the results were compared with the measured spectra. Based on the measured and calculated Raman spectra, and thermodynamic calculation, the formation of a diene structure from FA monomer is preferred over the formation of a diketone structure. The rate of FA polymerization was decreased with increasing solvent concentrations and was controlled by the FA/solvents molar ratio.

Acknowledgement

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

References

New Insight into the Surface Species During Water Electrolysis by in-situ AP-XPS


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Introduction and Objectives

Ambient pressure XPS (AP-XPS) is a well-established tool for the surface characterization of heterogeneous catalysts under reactive environment in the pressure range up to 0.5 mbar [1]. Such a technique is also suitable to investigate the electrode surface under the electrochemical activation of a molecule. In this work, we present a cell-concept, which allows to characterize the surface of a Pt/NAFION-based electrode for electrochemical water splitting by means of the AP-XPS end-station at the ISIS beamline (HZB/BESSY II), in the water total pressure range of $10^{-2}$ mbar. The NAFION membrane is sputter-coated on both sides by the electro-active element, functioning as cathode on one side and anode on the other side. The cell presents a reservoir for liquid, which is leak-tight sealed through the coated-NAFION membrane. The use of liquid water in the reservoir is two-fold: on one hand it supplies the reactant molecules to both the electrodes due to the permeability of the NAFION membrane to water, on the other hand it guarantees a good hydration of the membrane which is fundamental for achieving a significant current. The electrode directly in contact with the liquid water functions as counter electrode, while the electrode exposed to photons is the working electrode (we). The water transport through the NAFION membrane results in a total pressure up to $10^{-2}$ mbar in the XPS chamber. Sketch of the cell is reported in Figure 1. Electrochemical techniques such as cyclic voltammetry (CV) and chrono-amperometry (CA) under relevant polarization are combined with simultaneous XPS investigation of the O1s, C1s and Pt4f core levels. In particular, the chemical state of the electro-active Pt and the oxygen surface species are investigated during water surface chemisorption, O2 evolution and H2 evolution. The gas composition is continuously monitored by mass spectrometry (online MS).

Results and Discussion

Figure 2 reports the cyclic voltammogram for the electrode/cell assemble in the in-situ XPS chamber. The gas phase analysis of the m/z 2 and m/z 32 MS traces at constant potential shows the response of the system when switching from open circuit condition to H2 evolution or O2 evolution condition. The current decreases when the liquid water in the reservoir is consumed and the pressure in the XPS cell decreases rapidly to $10^{-5}$ mbar.

Figure 1: sketch of the cell for the in-situ XPS investigation
Conclusions

The designed cell with the liquid reservoir was specially constructed to investigate by means of soft X-ray spectroscopy a Pt/NAFION electrode during in-situ electrochemical processes. The Pt4f shows that during OER, the Pt0/Pt+ ratio decreases indicating the progressive surface accumulation of Pt-O species. Such a system is suitable to be applied to investigate other electrocatalytic processes too.

References

In situ XAS of Pt Monolayer Model Fuel Cell Catalysts: Balance of Nanostructure and Bimetallic Interactions

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Introduction and Objectives

Bimetallic catalyst materials are of great interest due to the tunability of their (electro)catalytic properties, which is particularly important for oxygen reduction reaction (ORR) electrocatalysts in fuel cells, where a significant reduction of Pt loading is needed to achieve economic viability. Density functional theory (DFT) calculations have successfully predicted a volcano-type relation between ORR activity and the bond strength of the “descriptor” adsorbate atomic oxygen (O\textsubscript{ad}).\textsuperscript{1} Using x-ray absorption spectroscopy (XAS) at the Pt L\textsubscript{3} edge on a well-defined Pt model catalyst consisting of one monolayer Pt on a Rh(111) single-crystal substrate, we overcome the incompatibility between the high penetration depth of an \textit{in situ} technique and the required surface sensitivity, because only surface Pt atoms and their interactions with oxygen-containing species from the electrolyte are probed. By combining the High Energy Resolution Fluorescence Detection (HERFD) technique and \textit{ab initio} multiple-scattering calculations, we can establish unambiguous spectral fingerprints for the differentiation of chemisorbed oxygen-containing species and surface oxide formation.\textsuperscript{2,3} Here, we show our recent HERFD XAS results on two different Pt/Rh(111) model catalysts prepared by two different techniques that result either in a uniform two-dimensional Pt monolayer (2D Pt/Rh(111)) or in three-dimensional Pt islands (3D Pt/Rh(111)). Furthermore, we present an extensive DFT study on 3D Pt/Rh(111) where, in addition to the well-known strain and ligand effects, we identify an additional effect of under-coordinated Pt atoms near corners and edges of islands, which can strongly affect the overall ORR activity.

Results and Discussion

During sample preparation and subsequent characterization using EXAFS, we found that Pt evaporation in UHV onto a heated (600 K) Rh(111) substrate results in formation of 2D Pt/Rh(111) as already reported by Duisberg et al.,\textsuperscript{4} while a 3D island morphology was determined when Pt was deposited in a wet-chemical route\textsuperscript{5} using the galvanic displacement of a Cu monolayer.

Both samples were studied with \textit{in situ} HERFD XAS in 0.01 M HClO\textsubscript{4} electrolyte over a broad potential range, and the shape and intensity of the Pt 2p \textrightarrow 5d resonance (“white line”) was carefully analyzed to identify spectral signatures of chemisorbed species H\textsubscript{ad} and O/OH\textsubscript{ad}, as well as Pt oxide. Most remarkably, we found that both H\textsubscript{ad} at low potentials as well as O/OH\textsubscript{ad} at high potentials could not be detected at all on 2D Pt/Rh(111). This result may appear surprising for a Pt electrode, but can be explained with the strong ligand and strain effects of the Rh substrate which destabilize O\textsubscript{ad} by \textasciitilde0.6 eV. On 3D Pt/Rh(111),
the spectral signatures of H\textsubscript{ad} and O/\textsubscript{OH}

Conclusions

When HERFD XAS is applied to a well-defined monolayer model electrocatalyst, sufficient spectral resolution and surface sensitivity can be achieved to obtain the weak spectral signatures of chemisorbed oxygen-containing species. We have applied this technique to two Pt/Rh(111) model catalysts with different morphologies. The destabilization of O\textsubscript{ad} on 2D Pt/Rh(111) due to strain and ligand effects can be compensated to a large extent by changing the morphology of the Pt monolayer to that of small 3D islands. For individual adsorption sites near island edges, this compensation effect can be sufficient to reach up to \(~9.5\) times higher contribution to the ORR activity than a midterrace-site on Pt(111). We propose that tailored nanostructuring of size-and shape-selected islands could maximize this effect and make the choice of elements in a bimetallic system less dependent on ligand and strain effects.

References


Ambient Pressure Photoemission Investigations on PEM Fuel Cells In-Operando Conditions

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Introduction and Objectives

The hallmark in the field of surface chemistry and catalysis is the understanding of the role of the chemically active surfaces in operational conditions. Ultra high vacuum based XPS has been utilized extensively to characterize the composition and the electronic properties of the surfaces but its role in explaining the chemical function is to justify the stationary properties of the catalyst surfaces. It is a very well-known fact that in operational conditions; as the surfaces are at equilibrium with the gas or liquid phase interacting with, they are prone to change. Ambient Pressure Photoemission Spectroscopy (APPES) is a rather new type of an approach that makes in-situ XPS studies near ambient conditions possible.

Understanding the catalytic cycle of the oxygen reduction reaction (ORR), identification of the nature of the surface species in mass transfer limited and zero current regimes are important objectives in the improvement of fuel cell technology. Thus, investigations on the electronic and structural properties of the adsorbates and of catalyst materials on cathode and anode side of the PEMFCs in-operando conditions, i.e. as the fuel cell is running, is crucial.

We have studied the ORR reaction on Pt PEMFC in various operational conditions using APPES technique. Depending on the operational regime, we identified surface species present of Pt nanoparticles on PEMFC cathode.

Results and Discussion

APPES system located at Stanford Synchrotron Radiation Lightsource (SSRL, Beamline 13.2) houses a gas cell inside a chamber with differential pumping units. PEMFC samples can be transferred into the gas cell that contains a small nozzle required for acquiring photoelectrons emitted from the surfaces. Currently, XPS measurements can be performed in gas ambient up to 50 torr. As well as XPS, x-ray absorption measurements can be performed in near-ambient conditions.

Our prototype cell comprised a Nafion® membrane covered on both sides with carbon-supported Pt nanoparticles. The device was humidified by supplying water vapor from the anodic side of the membrane. The XPS spectra shown in figure below were collected while exposing the cathode to increasing pressures of oxygen gas (up to 5–10 torr) while recording the cell voltage and current. Clear changes in the composition of surface species as a function of both time and oxygen pressure are observed as the system moved from the kinetic- to the mass-transfer-limited regime. This is the first time in which the oxygen reduction reaction of a polymer electrolyte fuel cell has been measured in situ and in operando, and this is just the first of many systems that we will be able to probe by combining electrochemistry with APPES technique.
O 1s spectra as a function of time. The probed cathode surface was exposed to 0.4 Torr O\textsubscript{2} while the anodic surface was exposed to 40 Torr of forming gas. The sample moves from a kinetic-limited (bottom) to a mass-transfer-limited (top) regime.

The evolutions of the spectral features indicate that oxygen chemisorbed on Pt nanoparticles is correlated to the changes in the potential, i.e. different operational regimes of the fuel cell. Under the conditions studied formation of oxide was not observed.
Operando Characterization of Au/FeO\textsubscript{x}-CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Catalysts During Water Gas Shift Reaction

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Introduction and Objectives

In the past decade, research has demonstrated the high potential of fuel cells to replace the internal-combustion engine in vehicles and to provide power in stationary and portable power applications. The hydrogen and the fuel cells together, represent a radically different approach to energy conversion. Nowadays, hydrogen is mostly produced from fossil fuels by a multistep process that includes catalytic autothermal reforming, always followed by the water–gas shift reaction (WGSR). A crucial prerequisite for the techno-economic success of fuel cells, especially those that operate either at low temperatures or in mobile applications, is the discovery of improved reforming and WGS catalysts for the generation of hydrogen which are much more active than those used in chemical plants [1]. Gold catalysts are extensively used for the WGSR, however it is still difficult to find in the literature well performing and economically viable catalyst. In this work the development of gold based catalyst, essentially based on Ce-Fe mixed oxides-modified γ-alumina as support for the WGSR is proposed and compared to a gold catalyst iron oxide-promoted supported on a commercial CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}. Figure 1 shows a schematic representation of the prepared systems:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of the synthesized systems}
\end{figure}

The activity in the WGSR of the gold catalyst supported on the home-made support is remarkably higher than the Au catalyst supported on the iron-modified commercial support. In this scenario, the aim of this work is to understand the different behavior of these catalysts, under water gas shift reaction conditions, by employing several operando characterization techniques (XRD, EXAFS, DRIFTS, UV-Vis).

Results and Discussion

The catalytic activity of the studied systems is compared in Figure 2. Although both catalysts have comparable gold and ceria loadings their catalytic activities are completely different. Gold dispersed on the home-made support almost reached equilibrium conversion at 330°C while the catalyst prepared on the commercial support is hardly active in WGS. Operando XRD measurements (Figure 3) revealed two important differences between the catalysts that may explain the data shown in Figure 2.
First, gold nanoparticles are smaller in the homemade catalyst. Assuming that CO oxidation occurs with the participation of Au-OH species formed at a peripheral gold atom by transfer of a support hydroxide ion and that these species further reacts with CO molecules adsorbed on a low-coordination gold atom, it can be concluded that the smaller the gold particle size the higher the catalyst activity. Therefore, the homemade system composed of very small and well-dispersed gold nanoparticles does show a higher catalytic activity in the WGSR. In the presence of oxides with redox properties, Ce-Fe mixed oxides, CO oxidation may also occur by oxide ions transferred from the support.

Thus, iron oxide must play a role enhancing ceria redox properties favoring water dissociation that typically takes place on the support [2]. Our XRD data points to Ce-Fe solid solution in the homemade catalysts enhancing the reducibility of the ceria phase and favoring oxygen transfer reactions. On the contrary, the iron-promoted commercial support show diffraction lines associated to the presence of an iron spinel (Fe$_3$O$_4$) resulting in a less reducible support.

**Conclusions**

Operando experiments clarify that Au/FeO$_x$-CeO$_2$/Al$_2$O$_3$ catalysts can be a highly efficient for the WGSR if the formation of the iron spinel Fe$_3$O$_4$ (an inactive specie for WGSR) is avoided. Actually iron improves the ability of ceria to carry out the water dissociation only if it is able to maintain its maximum oxidation state facilitating ceria reduction.

**References**

High-pressure \textit{in situ} Mössbauer & X-ray Absorption Spectroscopy Studies of Hydrotreating and Fischer-Tropsch Catalysts

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Introduction and Objectives

Heterogeneous catalysts find large scale applications in many processes in (petro)chemical industry. Detailed characterization of such catalysts is required to derive structure-activity relations which teach us how to improve the process or the catalyst. Because important changes in the catalyst structure may occur going from the as-prepared state to the active state, it is important to characterize the structure of the catalyst under temperature and pressure conditions as close as possible to the conditions practiced in industrial reactors. Mössbauer and X-ray absorption spectroscopies are some of the few techniques that can be used for characterization of heterogeneous catalysts under working conditions. A state-of-the-art high-pressure \textit{in situ} reactor to investigate solid catalysts by Mössbauer spectroscopy at pressures and temperatures up to 40 bar and 773 K, respectively, was developed at the Reactor Institute Delft [1].

Results and Discussion

For the development of an economically attractive Fischer-Tropsch synthesis (FTS) process with high catalyst stability, detailed fundamental understanding of the deactivation mechanisms of the supported nano-sized cobalt crystallites is required. Recent results, obtained using our unique high-pressure Mössbauer reactor with Co-based FTS catalysts, clearly show the importance of characterization studies at industrially relevant pressures. Using in-situ Mössbauer spectroscopy we could unambiguously prove that oxidation of the nanoparticles by water will not occur at 20 bar and 493 K when hydrogen is present (Figure 1). Only in a water/argon atmosphere did oxidation take place, ruling out oxidation as deactivation mechanism in Fischer-Tropsch synthesis [2].

Hydroprocessing, mainly sulfur removal, remains one of the most important unit operations in the production of clean transportation fuels. The active phase (‘Co-Mo-S’) consists of Co sulfides dispersed over the edges of MoS\textsubscript{2} slabs. Most characterization has been carried out for samples sulfided at atmospheric pressure, yet sulfidation at elevated pressure is common industrial practice. An important distinction to be made when describing the active ‘Co-Mo-S’ phase is one in terms of type I (strong metal-support interaction) and type II (fully sulfided, no metal-support interaction). Type II is preferred in industrial catalysts. Conventionally, the use of chelating agents such as NTA is thought to result in fully sulfided type II ‘Co-Mo-S’ after sulfidation at 1 bar. \textit{In situ} Mössbauer and X-ray absorption spectroscopy show that sulfidation of a CoMo-NTA catalyst can be improved by increasing the sulfidation pressure. This results in a substantially more active hydrodesulfurization catalyst. Until now, it has not been possible to directly distinguish type I from type II phases other than by the activity criterion. Here we show that the EXAFS Mo-
S coordination number, which should closely correlate to the sulfidation degree of the MoS$_2$ slabs, appears to be a reasonable indicator for the approach of the active phase to type II ‘Co-Mo-S’ (Figure 2) [3].

Figure 1. Mössbauer spectra of Co/CNF catalyst at 20 bar and 493 K.

Figure 2. Relation between HDS activity and Mo-S coordination number.

Conclusions

High-pressure Mössbauer emission spectroscopy and X-ray absorption spectroscopy were successfully applied to the investigation of cobalt-based Fischer-Tropsch and hydrotreating catalysts. Water was shown to have a strong impact on catalyst deactivation by enabling the sintering of cobalt particles in Fischer-Tropsch synthesis. A fully sulfided and well-crystallized type II ‘Co-Mo-S’ phase with a weak support interaction was obtained after high-pressure sulfidation of a CoMo-NTA hydrodesulfurization catalyst.

References
Introduction and Objectives

As recently as 10-15 years ago, nanoparticles were described in qualitative terms: oblate, hemispherical, raft-like, random or core-shell. Today we are able to discriminate between the cuboctahedral and icosahedral motifs, establish quantitative shell structure (e.g., single or double layer) in binary or ternary nanoalloys, measure size, shape and morphology of clusters, and accurately characterize structural and thermal disorder in supported metal clusters. These advances are possible by using in situ x-ray absorption fine structure (XAFS) - a technique that is a premier tool for measuring structure, dynamics and electronic properties of nanomaterials.

Even the most advanced ab initio theories still rely on single crystal constructs, perfectly oriented cluster surfaces, and/or periodic and ordered systems to understand mechanisms of reactivity. While it is known that reaction barriers are directly related to adsorbate binding energies, very little is known about how the latter are affected by nanoscale effects and adsorbate coverage in real metal clusters. We will discuss thermodynamic properties, markedly non-bulklike, of supported clusters that can be extracted from XAFS data: the thermal expansion coefficient, Debye temperature, surface tension, strain energy and heat of adsorption. All results will be interpreted in the framework of a simple model that incorporates dominant factors of the three-phase (particle-support-adsorbate) system.

Results and Discussion

We investigated one of the most frequently used heterogeneous catalysts (Pt/γ-Al₂O₃) under steady state conditions of varying temperature and gas pressure. Our analysis modeled the electronic contributions to the integrated difference spectra of the x-ray absorption near-edge structure (ΔXANES) signal S in the following form: \( S(T, P) = A\theta(T, P) + BT + C(P) \). This formula recognizes that electronic changes in the system originate from adsorbate-particle (first term), particle-support (second term), and gas-support (third term) interactions. Intraparticle strain energy was calculated using static Debye-Waller factors obtained by temperature-dependent extended x-ray absorption fine structure (EXAFS) analysis. We determined that the strain energy can be a significant fraction (10-20%) of the heat of adsorption.

Conclusions

We have demonstrated the ability of XAFS to acquire thermodynamic parameters under catalytic conditions: the heat of adsorption for H₂ and CO were derived using the ΔXANES technique, while the intraparticle strain and the pressure-dependent shape change were determined by EXAFS. The support and adsorbate-induced strain is a large and important factor affecting catalyst binding energy and reactivity.
References


An Integrated AFM-Raman Instrument for Studying Heterogeneous Catalytic Systems: A First Showcase

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Introduction and Objectives

Supported metal nanoparticles are important heterogeneous catalysts in many industrial processes. A thorough understanding of which specific surfaces have the highest catalytic activity is required in order to tune the shape and size of nanoparticles to reach the maximum catalytic activity. [1]

Raman spectroscopy has proven to be a powerful and versatile tool for the study of chemical reactions, but lacks sensitivity under normal measurement circumstances. The use of surface enhancement makes Raman spectroscopy a much more sensitive and versatile tool for the study of chemical reactions. Surface Enhanced Raman Scattering (SERS) occurs principally on roughened noble metal surfaces or noble metal NPs, and allows chemical imaging of adsorbate-surface interactions with high sensitivity. This makes it uniquely suited for investigations of reactions at a catalytic surface. The integration of Atomic Force Microscopy (AFM) with Raman spectroscopy forms a powerful new tool for nano-scale chemical imaging of catalytic solids, allowing nano-scale morphological features to be correlated directly to chemical information. [2]

Results and Discussion

Figure 1: Simultaneous AFM and Raman imaging of an Al2O3 wafer coated with Ag nano-cubes and Rh6G in air using a 633 nm laser, laser power 500 mW at sample; (A) AFM height image of surface; (B) AFM magnification of an area over which Raman intensity was followed (scale bar = 400 nm); (C) Raman spectra followed over time from area B; (D) Raman intensity map of the Rh6G band at 1512 cm⁻¹.
Conclusions
The potential of an integrated AFM-Raman instrument for identifying which nano-particle clusters are the most active through a study of the photo-oxidation of rhodamine-6G (Rh6G) over Ag nanoparticles is explored. We show that it is possible to follow the reactants or products of a reaction under in-situ conditions, varying both atmosphere and temperature, and pinpoint the active section of a catalyst on the nanoscale.

References
Model Studies of Chirality Transfer Reactions on Platinum


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Introduction and Objectives

This study deals with chirality transfer to prochiral substrates at sites created by chemisorbing optically active compounds, called chiral modifiers, on platinum. We describe a newly developed approach to study large populations of individual chirality transfer preorganization complexes [1]. The method combines sub-molecularly resolved dynamic STM measurements, intensive DFT input, surface vibrational spectroscopy (RAIRS) and parallel catalytic runs using chirally modified supported metal particles. The experimental conditions and the reaction systems are chosen so as to maximize the relevance of the surface science data to the catalytic reactions under study. STM measurements are taken at the reaction temperature (∼room temp.) so as to distill out information that is relevant to the catalytic stereoselective reaction. The Pt(111) surface is used because shaped nanoparticle studies show that other faces lead to hydrogenation of the chiral modifier [2].

Results and Discussion

Chirality transfer preorganization structures formed by (R)-(+)-(1-naphthyl)ethylamine, (R)-NEA, and 2,2,2-trifluoroacetophenone, TFAP, on Pt(111) were studied and compared to data for other modifier-substrate pairs. The DFT calculations show that asymmetric induction in the TFAP/(R)-NEA system is controlled by a hierarchy of forces: strong chemisorption of the TFAP phenyl group, modifier-substrate NH₂...OC bonding, and weak stereodirecting steric interactions involving the phenyl group of TFAP. A different picture emerges on studying α-ketoester substrates. Sub-molecularly resolved work on (R)-NEA + α-ketoester complexes shows two binding interactions: an NH₂...OC interaction, as for TFAP, and an aryl-CH...OC interaction.

Conclusions

Single site and single molecule studies, coupled with catalytic tests, are used to gain increased mechanistic understanding and control of heterogeneous enantioselective catalysis.

References


Oxidation of Pt(111) Under Near-ambient Conditions

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Introduction and Objectives

Atomically thin oxide layers can form on the surfaces of Pt-group metals under oxidizing conditions [1]. These surface oxides frequently exhibit markedly different reactivity than the underlying metallic substrate and have been proposed to influence the activity of Pt-based materials in a number of important industrial processes, including CO oxidation in catalytic converters and the electrochemical oxygen reduction reaction (ORR). However, Pt oxidation has proven difficult to examine using surface-sensitive techniques that can distinguish different oxidation states, owing to the compatibility of conventional electron-based spectroscopies with the elevated O2 pressures (>10^-5 Torr) required to oxidize Pt. Consequently, even though (111)-oriented facets are the most abundant close-packed surfaces on the Pt nanoparticles typically employed in industrial catalysis, oxide growth on Pt(111) remains poorly understood. This study [2] employed a photoemission system that can operate at near-ambient pressures [3] (< 5 Torr) in order both to characterize the surface-oxygen phases that form on Pt(111) and to examine the reactivity of these phases toward H2 and CO.

The oxidation of Pt(111) as a function of both temperature and O2 pressure was monitored in situ in the presence of up to 5 Torr O2 using X-ray photoelectron spectroscopy (XPS) and ex situ (i.e., after evacuating O2) using X-ray absorption spectroscopy (XAS). Both XPS and XAS reveal significant pressure- and temperature-dependent changes of the Pt–O interaction.

Results and Discussion

Above a critical oxygen coverage of 0.6 ML [1 ML = 1 O atom per Pt atom in a (111) layer], there is a phase transition from a high-coverage chemisorbed phase (~0.5 ML) to a surface oxide, as indicated by the emergence of a high-binding-energy shoulder in Pt 4f7/2 XPS. Accompanying ex situ XAS measurements (Fig. 1) at the oxygen K-edge indicate that this new phase is associated with drastic changes in the polarization dependence of the X-ray absorption cross section. In particular, the single absorption feature associated with chemisorbed oxygen is replaced by a strongly polarization-dependent double-peaked structure. On the basis of XAS simulations using the GPAW [4] code (Fig. 1), we attribute this XAS structure to a PtO-like surface oxide with square-planar Pt coordination. Repeated cycles of heating and cooling under the most aggressive oxidizing conditions we could access [P(O2) < 5 Torr] induced further oxidation of the PtO-like phase, as confirmed by the two new Pt 4f7/2 features at high binding energy (72.1 and 73.5 eV), together with the drastically broadened O 1s peak. The resulting changes in XAS are well reproduced by a model structure comprising a single trilayer of α-PtO2(0001) on Pt(111).

The reactivity of the three surface-oxygen phases characterized in this study—chemisorbed O and the PtO- and PtO2-like surface oxides—toward hydrogen and carbon monoxide was investigated. From the
rate of disappearance of surface oxygen at a fixed temperature and CO/H₂ flux, we have determined that the reactivity of the surface toward the oxidation of either species decreases with increasing oxygen coverage.

Figure 2: Experimental O K-edge XAS spectra (solid lines) are shown in (a) and compared in (b) against simulations (dashed) of the adjacent model structures; side views of the model structures are cross sections along the dashed white lines. The dashed-dotted lines show theoretical results for the 0.5 ML oxide stripe.

Conclusions
The oxidation of Pt(111) at elevated O₂ pressures has been characterized using a high-pressure photoemission setup. Beyond a critical chemisorbed coverage of ~0.5 ML, oxidation proceeds via a PtO-like surface oxide, followed by PtO₂-like trilayers that are the precursor to bulk oxidation. Both surface oxides are less reactive than chemisorbed oxygen for either CO or H₂ oxidation.

References
The Chemistry of Palladium Modified by Foreign Species X (H, C, Ga, N)

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Introduction and Objectives

Palladium is a well-known heterogeneous catalyst of various reactions; among them we consider alkene and alkyne hydrogenation, cis-trans isomerization and oxidative dehydrogenation here. This project reviews recent findings gathered in our laboratories when studying the above reactions, and our focus will be on the role of foreign species X (H, C, Ga, N) influencing the prevailing reaction path. It has often been recognized that palladium allows the incorporation of feed components, like O, H, C in its subsurface and bulk, additives gives rise to enhanced catalytic performance, and alloying with second metals has also been numerously reported to make drastic effect on reactivity and selectivity. By walking through various examples studied with the toolkit of in situ spectroscopic characterization, I'm going to give a short overview of the role of foreign species.

By applying in situ (operando) techniques we collected complementary information on the working state of palladium catalysts and used density functional theory to understand atomistic details of hydrogen and carbon incorporation into Pd.

Results and Discussion

In alkyne hydrogenation we have used high-pressure XPS to establish the chemical state of the surface, and found that carbon incorporates into the surface and subsurface under selective hydrogenation. This incorporation was absent when alkenes were hydrogenated. We utilized the strength of in situ Prompt-Gamma Activation Analysis to quantify the amount of hydrogen dissolved in Pd, and concluded that in selective alkyne hydrogenation the reaction was not the function of H/Pd, whereas unselective reaction or alken hydrogenation proceeded always with bulk H saturation. Performing molecular beam experiments on well-characterized Pd model catalysts provided us with the direct evidence that alkene hydrogenation requires the presence of H in the subsurface region. Cis-trans isomerization of alkenes, however, does not rely on subsurface hydrogen and proceeds using surface hydrogen. The permeability of the surface to facilitate or block fast surface penetration and subsurface H population can be strongly modulated by surface modifiers. While carbon deposits on low-coordination sites enable facile H diffusion \cite{1}, adsorbed CO \cite{2} for example strongly hiders hydrogen dissolution. Another widely used example is the technical system, Pd-Ag, where the Pd d-band is shifted to lower energies and the density of states at the Fermi level is diminished to destabilize H adsorption and subsurface population. Note that carbon incorporation
into the subsurface gives rise to the same effect, though this state can be easily driven out of stability at high hydrogen chemical potentials. Intentional modification of palladium by Ga, in which Pd-Ga intermetallic compounds form, gives rise to the advantage of selective and long-term stable catalysts for alkyne hydrogenation [3]. In situ XPS, XRD and EXAFS experiments assisted us to establish phase and structural information under controlled chemical environments. Although Ga is prone to some surface oxidation, in hydrogen and under hydrogenation PdGa and Pd$_2$Ga was found to possess high structural stability both in its bulk and on its surface. The covalent interaction between Pd and Ga, even with nanoparticles of Pd$_2$Ga supported on CNTs, does not allow reaction induced segregation and any subsurface chemistry is essentially eliminated. In my talk I will give further examples to illustrate the role of N modifiers.

*Figure 1: In situ EXAFS example of Pd/CNT (left) and Pd$_2$Ga/CNT (right) at different conditions*

**Conclusions**

A broad and consistent view on the role of foreign modifier species exerting on Pd has been attained over the years highlighting that subtle changes of the catalyst can dramatically modify performance. These achievements rely on multiple in situ methodologies.

**References**

Characterization by in situ DRIFTS: Toluene Adsorption and Oxidation over ZrO₂

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Introduction and Objectives

The adsorption of reactant molecules combined with in situ spectroscopic methods provides essential information about the surface chemistry and elementary reactions [1] for even highly complex systems such as catalytic cleaning of gasification gas. The gasification of biomass is an environmentally attractive way to produce electricity, heat and synthesis gas. However, the produced gas contains impurities, such as tar, and has to be cleaned before further use. When oxygen is added to this product gas, ZrO₂-based catalysts are known to be active in tar decomposition [e.g. 2]. Adsorption and total oxidation of toluene (as model compound for tar) was characterized by in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy). The objective of this study was to demonstrate the significant difference in interpretations of toluene adsorption spectra obtained at 30 and 600 °C (actual gasification gas clean-up temperature) for determination of the first step in the decomposition of toluene in gasification gas clean-up.

Results and Discussion

Adsorption and oxidation of toluene on calcined and reduced ZrO₂ was studied by in situ DRIFTS: Toluene (750 ppm toluene in He) was adsorbed i) at 30 °C or ii) at 600 °C. After 30 min the sample cell was i) flushed with nitrogen for 30 min at 30 °C or ii) flushed with nitrogen for 10 min at 600 °C and then cooled down to 30 °C in nitrogen to obtain a spectrum without the contribution of gas-phase toluene. The spectrum of an aluminium mirror measured under nitrogen flow was used as the background. Next oxygen (2% O₂/N₂) was admitted to the sample cell and temperature was increased stepwise from 30 °C to 600 °C (spectra were collected every 25 °C).

Adsorption of toluene at 30 °C on ZrO₂ was found to be molecular (non-dissociative). The peaks (on the left in Fig. 1) appearing at 3100-3000 (not shown), 1604, 1545 and 1498 cm⁻¹ are characteristic for the aromatic ring and the peaks at 2924 and 2872 (not shown), 1452 and 1372 cm⁻¹ for the methyl group [3]. Interestingly, the original peak of ZrO₂ at ca. 3770 cm⁻¹ (not shown) assigned previously to terminal OH groups of ZrO₂ [2], disappeared. In addition, an extremely broad peak appeared throughout the spectrum of ZrO₂ (not shown), suggesting the formation of adsorbed water on the surface at 30 °C.

Toluene adsorption at 600 °C (on the left in Fig. 1) brought out sharp peaks appearing at 1532 and 1420 cm⁻¹. These peaks are assigned to asymmetric and symmetric stretching modes of adsorbed benzoate species, whose presence indicate that the C-H bonds in the methyl group of toluene can dissociate [4]. Adsorbed benzoate species are formed through abstraction of hydrogen from the methyl group of toluene, followed by reaction between the anion (C₆H₅CH₂⁻) and two surface oxygen atoms of ZrO₂ to form adsorbed benzoate ion [4]. In addition, the band appearing at 1594 cm⁻¹ is assigned to the skeleton vibrations of the aromatic ring [3, 4]. When oxygen (on the right in Fig. 1) was admitted to the reaction cell...
and temperature was increased stepwise from 30 to 600 °C, the adsorbed species on ZrO$_2$ surface did not vanish until at temperatures above 575 °C.

![DRIFTS spectra of ZrO$_2$ sample after toluene adsorption at 30 °C and 600 °C.](image)

**Figure 1.** Left: DRIFTS spectra of ZrO$_2$ sample after a) toluene adsorption at 30 °C and b) toluene adsorption at 600 °C and cooling to 30 °C. Right: Spectra of ZrO$_2$ during toluene oxidation from 500 to 600 °C.

**Conclusions**

At 30 °C, toluene was found to adsorb molecularly on the surface of ZrO$_2$. At 600 °C, toluene adsorbed dissociatively on ZrO$_2$ forming adsorbed benzoate species with surface oxygen atoms. Therefore, it is speculated that the first step in the decomposition of toluene during gasification gas cleaning over ZrO$_2$ is the activated adsorption of these benzoate species. This cannot be concluded from the adsorption of toluene at 30 °C, therefore indicating the significance of in situ characterization applied in/near the actual reaction conditions.

**References**

The State of Promotors in Fischer-Tropsch Catalysts at Reaction Conditions

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Introduction and Objectives

Supported cobalt catalysts are widely studied and applied for conversion of synthesis gas in low temperature Fischer-Tropsch synthesis. It is common practice to add a noble metal promoter to optimize the performance of the catalysts. Recently, more attention has been directed towards a fundamental understanding of the promotion.

This study focuses on the state of promotors in Fischer-Tropsch catalysts. Especially at reaction conditions, the nature and location of the promoter itself is unclear which leads to the utilization of in situ techniques [1]. Modulation enhanced spectroscopy (MES) applied to in situ XAS on Co FT catalysts enables a bulk technique to become surface sensitive.

Results and Discussion

Promotion of the FT catalysts produces a variety of effects on the structure and catalytic performance. If this is due to the formation of bimetallic particles is a question which can only be answered by collecting more information about the state of the promoter metal under reaction conditions [2]. Additionally, it has been found that alloy formation between catalyst-metal and promoter-metal changes adsorption properties due to interactions in the outer shell orbitals [3]. The detailed nanostructure, however, is unknown and further investigations are necessary.

Investigations of the oxidation state, focusing on Re as promoter metal show that approx. 20% of Re is present in low oxidation states and reduction takes place at approx. the same temperature as the 2nd Co reduction step from CoO to Co. XANES studies show that the unreduced Re fraction remains in oxidised form and there are no indications of bulk changes in the local environment around Re. The catalytic behaviour of Re and Ni promoted Co-FT catalysts has been investigated using modulation enhanced spectroscopy. The changes in behaviour for promoted and noble-metal promoted catalysts are discussed in comparison with their unpromoted counterparts.

Figure 1 shows the application of modulation excitation applied on the EXAFS signal investigating Co FT catalysts. After demodulation (not shown here) the technique allows to selectively investigate the changes on the surface fraction of the catalyst.
Abstracts

Figure 1: Modulation excitation spectroscopy (MES) applied to in situ EXAFS on Co FT catalyst (T = 483 K, alternating between H₂ flow and O₂/He flow of 2.5 mL/min).

Conclusions

MES allows for sensitive and selective detection and monitoring of the dynamic behaviour of species directly involved in the reaction [4]. The set-up is capable of performing a surface-sensitive experiment at industrially relevant FT conditions, therefore bridging the gap between model and industrial conditions.

References

Introduction and Objectives

The catalyst body can be considered to be the workhorse of industrial catalysis. These mm-sized catalysts owe their activity to the formation of highly dispersed metal/metal oxide species with particular oxidation states and coordination environments.[1] Their efficiency depends on the speciation, micro-distribution and stability of the active species. It is therefore of importance to understand the physical and chemical processes involved in their preparation. Recently, space and time resolved techniques have been developed and applied to study the interactions between active species and the support surface. Raman and UV-Vis techniques in particular are commonly used for characterising the precursor species during impregnation and calcination although this is normally achieved via bisection. Techniques such as MRI and X-ray tomography have the advantage in that they can be employed non-invasively although the former is an indirect method using the \(^1\)H NMR signal intensity of species that interact with water, whereas the latter either probes the elemental or crystalline phase distribution.[2] Recently, Spatially Offset Raman Spectroscopy (SORS) has been developed for obtaining Raman spectra beneath the surface of turbid media.[3] Catalyst bodies can also be considered a type of turbid media and readily amenable to interrogation by SORS. For this purpose we developed the method of Diagonally Offset Raman spectroscopy (DORS), a variant of SORS, which allows for spatiotemporal in situ studies of catalyst bodies revealing the chemistry therein in a noninvasive manner. We demonstrate this method for studying the Mo species that form during incipient wetness impregnation of a 3 mm cylindrical \(\gamma\)-Al\(_2\)O\(_3\) extrudate impregnated with a solution containing 1.3 M [Mo] ammonium heptamolybdate (AHM) and 0.65 M phosphoric acid.

Results and Discussion

2D back-scatter Raman maps of the bisected extrudate were obtained by a Raman scanning method. These maps, shown in Figure 1a demonstrate the presence of an exterior ring containing \(\text{HP}_2\text{Mo}_5\text{O}_{23}^{5-}\) (Mo-P) with bands located at 370, 395, 885, and 936 cm\(^{-1}\). The backscatter Raman spectra recorded at the core of the extrudate displays bands at 936 and 950 cm\(^{-1}\), although the latter band is the most intense. The two bands signify a mixture of Mo-P and \((\text{NH}_4)_3[\text{Al(OH)}_6\text{Mo}_6\text{O}_{18}]\), an Anderson-type heteropolyanion with bands at 375, 570, 900 and 950 cm\(^{-1}\), referred to as Al-Mo.[4] A DORS measurement before bisection was conducted rotating the extrudate by 360\(^\circ\) with three xy-positions. The positions of the points of illumination and point of collection on the extrudate are schematically shown by the crosses in the 2D maps in Figure 1a. These positions allow us to probe loosely defined domains of the surface, sub-surface and bulk. The surface of the extrudate is measured when the point of illumination and collection overlap (green cross). The corresponding DORS Raman spectrum (Figure 1c) is similar to that obtained in backscatter mode near the surface (Figure 1b) demonstrating that mainly Mo-P is present. The subsurface is measured when the distance between point of illumination and collection overlap (red crosses). The shoulder at 950 cm\(^{-1}\) in the Raman spectrum increases relative to the band at 936 cm\(^{-1}\) corresponding to the increasing concentration of Al-Mo towards the core of the extrudate. The third position is depicted by the yellow crosses. The intensity of the Raman bands of Al-Mo has increased relative to that of Mo-P, showing that for this xy position the bulk (surface + interior) is measured. The spatial resolution is close to the spot size for a surface DORS measurement. It increases to the mm range when the bulk is measured due to scattering of photons through the sample. However, the results demonstrate that it is possible to discriminate between surface and bulk by DORS in an industrially relevant catalyst extrudate.
DORS was used to measure dynamically an incipient wetness impregnation of a cylindrical γ-Al2O3 extrudate with a solution containing 1.3 M [Mo] AHM. 0.75 M NH4NO3 was added as an internal standard. Before impregnation, the solution at pH 5 mainly contains heptamolybdate (MoO72-) with Raman bands located at 896 and 942 cm⁻¹. The impregnation was carried out in situ on an extrudate in glassware mounted in the DORS setup. 5 to 75 min of equilibration was investigated in 10 min intervals. Three xy positions of the sample were used to study surface, subsurface and bulk identical to the positions depicted by the crosses in Figure 1a. The sample was rotated to three positions within a 45° angle in 22.5° steps. Upon impregnation, hydration of the alumina surface into aluminum hydroxide-like layers occurs - MoO24²⁻ species react with alumina under acidic conditions to form Al(OH)₆Mo₆O₁₈³⁻ with Raman bands at 570, 898 and 947 cm⁻¹.[4,5] The Raman intensity of Al-Mo increases with equilibration time, especially after 45 min equilibration, especially near the surface. A Raman band at 900 cm⁻¹ was used to identify the presence of Al-Mo near the surface of the extrudate and suggests a gradient of Al-Mo towards the core of the extrudate. 2D Raman scans of bisected extrudates after 2.5 min, 30 min and 125 min equilibration and subsequent drying confirmed that Al-Mo is mostly present in the outer shell in the form of hotspots (areas of ~0.1 mm in diameter) and near or at the exterior surface of the extrudate confirming the results obtained by the DORS measurement.[6]

Conclusions

The DORS technique has been successfully demonstrated for characterising the chemistry occurring at the periphery, sub-surface and bulk of catalyst bodies under both static and dynamic conditions. Most importantly this measurement technique is non-invasive and can be readily combined with other techniques that yield complementary information.

References

Selective Catalytic Reduction of NO\textsubscript{x} over Cu-SSZ-13: a Combined \textit{in situ} DRIFTS/MS Study

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Introduction and Objectives

Enhanced fuel efficiency of internal combustion engines can be achieved by increasing the air/fuel ratio. However, due to the high oxygen concentration in the exhaust gas mixture, traditional three way catalysts are ineffective in the reduction of NO\textsubscript{x} under these conditions. The recent reports on copper ion-exchanged SSZ-13 zeolites indicated high hydrothermal stability, improved low temperature activity and selectivity to N\textsubscript{2} in ammonia selective catalytic reduction of NO\textsubscript{x} reaction in comparison to other copper ion-exchanged zeolites catalysts, such as Cu-ZSM-5 and Cu-Y. [1, 2] However, the mechanism of NH\textsubscript{3}-SCR of NO\textsubscript{x} over Cu-SSZ-13 zeolite and the status of active species (copper ions) during the reaction are poorly understood.

Results and Discussion

In this work, the combination of DRIFTS and MS was used to investigate the reactions of adsorbed ammonia with different oxidants, such as NO\textsubscript{2}, NO+O\textsubscript{2}, NO+NO\textsubscript{2}, N\textsubscript{2}O, NO and O\textsubscript{2}. IR spectroscopy identified two different adsorbed ammonia species over the Cu-SSZ-13 zeolites, i.e. copper- and proton-adsorbed ammonia species, which presented different behaviors during oxidation. Although the oxidation of these adsorbed species were dependent on the oxidant used, it still could be concluded that copper sites-adsorbed ammonia species showed better low temperature activity and selectivity to N\textsubscript{2} than proton sites-adsorbed ones. For example, figure 1A shows DRIFTS results obtained during the oxidation of adsorbed ammonia by NO\textsubscript{2} in the range of 1800-1200 cm\textsuperscript{-1} at 423 K. The features at 1620 and 1454 cm\textsuperscript{-1} could be attributed to copper and proton adsorbed ammonia species, respectively. The feature at 1620 cm\textsuperscript{-1} decreased first with NO\textsubscript{2} exposure time and disappeared after 30 minutes at 423 K, indicating the oxidation of copper-adsorbed ammonia species. It is worth noting that the feature of proton-adsorbed ammonia at 1454 cm\textsuperscript{-1} increased slightly with NO\textsubscript{2} exposure time until the disappearance of the feature for copper-adsorbed ammonia, implying that proton adsorbed ammonia species are less active than the copper-adsorbed ones, and the transition of ammonia species from copper ions sites to proton sites might happen during ammonia oxidation. Mass spectra shown in figure 1B suggested that the water desorption was slower than N\textsubscript{2} production during ammonia oxidation, which might result in the formation of more proton sites during ammonia oxidation. In addition, mass spectra also confirmed the main products from the oxidation of copper-adsorbed ammonia species were water and N\textsubscript{2}. In this presentation we will provide the detailed results of the reaction of adsorbed NH\textsubscript{3} with a variety of oxidants in the sample temperature range of 423-673 K studied by \textit{in situ} DRIFTS and MS.
Acknowledgement

Financial support was provided by the US Department of Energy (DOE), Office of Freedom Car and Vehicle Technologies. Portions of this work were performed in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL). The EMSL is a national scientific user facility and supported by the US DOE, Office of Biological and Environmental Research. PNNL is a multi-program national laboratory operated for the US Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

References:


Figure 1 (A) DRIFT spectra of the oxidation of adsorbed ammonia species over Cu-SSZ-13 at 150 °C in the range of 1800-1200 cm⁻¹; (B) Mass spectra of spectra of the oxidation of adsorbed ammonia species over Cu-SSZ-13 at 150 °C.
A Spectroscopic Study of Cerium Oxide Nano-catalyst: Water Activation

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Introduction and Objectives

The drive for a fossil-fuel-alternative to produce hydrogen is one of the most critically important investigations at present. Steam reforming of bio-oil including the gasification of coke deposits in the presence of water is a conceptually promising alternative to generate hydrogen gas. In fact, it has already been reported that H₂O can be activated via the formation of hydroxyl groups (-OH) on oxides like ceria, which increases both the H₂ yield and the catalyst’s lifetime [1].

Cerium oxide is known to have unique catalytic behaviour because of its ability to undergo fast conversion between Ce⁴⁺ and Ce³⁺ in a stable fluorite structure [2]. In addition, the synthesis of CeO₂ nanoscopic shapes, such as rods, cubes, and wires, has been reported, with strong evidence of their enhanced reactivity towards CO oxidation [2-4]. So far, much attention has been focused on synthesing and testing the reactivity of these nano-shapes, but the in-depth characterisation of the surface species responsible for the enhanced activity is just emerging [4].

This paper reports on the investigation of the surface species on hydroxylated ceria, with specific attention to obtaining a detailed understanding of water activation and reaction into hydroxyl groups using in-situ vibrational spectroscopy.

Main Results

Different CeO₂ nanoshapes were synthesised using a hydrothermal method, following the procedure reported in [3]. The samples were further calcined at 500°C in synthetic air, resulting in BET surface areas of 96, 66 and 31m²/g, for rods, particles and cubes, respectively. A self-supporting wafer of the sample was placed into a purpose built stainless steel IR cell inside a Bruker Vector 22 with MCT detector. Infra-red spectra were recorded in-situ after drying at 200°C, subsequent reaction with CO and regeneration with water for each of the three different ceria morphologies.

As a typical example, the spectra obtained on ceria cubes are shown in Figure 1. After drying (black-solid spectrum), three different types of –OH groups are present on the catalyst surface, with bands at 3698 and 3642 cm⁻¹ attributed to isolated hydroxyl groups and broad band at 3554 cm⁻¹ due to hydrogen bonded –OH groups.
Subsequently, in the presence of CO/He (red-dash spectrum), a decline and shift in –OH peaks is noticed, resulting in five distinct O-H vibrations, caused by the interaction of CO with the active –OH species. The reaction between OH and CO also results in a variety of formate and carbonate surface species with vibrations between 3000-2800 cm⁻¹ and 1600-800 cm⁻¹, see inset in figure 1. Remarkably, these intermediates decompose upon exposure with H₂O, and hence restore the –OH groups on the catalyst, see Fig. 1 (blue-dot spectrum).

Similar experiments on ceria rods and particles led to the conclusion that the types of -OH species present are the same for each morphology, but with different relative intensities. Interestingly, the carbon surface species formed during exposure to CO clearly depend on the ceria morphology, as does the water activation and oxide surface re-hydration. Complementary to the FTIR experiments, Raman spectroscopy was performed, revealing the different oxygen storage capacity (OSC) and structural defects of these catalysts attributed to the different crystallographic terminations of ceria. Here we shall give a detailed description of the water activation as a function of ceria nano-shape.

References

**Reduction of Co/CeO₂-ZrO₂ Catalysts: a Quick-XANES Study with Implication for on-board Hydrogen Production by Iso-octane Reforming**

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**Introduction and Objectives**

Ceria-zirconia solid solutions are of great interest in various fields of catalysis thanks to their ability to store and release oxygen under reaction conditions (Oxygen storage Capacity, OSC). [1] Taking advantage of this performance, these mixed oxides have been studied for on-board hydrogen production by catalytic reforming of co-fed gasoline by exhaust-gases through EGR system (Exhaust Gas Recirculation) assuming that adding hydrogen in internal combustion engines would reduce fuel consumption and gas emissions as CO, CO₂, and NOx. [2-3] Additionally, Cobalt insertion in ceria-zirconia (CZ) has proved to enhance hydrogen production in hydrocarbon reforming by improving the reducibility of the mixed oxides. Optimization of these systems requires a precise understanding of their microstructure (speciation and oxidation state) with respect to the metallic elements (Co and Ce) included in their composition in the as-prepared catalysts as well as upon their thermal activation. [4] In-situ time-resolved X-ray absorption spectroscopy experiments in reductive atmosphere (10% H₂/He) has been performed to understand the effect of cobalt insertion on promotion of the reducibility of CZ solid solutions.

**Results and Discussion**

The order/disorder of the oxygen sub-lattice, generated by insertion of low-valence cations (Co²⁺) into the fluorite-like lattice of (Ce,Zr)O₂ is known to be key for promoting the reducibility of CZ solid solutions. Hence, Temperature Programmed Reduction (TPR) experiments have shown that cobalt insertion enhances the reducibility of the (Ce,Zr)O₂ system. In order to elucidate the state of cobalt (inserted or rejected from the lattice) and the reduction properties of the mixed oxides, Quick-XANES spectra of various catalysts made of CZ or Co containing CZ have been recorded at the Ce LIII-edge and Co K-edge during in-situ experiments in hydrogen while increasing the temperature up to 500°C.

A representative example of the reduction of a CZ(58%CeO₂-42%ZrO₂) mixed oxide containing 5wt% Co, i.e. CZ(58-42)Co(5%), is shown in Fig. 1. Quantitative linear combination of individual XANES spectra obtained with a temporal resolution of 1s shows that Ce(IV) is obviously dominant at room temperature while a nearly quantitative reduction of Ce(IV) to Ce(III) is observed at 500°C. Modification of the EXAFS region between room temperature and 500°C confirms a structural change in the CZ matrix after reduction. Co K-edge experiments have shown that cobalt occurs as a combination of isolated Co(II) inserted into the CZ structure and rejected cobalt as cobalt oxide (Co₃O₄). After hydrogen treatment Co is completely reduced to metallic cobalt (not shown here).
Experiments with different Co loadings have shown that the onset of reduction of Ce in CZ occurs at about the same temperature (ca. 200°C) for samples with the same ratio of ceria to zirconia. However, the rate of reduction drastically increases with the Co content and an enhanced proportion of reduced cerium is observed at lower temperature with the presence of inserted cobalt.

**Conclusions**

Quick-XANES spectra obtained with a 1s temporal resolution show that insertion of octahedral Co$^{2+}$ in the Ceria-Zirconia lattice greatly improves the reducibility of the mixed oxides. Moreover, integration of cobalt in the fluorite lattice prevents its leaching from the catalyst for onboard application in EGR. The impact of enhanced reducibility on isooctane reforming for hydrogen production will be discussed.

**Acknowledgments**

The authors acknowledge SOLEIL for provision of synchrotron radiation and express thanks to the staff of the SAMBA beamline for helpful assistance.

**References**

**XPS and in situ XANES Investigation of Nickel-supported Catalysts Applied to Ethanol Steam Reforming**

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**Introduction and Objectives**

Besides the importance of Hydrogen for many industrial processes, it can be crucial to reduce the impact of fossil fuel usage, calling then for new technologies/materials to fulfill its high demand. Catalytic processes can be used for increasing the H₂ production at reduced costs, and among many processes, the ethanol steam reforming is one highly attractive route because the H₂ can be obtained from a renewable source. Many questions about the nature of active sites and catalyst deactivation still remain and, for this reason, it is the aim of this work to study the active phase structure and surface properties of catalysts under each step of reaction (as-prepared, during activation and under _operando_ conditions) in order to control the properties of these materials.

**Results and Discussion**

The Ni-supported catalysts in alumina modified by Zn and/or Co were studied by XANES during the activation process (reduction of NiO). In Figure 1 is shown the _in situ_ Ni K-edge temperature-resolved XANES spectra of the NiCoZnAl catalyst (20-500°C under 5% of H₂ in He), which argue that the reduction of NiO is sensitive to the Zn and Co presence. While the reference NiAl sample starts its activation at ~415°C and lasts 1h40min after that, the addiction of Zn (NiZnAl) decreases significantly this time to 1h keeping the same initial temperature and the Co-modified sample (NiCoAl) presents the same activation time but significantly decreases the initial temperature to ~338°C. The spectra at the reaction’s end indicate different Ni species: while the NiAl spectrum is similar to the NiO albeit with a less intense white line and the Zn presence (NiZnAl and NiCoZnAl) leads to the partial reduction of NiO with a mixture of Ni²⁺ and Ni⁰ sites, only the NiCoAl is fully reduced to Ni⁰. The materials were also characterized by XPS, as summarized by results on Ni 2p₃/₂ region, shown in figure 2, corresponding to the NiCoZnAl catalyst before and after the activation. The peak at 855.3eV, and its satellite at 861.5eV, ascribed to NiO in the as-prepared sample decrease after the reduction. A peak at 852.0eV referring to Ni⁰ and the peaks referring to NiO are present after the activation, which indicate that a mixture of Ni²⁺ and Ni⁰ is obtained, in agreement with the XANES results. The NiCoAl and NiAl samples were completely reduced to Ni⁰ while the NiZnAl presents a residual peak referring to Ni²⁺.
The same degree of reduction is observed from both XANES and XPS, with except of the NiAl sample: the surface sensitive XPS experiment indicates a large concentration of Ni\textsuperscript{0} while XANES indicates only a decrease of the white line of NiO spectra under the used conditions, what indicate that this reduction was performed only at the surface for this sample. Mass spectrometry measurements, simultaneous to XANES, where performed to further understand these differences by following the H\textsubscript{2} production under operando conditions (200-500\degree\textsuperscript{C}, ethanol+water steam). These data confirm the lower H\textsubscript{2} yield for the NiAl sample, which is expected for a non-activated catalyst, as observed by XANES. The comparative analysis indicates that the Zn-modified samples (NiZnAl and NiCoZnAl) present similar H\textsubscript{2} yield at 500\degree\textsuperscript{C} and superior to the non-modified samples. In that conditions, XANES and XPS show a partial reduction of Ni, indicating that the mixture Ni\textsuperscript{0} and Ni\textsuperscript{2\textsuperscript{+}} may be responsible for the catalytic activity in these compositions. At all other temperatures (200 to 450\degree\textsuperscript{C}) the NiZnAl sample presents superior H\textsubscript{2} production.

Conclusions

Combining operando XANES experiments with catalytic tests and XPS analysis it is concluded that the active phase of the NiCoZnAl and NiZnAl is represented by a mixture of Ni\textsuperscript{2\textsuperscript{+}} and Ni\textsuperscript{0}. It is shown that the Zn presence in these catalysts significantly decreases the activation time, and increases the H\textsubscript{2} yield from ethanol steam reforming at 500\degree\textsuperscript{C} compared to the other samples. The Co insertion decreases the temperature for the beginning of the activation in the NiCoAl catalyst.

References

Introduction and Objectives

Biomass is considered to play a fundamental role in our future supply of so-called "green energy". Producing biofuels from these materials proves to be sustainable, given that proper conversion technology is used. As biomass typically contains high amounts of water, dry conversion processes are rendered rather inefficient, due to the required biomass drying.

Since hydrothermal processing does not require dry biomass, it offers great potential for producing biofuels and bio-chemicals from various types of biomass. A prime example for such a process is the hydrothermal gasification of biomass in supercritical water (SCWG), producing mixtures of methane, hydrogen and carbon dioxide. The involved chemistry, performed near and above the critical point of water (T_c = 374 °C, p_c = 22.1 MPa), is of fundamental interest, owing to the exceptional behavior of water under these conditions.

Under SCW conditions, biomass can be converted into a product gas rich in methane, called synthetic natural gas (SNG). A catalyst based on carbon-supported ruthenium nanoparticles was shown to be a highly efficient methanation catalyst under these conditions and has been studied extensively in lab-scale gasification plants [1-3]. Here, model biomass such as glycerol as well as real biomass has been successfully converted into SNG. We have recently shown that the catalyst is fully reduced under these conditions [4]. However, the mechanistic details of the catalyst-biomass interaction, catalyst deactivation and poisoning are still poorly understood.

Results and Discussion

To shed light on these phenomena, we developed a novel continuous flow reactor that allowed us to study the carbon supported Ru catalyst under in situ conditions, using extended X-ray absorption fine structure (EXAFS) spectroscopy. The reactor was constructed from aluminum nitride, a polycrystalline ceramic, able to withstand pressures and temperatures up to 30 MPa and 750 K, respectively. For the first time, we were able to record EXAFS spectra of a supported metal catalyst during continuous operation in SCW. Ethanol (7.5% in water) was chosen as model biomass for SCWG and catalyst activation as well as deactivation by S-poisoning during continuous SCWG were studied at the SuperXAS beamline of the Swiss Light Source (SLS).

During activation between 130°C and 200°C, the catalyst was reduced from as-prepared RuO_2 to metallic Ru. Ru° represents the active state under supercritical conditions and remains fully reduced during SCWG. Fitting of the EXAFS spectra yielded a particle size of about 1.4 nm (55 atoms, based on a spherical Ru particle) for the activated catalyst under SCWG conditions. This corresponds well to particle sizes...
of the as-prepared catalyst observed by TEM, indicating that no significant particle growth took place during activation and gasification.

An EtOH/H₂O feed containing 80 ppm of sulfur in the form of dimethyl sulfoxide lead to a stark decrease in catalytic activity. However, even during prolonged poisoning periods, no bulk sulfidation was observed. Structural data obtained from the EXAFS spectra suggests a stoichiometry of RuS₀.₅ for the poisoned catalyst, corresponding to a sulfur surface coverage of roughly 65%.

Using isotope labeling, the effect of S-poisoning on the catalyst’s surface reactions was studied by batch gasification of MeOH in heavy water. We observed drastic differences in the substitution pattern of methane produced by an active and poisoned catalyst, respectively, suggesting a change in reaction mechanism and binding energies of adsorbed carbon species.

Conclusions

Using a ceramic continuous flow reactor, we were able to record the first in-situ EXAFS spectra of an active catalyst in supercritical water. The structure of the active Ru/C catalyst as well as structural changes due to catalyst poisoning by sulfur species were studied during the SCWG of ethanol. Changes in reaction mechanism and binding energies of adsorbed carbon species were investigated by gasifying methanol in SC heavy water, producing isotope-labeled methane.

Combining the latter technique with EXAFS spectroscopy allows us to directly probe for the nature of adsorbed carbon species on the catalyst’s surface by chemical means, combined with the concomitant acquisition of structural data through EXAFS spectroscopy.

References

Monitoring of the Hydrogenation of Biomass with Online ATR mid-IR Spectroscopy

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Introduction and Objectives

The change from fossil to renewable energy sources such as wood and foliage requires alterations in research as well as industry. Among other challenges, new concepts for process analytics have to be found where established methods are not applicable any more.

Online ATR (attenuated total reflection) spectroscopy with probes has been introduced as a promising alternative for some time, as much because of its adaptability to production sites as because of its applicability at reaction conditions such as high temperatures and pressures. In addition, data acquisition and analysis are carried out in real time, so that the results can be used for process control as well as monitoring. Still, convincing methods to analyse bioconversion processes with online spectroscopy remain to be developed.

The catalytic hydrogenation of glucose (from cellulose) to D-sorbitol (Fig. 1) is a good example of the problems that have to be approached. Both sugars show similar structural features and functional groups, so that a spectral region with high structural resolution should be used. The reaction takes place in water, which rules out NIR (near infrared) because of the strong absorption in this spectroscopic region. A suspended catalyst renders transmission spectroscopy impossible. For these reasons, ATR mid-IR spectroscopy and a multivariate analysis method were chosen as the most promising techniques.

Reaction

The reaction of glucose to D-sorbitol was carried out in water as a solvent. This hinders the further dehydration step to sorbitan.

As a catalyst, ruthenium nanoparticles were stabilised with acidic ionic liquids and fixed on a silica support. The hydrogenation took place in an autoclave at 60 °C with 60 bar of H₂. A gold-coated fibre-optic mid-IR probe with diamond tip was inserted into the reaction mixture for reaction monitoring. To obtain time resolved reference data, the reaction was stopped by quenching after different reaction times and analysed via HPLC.

Figure 1: Hydrogenation of glucose to D-sorbitol and possible further dehydration to sorbitan
Analysis and Results

A quantitative method was developed. Although the glucose and sorbitol spectra are very similar and overlaid with water peaks, an $R^2$ of 99.87% for sorbitol and 99.97% for glucose could be achieved. This quantification method was first used in the analysis of a 24 h run with low conversions up to 20% and compared to the HPLC data collected at different times. The results fit well and confirm the quantification method.

Investigations of the temperature and pressure dependence of the reaction were then carried out with the same quantification method. At higher pressures, the observed rate coefficient, which includes reaction and transport effects\cite{2}, increases while the conversion stays constant. This suggests that the reaction is transport limited and profits from the higher amount of hydrogen available. The temperature variation showed that the reaction becomes faster when the temperature is raised, as was expected. This is also visible from the slope of the decline, which is much steeper at higher temperatures. Experiments also revealed that a catalyst concentration of only 0.003 mol-% (literature: 10 mol-%\cite{3}) referred to the substrate leads to good results.

Conclusions

The comparison of HPLC and IR spectroscopy results for the catalytic hydrogenation of glucose showed that even such similar substances can be quantified when using the right quantification method. The use of an aqueous solution and suspended catalyst particles can be dealt with by applying ATR mid-IR spectroscopy. The high $R^2$ value for the quantification method and the good agreement between the two analytical methods raise hopes that this concept is also adaptable to other bioconversion reactions with the same kind of challenges.

The examination of the pressure and temperature dependence of the reaction showed that both parameters have a strong influence and can help to shorten the reaction time significantly. The acceleration of the reaction with increasing pressure and a constant conversion suggest that the reaction is transport limited. Studies also showed that not only the reaction time, but also the catalyst concentration can be decreased strongly, which is important for a further scale up towards industrial applications.

References

In situ XRD and XAS of the Carburization Process of Tungsten Carbides
Catalysts to Apply in Cellulose Conversion

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Introduction and Objectives
Tungsten carbide has been shown to be an effective catalyst for reactions catalyzed by noble metals such as Pt, Pd and Ru. Besides, it has been reported that catalysts based on tungsten carbides supported on carbon have great potential for biomass transformation [1]. The transition metal carbides are obtained when carbon atoms are incorporated into transition metal interstitial sites. Typically, the transition metal precursor is exposed to a 10-20%CH\textsubscript{4}/H\textsubscript{2} gas mixture, while been heated under controlled flow of the gases and heating rates. Normally, the tungsten carbides formation involves the sequence WO\textsubscript{3}\rightarrow WO\textsubscript{2}\rightarrow W\rightarrow W\textsubscript{2}C\rightarrow WC. Generally, the W\textsubscript{2}C phase is formed around 650-800 °C and the WC above 800 °C [1]. Two important aspects that must be overcome in order to apply tungsten carbides in industrial processes are the severe conditions to promote the carburization process - high temperature and high level of H\textsubscript{2} and/or CH\textsubscript{4} - and the avoidance of carbon deposition on the surface of the active sites. In this work \textit{in situ} XRD and XAS measurement was applied to study the phase transition during the carburization process of tungsten carbides under flow of the diluted H\textsubscript{2}/CH\textsubscript{4}/He gas mixture. In addition, the promoting effect of the Ni in the structural changes of the samples was evaluated as a function of the Ni loading. The surface characteristics were determined by XPS and catalytic properties are evaluated in the cellulose transformation using a batch reactor.

Experimental
The tungsten carbides supported on carbon and promoted by nickel samples were prepared with 30 wt. % of the W\textsubscript{x}C (1\leq x\leq 2) and 0, 1, 2 and 3 wt. % of the Ni by dry impregnation of the chemical precursor on active commercial carbon (Merck). The carburization process was performed at the X-ray diffraction beamline XRD1 at the LNLS-Brazil with energy of the 8keV (λ=1.5498Å), using a furnace installed in the Huber goniometer, a mass spectrometer connected to the outlet of the furnace and one-dimensional Mythen detector. The carburization was carried out under diluted H\textsubscript{2} and CH\textsubscript{4} concentrations due to the restriction to use inflammable gases inside the LNLS. A total flow of 100mL/min of the 1%H\textsubscript{2}/5%CH\textsubscript{4}/He gas mixture was applied under a heating rate of the 8°C/min until 890°C. In this condition each XRD pattern (2θ=30 to 52°) was obtained in 1 min. The same \textit{in situ} studies were performed in the X-ray absorption beamlines XAFS1 and DXAS at the LNLS in the Ni K-edge but using a capillary furnace and total flow of 15mL/min of the diluted gas mixture. The carburization conditions applied to \textit{in situ} XRD analysis were transferred to the carburization reactor and the catalysts have been tested in cellulose conversion using a batch reactor.
Results and Discussion

The in situ XRD results showed that it was possible to promote the carburization to form W2C and WC phases using very low concentration of H2 and CH4. The phase transition sequence in the Wx/C/C sample is WO3 → WO2 → W (Fig. 1, top), but the formation of the W2C, WC1-x and WC phase occurs at the same temperature (∼860°C), and these phases are stable up to 890°C. On the other hand, in the Ni-promoted samples, the carbides phase starts to form at lower temperatures (536, 484 and 448°C, for 1, 2 and 3% of Ni, respectively) (Fig. 1, bottom). The presence of Ni promotes the hydrogen dissociation at lower temperatures and leads to the WOx reduction and WxC formation at lower temperatures. The W2C is predominant and small amounts of Ni6W6C, WC1-x, WC phases are formed. The W2C is stable up to 890°C, which indicates that Ni promotes the stabilization of this phase.

The in situ Ni K-edge XANES results showed that the oxidation state of Ni changes during the carburization process, but it is different from metallic Ni. According to the quantitative XPS analysis, the W concentration increases on the surface in the Ni-promoted samples. The milder carburization conditions applied to in situ XRD analysis were successfully transferred to the carburization reactor and the catalyst has been tested in cellulose conversion. Preliminary results showed that the tungsten carbides catalysts were able to convert 100% of cellulose and acetal is the major yield.

Figure 1: In situ XDR patterns of the tungsten carbides catalysts, top WxC/C and bottom 3%NiWxC/C: ○ W2C; ● W; ★ WC1-x and □ Ni6W6C.

Conclusions

Thanks to the restrictions on the use of pure inflammable gases in the beamlines at the LNLS-Brazil, catalysts based on tungsten carbides supported on carbon were obtained in mild carburization condition of gases: 1%H2/5%CH4/96%He. Nickel was effective in decreasing the carburization temperature, in stabilizing the W2C phase and in increasing the active phase on the surface of the catalyst. Preliminary catalytic reaction showed that the tungsten carbides are active in cellulose conversion.

References


Acknowledgements: LNLS, the Brazilian Bioethanol Science and Technology Laboratory (CTBE) and Rhodia-Brazil.
Intermediate –Energy X-ray Catalysis Research at Advanced Photon Source
Beamline 9-BM

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Introduction and Objectives

It is well-known that XAFS (X-ray Absorption Fine Structure) is a useful “workhorse” technique for characterizing supported 3d and 4d transition metal catalysts. In-situ characterization of many catalytic materials is often not trivial as they typically operate at conditions far from ambient. These conditions typically involve high temperature, treatment with various gases, and the presence of reactants that might not be stable in air and/or moisture. Therefore, in-situ sample cells have to be designed such that the sample is subjected to carefully-controlled conditions before and after the actual experiment at the beamline. This involves the need for specialized equipment and their required infrastructure, such as a mass-spectrometer, furnaces, temperature controllers, gas handling system, exhaust system, flammable cabinets, good glove boxes, etc.

In order to broaden catalysis research opportunities at the APS, significant infrastructure upgrades during FY2009 and FY2010 have been carried out on the APS beamline 9-BM for basic in-situ catalyst studies using XAFS.

9-BM is unique to the APS in that it is the only beamline that can perform XAS experiments at energies as low as 2.1 keV. Reaching the relatively low-energies corresponding to the L-edges of 4d metals (such as Pd and Ag) is easily achieved. In order to probe the L-edges in-situ, a specialized reaction cell is needed. Designing an in-situ sample cell for lower-energy XAFS is more difficult than designing a cell for higher-energy (above 6-7 keV) due to various sources of beam absorption, such as windows and gases. The cell has to be leak-proof while allowing the x-rays to penetrate through to the sample. We demonstrate that the use of an in-situ cell for the “tender” (2.1 keV to 5 keV) energy regime works well at 9-BM and provide some research examples.

Results and Discussion

Supported bimetallic, transition metal catalysts are chosen due to their superior performance, but the nature of the metal interactions and their effect on catalyst performance is not well understood. Using an adaptation of a specially-designed cell[1], capable of reaching temperatures above 500 degrees C while flowing gases over the catalyst, in-situ measurements at the Pd LII and LIII edges (~3.2 keV) were performed on a suite of Pd-M (M = Pt, Au, Cu, Zn) samples in order to determine the changes in the XANES due to alloy formation. In addition, the spectra of the catalysts with adsorbed CO were also acquired. Both alloy and surface bond formation resulted in significant shifts in the XANES shape and edge position. The fact that bimetallic Pd-M catalysts show significant changes in the XANES spectra compared to that of Pd-only catalyst indicates that there is a significant modification of the Pd electronic structure [2]. In Pd-Pt bimetallic nanoparticles, for example, the shift in the energy of the Pt L3 edge is opposite to that at the Pd L3 suggesting some electron transfer between the two metals. L edge XANES are also
strongly modified upon chemisorption, for example with CO [3]. Figure 1 shows the effect of CO adsorption on a selection of alloys.

Conclusions

The successful use of an in-situ intermediate-energy-range x-ray cell has been demonstrated, and has led to new insight about how L-edge XANES for 4d transition metals can aid in determining the role alloy formation has on orbital hybridization, the DOS, and which metals in alloys are more active in bond formations. It is expected that many more experiments of this type will follow.

References


Figure 1. LIII spectra of the catalysts with adsorbed CO. Both alloy and surface bond formation resulted in significant shifts in the XANES shape and edge position.
The Mechanism of Water Reduction/oxidation on Titanium Complexes Assessed by a Multi-technique \textit{in situ} Approach

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Introduction and Objectives

Chemical reaction monitoring with \textit{in situ} and \textit{operando} spectroscopy is a versatile approach for the elucidation of homogeneous and heterogeneous reaction mechanisms. However, in photocatalytic reactions \textit{in situ} spectroscopy is rarely applied. Recently we introduced for the first time coupled \textit{in situ} EPR/Raman spectroscopy to elucidate the mechanism of homogeneous water reduction [1]. EPR spectroscopy detects paramagnetic species (metal ions, radicals), however, structural information is limited. This drawback was compensated by Raman spectroscopy which provides access to the structure of functional groups and coordination. To widen the application potential of \textit{in situ} vibrational spectroscopy for photocatalysis, we developed a dedicated \textit{in situ} ATR-FTIR photocell (Figure 1) which enables future simultaneous Raman and UV-vis spectroscopic measurements. This was used together with \textit{in situ} EPR to study the mechanism of water reduction and oxidation by decamethyltitanocene(III) triflate [Cp*$_2$ Ti(OTf)] (1a) separately. As published by Rosenthal et al. [2] (Scheme 1, blue arrow), water reduction can occur already in the dark, while water oxidation is more difficult and needs activation by light. It is the aim of this work to identify possible reaction intermediates and deactivation pathways.

\textbf{Figure 1.} \textit{In situ} ATR-FTIR spectroscopy setup.

\textbf{Scheme 1.} Elemental steps of photocatalytic water splitting without (blue) and with light irradiation (red).
**Results and Discussion**

During water reduction by hydrolysis of 1a in the dark, [Cp*₂Ti(OH)(OTf)] (2a) is formed and hydrogen is released. Besides EPR spectroscopy, in situ ATR-FTIR investigations revealed the formation of different intermediates. In Figure 2, the corresponding difference spectra (THF-subtracted) during the first 6 h are shown. Upon transformation of complex 1a to complex 2a the band at 1201 cm⁻¹ vanished and the band at 1234 cm⁻¹ was shifted to 1238 cm⁻¹. Moreover, two new bands appear at 1158 and 1221 cm⁻¹, respectively. Currently the assignment of these bands with separately prepared reference compounds is still under study. A characteristic Ti-OH vibration band at 3577 cm⁻¹, as well as a water band at 3500 cm⁻¹ can be detected. The formation of 2a was also confirmed by the absence of any Ti(III) compound (EPR spectroscopy).

To elucidate the light-driven water oxidation step, the photoreaction of 2b was monitored by EPR spectroscopy (Figure 3). Without light, no EPR signal is observed. Under light irradiation, the Ti(III) compound [Cp*₂Ti(OH)₂] (3, $g=1.977$, $A_{Ti}=10G$, $2x_{Ti}=2.2G$, $\Delta B=1.8G$) was formed by Cp*⁻ elimination which is slowly degraded to the Ti(IV) cluster 4. However, recent results indicate that the Ti-OH bond can be cleaved to close the catalytic cycle (Scheme 1). During VIS irradiation of complex 2b, formation of 1b was observed.

**Conclusions**

A dedicated photocatalytic in situ ATR-FTIR cell has been developed and used together with photocatalytic in situ EPR spectroscopy for elucidating the reaction mechanism in homogeneous water splitting with Ti(IV)/Ti(III) compounds. This new ATR-FTIR setup can also be used for solid catalysts. Coupling with fibre-optical probes for Raman and UV-vis spectroscopy will be tested in the future.

**References**


ATR-IR Reveals Different pH Effect on Nitrite Reduction for $Pd/Al_2O_3$ and $Pt/Al_2O_3$

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Introduction and Objectives

Increasing nitrite and nitrate levels in ground water cause environmental concerns and increasingly strict water quality regulations require removal of nitrite and nitrate from ground water. Previously it was shown that hydrogenation of nitrate and nitrite over noble metals is most promising, although initially not much was known about the exact reaction steps in the mechanism.\(^1\) It was shown that in-situ ATR-spectroscopy is a valuable tool to identify adsorbed species on Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ during the hydrogenation of nitrite, which could not be observed before.\(^2\) Clearly, the nitrite mechanism is complex and involves a number of pathways, some of them connected via joint adsorbed species, and leading to ammonia, $N_2$ and $N_2O$. The present study shows that although the reaction pathways on platinum and palladium seem rather similar, the rate determining steps are definitely different, resulting in different reaction selectivity as a function of pH.

Results and Discussion

Thin catalyst layers of either 5 wt% Pt/Al$_2$O$_3$ or Pd/Al$_2$O$_3$ were immobilized on ZnSe Internal Reflection Elements (IRE). After calcination and reduction, the catalyst film was ready to be used. Attenuated Total Reflection Infrared (ATR-IR) spectra were recorded with a Tensor FTIR spectrometer (Bruker) at room temperature using a home built stainless steel flow through ATR-cell.\(^3\) After assembling the ATR-IR cell with the coated IRE, the cell was flushed with H$_2$/H$_2$O to reduce the catalyst in-situ at pH values corresponding to the subsequent experiments. After flushing, a solution of $4.3 \times 10^{-4}$ mol.L$^{-1}$ NO$_2^-$ (aq) was introduced to the cell at the same pH to follow the consumption of pre-adsorbed hydrogen. Subsequently, the newly formed adsorbates were reduced by exposing the catalyst to H$_2$/H$_2$O.

As a typical example, Figure 1a shows the in-situ ATR-IR spectra for the adsorption of nitrite on reduced $H$-Pd/Al$_2$O$_3$ at different pH. Figure 1b and c show the integrated intensities of the surface species observed as a function of time for pH 5 and 9. The most striking differences are observed when the pH was decreased below 6. The amount of adsorbed NO largely increased with lower pH, and adsorbed NO$_x$ species were observed. On both Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ a clear influence of pH is observed on adsorption and subsequent hydrogenation of nitrite in water (not shown here).
For H-Pt/Al₂O₃ larger amounts of reaction intermediates like NO₃⁻ steps at 1620 cm⁻¹ and faster hydrogenation rates were found at lower pH explaining the higher TOF at lower pH as reported in literature. On H-Pd/Al₂O₃ the effect of pH on selectivity is controlled by the rate constants of formation and subsequent hydrogenation of the most stable reaction intermediates to N₂ (NO (ads) and NH₄⁺ (NH₂ (ads)).

In this contribution the differences and similarities between adsorption and hydrogenation on both catalysts will be discussed and an improved reaction scheme will be presented.

Conclusions

This ATR-IR spectroscopy study shows that the change in selectivity with pH observed during nitrite hydrogenation over palladium catalysts in batch reactors is directly related to changes in individual rate constants for the formation and hydrogenation of the most stable surface intermediate species. For H-Pt/Al₂O₃ the situation is more complex because of entangled reaction paths that influence each other intriguingly.

References

On the Role of Palladium Hydride in Selective Nitrile Hydrogenation Over Pd Nanocatalysts

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\section*{Introduction and Objectives}

Food security is a major global challenge, with world population growth of 45\% predicted by 2050. Increased crop productivity is essential to meet this need, particularly in developing countries, necessitating next generation pesticides/fertilisers. Selective nitrile hydrogenation is a key source of primary amines, which form the active ingredient in many herbicides used in crop protection.\textsuperscript{1} Nitrile hydrogenation is also employed in dye, solvents, agrochemicals, pharmaceuticals and pigment manufacture. Conventional processes use hazardous reagents e.g. pyrophoric LiAlH\textsubscript{4}, hence there is great academic and industrial interest in developing heterogeneous clean catalytic technologies for these selective hydrogenations. While significant progress has been made in enhancing catalyst activity and selectivity for such reactions, deactivation hinders their commercial implementation.\textsuperscript{2} Catalytic hydrogenation of unsaturated nitriles is difficult, with low selectivity to the unsaturated primary amine common (Fig. 1).\textsuperscript{3} Pd nanoparticles (NPs) are promising catalysts, but require improved activity and selectivity.

Recent model studies of Pd-catalysed alkene/alkyne hydrogenation suggest a subtle interplay between interstitial PdH and PdC formation and resulting selectivity;\textsuperscript{4} in-situ PdH formation promotes C=C hydrogenation, while PdC genesis suppresses subsurface H\textsubscript{s}, turning off this undesired reaction pathway. Pd-βH stability is also particle size dependent, with Pd metal favoured for small NPs thus reaction selectivity may be expected to be particle size dependent.\textsuperscript{5,6} Here we report on the impact of reaction-induced catalyst restructuring/phase transitions during liquid phase nitrile hydrogenation over supported Pd NPs and investigate whether the formation of stable hydrides can be correlated with selectivity towards amine formation.

\section*{Results and Discussion}

Operando Pd K edge XAS measurements were performed using our purpose built liquid reaction cell (Fig. 2),\textsuperscript{7} in which our Pd/C catalyst was circulated in a methanol slurry prior to solvent saturation with 2 bar H\textsubscript{2}. Solvent and hydrogen-induced catalyst restructuring was monitored by time resolved Pd K-edge XAS. Palladium was stable under methanol, but XANES reveals progressive reduction of the initially partially-oxidised Pd nanoparticles, with EXAFS analysis demonstrating a coincident expansion of Pd-Pd scattering distances, which we attribute to hydride formation. The introduction of crotononitrile, and co-

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{Crotononitrile hydrogenation pathways}
\end{figure}

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incident consumption of hydrogen, initially reverses this expansion, possibly reflecting extraction of interstitial hydrogen or PdC formation. These structural transitions have a profound impact on selective nitrile hydrogenation. Complementary in-situ XPS measurements of crotononitrile adsorption and thermally-induced hydrogenation versus decomposition pathways shed valuable insight on the surface reaction mechanism and coke deposition.

Conclusions

Operando XAS measurements of liquid phase crotononitrile hydrogenation over supported Pd catalysts reveal reactant-induced restructuring structural accompanying hydride and carbide formation, and surface coking. Selectivity towards C=C versus C≡N hydrogenation is discussed with respect to the resulting structure-function relationships.

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Design and Optimization of a Flow-through ATR-FTIR Cell for Transient and Modulated Operando Experiments

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Introduction

Attenuated total reflection (ATR) infrared (IR) spectroscopy is a powerful tool for the investigation of reaction pathways in solid(catalyst)/liquid(reactive) systems, because it provides the detection of species adsorbed on a catalyst under reaction conditions. However, the presence of strongly absorbent solvents, spectator species and/or the catalyst itself can make very difficult or preclude the identification and tracking of the true active species, that is, the reaction intermediates. Then, transient experiments are widely applied in the analysis of reaction intermediates by perturbing a catalytic system working under steady state conditions (ss). More recently, modulation excitation spectroscopy (MES) with phase sensitive detection (PSD) have proved to be an adequate methodology to separate a weak response from a strong background signal [1]. MES experiments are based on the disturbance of a ss system by the periodical variation of an external parameter such as the temperature, the pressure, or the concentration of a reactant. Therefore, all the species in the system that are affected by this parameter will also change periodically with the same frequency of the perturbation, but with a phase lag. Thus, MES, coupled with PSD analysis, applied to in situ ATR-IR experiments can allow the sensitive and selective detection of species directly involved in a reaction at the liquid/solid interface, and the monitoring of their dynamic behaviors.

In this work we present an optimized design of a flow-through ATR cell for transient and operando-modulated experiments in the solid-liquid interface. Examples of application are also shown [3].

Results and Discussion

An optimized flow-through ATR cell was designed and constructed considering the following requirements for a proper operation of the transient/MES experiments: a) the volume of the cell should be small enough to allow a rapid exchange of reagents, in order to perturb the system in a wide range of frequencies; b) the concentration profiles and speed of the fluid into the cell should be as flat as possible to simplify data analysis, and c) the length/width ratio should be such that resembles a plug flow reactor.

To this end a series of 3D simulations of the flow into the cell with different geometric configuration were carried out by using PETSc-FEM, a parallel multiphysics code primarily targeted to 2D and 3D finite elements computations on general unstructured grids [2]. Particularly, the geometry of the inlet and outlet ports, as well the height of the cell were optimized to avoid dead volumes and prevent backflow zones. As an example, Figure 1 shows the calculated flow lines in one of the geometries considered. Once optimized, the body of the cell was micro-mechanized in 316L stainless steel. The cell was fitted with a 45° trapezoidal AMTIR crystal (80 x 10 x 4 mm), providing 10 internal reflections at the liquid/crystal interface. The crystal was fixed to the cell body by means of a Viton O-ring, defining a total volume of the cell of 60 µL. The temperature of the cell was controlled by a thermostatted water bath (±0.5 K) connected to the liquid-jacket drilled in the stainless steel cell body. A FTIR spectrometer Nicolet 8700 (Thermo-Electron) with a cryogenic MCT detector was used to collect time-resolved IR at a resolution of 4 cm⁻¹ (up to 50 scans/sec).
Transient and modulation-concentration experiments were performed by flowing solvents or dissolved reactants by means of a peristaltic pump located at the end of the cell. A pneumatically actuated three-way valve controlled by a computer software allowed to switch the stream of reactants. Repetitive square-wave stimulations with flow rates from 0.5 to 2 mL/min and modulation frequencies up to 200 mHz could be generated into the ATR cell with this experimental setup. Axial-mixing was not detected changing between soluble (iso-propanol/water) insoluble (carbon tetrachloride/water) solvents.

The performance of the ATR cell was checked by carrying out MES-concentration experiments on: i) the activation of acetic anhydride on a heteropoly-acid catalyst, and ii) the changes of the secondary structure of a lipase protein by exposing it to solvents with different hydrophobicity (log P).

**Conclusions**

The optimized design of a flow-through ATR cell allow performing transient and modulated experiments to investigate the reaction intermediaries and system changes. Results obtained in the selected examples showed that: i) acetic anhydride is decomposed on the a heteropoly-acid catalyst producing very reactive acetyl species (which IR bands can be observed after PSD analysis of the spectra) [3], and ii) very subtle changes in the secondary structure of a lipase by contact with solvents could be observed in the Amide I band.

**References**

In situ Real-time Attenuated Total Reflection FTIR Spectroscopy for Monitoring Glycerol Carbonate Synthesis

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Introduction and Objectives

Glycerol is a renewable and inexpensive raw chemical, which use depends on its efficient conversion to value-added materials. In particular, glycerol carbonate and its derivatives have received increasing attention during the last years due to their potential end use as solvent and for plastics. The synthesis of glycerol carbonate by carbonylation of glycerol was studied by in situ Attenuated Total Reflectance FTIR spectroscopy [1]. Urea is a particularly attractive carbonylating agent to be used in this reaction due to the mild reaction conditions and high selectivity [1,2]. To carry out these experiments cobalt oxide nanoparticles, Co\textsubscript{3}O\textsubscript{4}, hierarchically dispersed on zinc oxide microparticles, ZnO, were used as catalysts. They were deposited on a diamond internal reflection element incorporated in a heated base plate, and the reaction carried out in a home made liquid cell. In situ real-time ATR-FTIR spectroscopy is a valuable tool for monitoring reaction progress and analyzing the reaction mechanism of the synthesis of glycerol carbonate.

Results and Discussion

The present work demonstrates that Co\textsubscript{3}O\textsubscript{4}/ZnO catalysts show differences in reactivity during the carbonylation reaction of glycerol with urea monitored by ATR-FTIR spectroscopy. Figure 1 plots the evolution during reaction at 145 °C (4 hours) of the most representative bands of urea (reactant) at 1664 cm\textsuperscript{-1}, glycerol urethane (reaction intermediate) at 2843 cm\textsuperscript{-1} and glycerol carbonate (product) at 1791 cm\textsuperscript{-1}, using the RT-10CoZn catalyst. The characteristic band of urea decreases initially rapidly with reaction time, reflecting its consumption; concomitantly the band corresponding to glycerol carbonate increases with time, evidencing the formation of this reaction product. During ca. the first hour of reaction time, the characteristic band of the reaction intermediate (glycerol urethane) follows a trend similar to that corresponding to the product; thus the glycerol urethane forms quickly and then is converted rather slowly into the glycerol carbonate product. This confirms that the urethane is an intermediate in the formation of the carbonate and agrees with the mechanism suggested for this reaction [2]; the fast step of the reaction is the conversion of glycerol to glycerol urethane and the slow step of the reaction is the conversion of glycerol urethane to glycerol carbonate. Glycerol urethane intensity passes through a maximum with reaction time; while the glycerol carbonate signal
keeps on increasing with reaction time. Further insight is illustrated in Figure 2 where the evolution of the bands at 1716 cm⁻¹ (glycerol urethane intermediate) and at 1664 cm⁻¹ (urea reactant) defines an isosbestic point at 1690 cm⁻¹. Such an isosbestic point underlines that the conversion of urea to glycerol urethane is direct, with no other reaction intermediate during this first step of reaction [3]. At 115 min time-of-reaction glycerol urethane (intermediate) begins to be fully converted into the product, however, the signal of glycerol urethane remains constant. It is an equilibrium-limited reaction due to the fast reversible conversion of glycerol and urea to glycerol urethane [4]; glycerol urethane will be present (and monitored) as long as ammonia remains in solution. Thus, a combination of NH₃-limiting conditions and of a slow second reaction step to form the carbonate would account for the presence of glycerol urethane intermediate for such a prolonged period after the initial rapid concentration changes.

![Figure 1](image1.jpg)

![Figure 2](image2.jpg)

**References**


Modelling and Optimization of IR Cell Devoted to in situ and Operando Characterization of Catalyst

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Introduction

The characterization of catalyst in reaction conditions is widely used at laboratory scale and provides useful information that generally leads to the proposition of reaction mechanisms. Infrared spectroscopy is very powerful due to the high sensibility to adsorbed species detection. Both transmission and DRIFT modes can be used and generally the specific geometry of the sample in transmission mode (wafer of catalyst) appears far from an ideal plug flow reactor. However few studies deal with the optimization of this category of reactors [1]. The present study combines response time distribution measurements and modelling of different reactor geometry. Two types of reactors in particular are compared with two different geometries: a circular pellet and a square pellet with a specific sample holder.

Experimental

γ-alumina obtained by sol–gel method using alkoxide precursors was used to make the pellet. The catalyst was loaded in the IR cell and connected to an automatic setup which allowed the transient pulse of N₂O in helium during 2 seconds at 25°C, 10 mL/min and atmospheric pressure. A quadruple mass spectrometer was connected either at the entrance of the cell or at the exit of the cell. Modelling of the cell was performed by means of Comsol software, version 3.5a with Chemical Engineering Module, and version 4.0, using 3D geometry. Gas flow was firstly treated by steady-state incompressible Navier-Stokes equations, followed by transient modelling of convection and diffusion.

Results

Two configurations of the sample holder were used in this study, Figure 1. The circular geometry is similar to other operando reactors using FTIR transmission spectroscopy described in the literature [3]. A cylindrical body made of stainless steel maintained a cylindrical wafer of catalyst, 16 mm of diameter and about 40-60 μm of thickness. Only one quarter of the actual cell is represented because of the symmetry of the reactor. Alternately, we developed a square geometry for the sample holder. In this case, the self-supported sample was square wafer of catalyst with 12 mm edge. Half of the wafer holder is represented for the modelling because of the symmetry of the reactor. The Reynolds number was calculated to determine the character of flow in the cell, by taking into account the places where the gas velocities were highest (entry and exit holes). These values are lower than 1, therefore the consideration of laminar flow remains valid for both geometries. Profiles of gas velocity obtained from modelling with module CFD clearly discriminates both geometries. The distribution of gas velocity near the
circular wafer suggests that the construction of the circular reactor is far from ideal. By contrast, this deviation was corrected when a square geometry was used.

The transient pulses of N₂O were modelled and compared to experimental signals (Figure 2). As observed, a good agreement between experimental and theoretical signals is obtained and it can be related to the volume of the sample holder, geometry and dispersion of the gas into the cell. The existence of dead volumes is highlighted by the observation of a tailing peak in the experimental and modelled curves. This effect is a little bit more marked in the circular geometry, which can be related to the presence of complex hydrodynamic phenomena.

The relative importance of dead volumes was also evaluated and suggested that the inlet and outlet of square geometry could be improved. Alternately, the tracer’s concentration was measured in the reactor in selected areas in order to estimate the local concentrations during pulses of N₂O. Finally, the consequences of the geometry to the amount of adsorbed species will be examined in future for further applications in operando IR spectroscopy.

**Conclusion**

The design of operando reactors is a key point for further development of infrared spectroscopy applied to kinetic measurements. The comparison of the two geometries clearly underlines that a deviation of gas velocity is put into evidence near the catalyst surface when a classical circular geometry is used. The new design with square geometry leads to a significant improvement with homogeneous gas velocity.

**References**

Development of a New in situ FTIR Reactor for Operando Studies in Photocatalysis

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Introduction and Objectives

For many years, photocatalysis has been proposed as one of the promising techniques to abate environmental pollutants. There are, however, still some issues to be resolved before this technique can have a major influence on today’s society. One of those issues is the improvement of the currently obtained catalytic efficiencies. For this, it is vital to know the reaction mechanism of the photocatalytic degradation, an area where \textit{operando} spectroscopy is vital. The main objective of this work was thus to develop a versatile Fourier Transform infrared (FTIR) \textit{in situ} reactor that enables the study of the catalyst surface at the very moment the reactions are occurring on that surface.

One of the major issues to be considered when working with \textit{operando} studies for photocatalysis, is the fact that the catalyst must be activated by light, commonly UV light. It is therefore important that the used spectroscopic technique does not interfere with the necessary UV light. Most of the currently described reactors, however, avoid this issue by first activating the catalyst, after which FTIR measurements are performed to obtain data of the adsorbed species, e.g. [1]. This is in fact not really \textit{operando} and must thus be avoided in the study of reaction pathways. Other reactors, however, do comply with the \textit{operando} aspect, but use an external UV lamp making them prone to damage (due to the use of quartz [2]). In order to avoid all the aforementioned problems, we chose to work with an internal UV light source: namely, UV LEDs (375 nm; 10 mW at 20 mA; Roithner LaserTechnik), which makes it possible to illuminate the catalyst while it is recorded.

Once the reactor was built, it was validated by using it to investigate the photocatalytic reaction mechanism of nitric oxide (NO) [3] and comparing these results with those already described in literature [4]. After validating this new reactor, it was then used to elucidate the reaction pathways of some simple volatile organic model compounds, like ethylene [5] and acetaldehyde [6].

Results and Discussion

The aim of this study was to develop, validate and use an FTIR \textit{in situ} reactor that can be used in the research of photocatalytic reaction mechanisms. A cylindrical reactor design (\(\varnothing = 50\) mm) was chosen because of its low amount of dead volume. It was completely made of stainless steel 316 (Caseo), for its low adsorption properties. Further details of the reactor can be found in Figure 1, which shows a schematic diagram of the as developed reactor [3].
After its validation with NO, the reactor was used to elucidate the photocatalytic reaction mechanism of ethylene degradation. This new approach revealed some exciting new insights in the photocatalytic oxidation reaction of ethylene. It was, for instance, found that there is a change in dipole moment of the ethylene molecule when it is brought close to the catalyst. From this finding, a hypothesis was formulated on how the CC-bond of ethylene will break. This hypothesis was then confirmed by the obtained data, showing the great potential of the newly developed FTIR \textit{in situ} reactor.

Conclusions

The internal UV illumination, provided by the UV LEDs, makes it possible to study the photocatalytic reactions \textit{in situ} with real time monitoring under realistic conditions of temperature and pressure, which was proven in unravelling the reaction mechanism of some simple organic pollutants, like ethylene.

References

In-situ Quantitative Identification of Intermediate Species During the Genesis of Active Phases in Cobalt Fischer-Tropsch Catalysts

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Introduction and Objectives

Fischer-Tropsch (FT) synthesis produces ultraclean alternative fuels from renewable and fossil resources. The catalytic performance of cobalt FT catalysts is a function of cobalt dispersion, reducibility and stability of active phases under operating conditions. The catalysts are typically prepared by impregnation, followed by calcination in oxidizing atmosphere and activation in hydrogen. Previous reports \cite{1, 2} suggest that decomposition of cobalt nitrate is a decisive step in the genesis of active phase and could involve several short-living intermediate species. These intermediate species could influence nucleation, growth and sizes of cobalt oxide nanocrystallites. The ex-situ characterisation however, could not provide any detailed information about the structure of these intermediates and exact conditions of their emergence in the catalysts. Note that identification of unknown intermediate species is a challenge for many chemical reactions and usually requires in-situ highly sensitive and time-resolved techniques.

In the present work, in-situ quick X-ray absorption spectroscopy (QXAS) in combination with other in-situ and ex-situ techniques has been used to monitor the transformations of dispersed phases in silica-supported cobalt catalysts prepared using either activation under 5\%NO/He or sub-stoichiometric addition of sorbitol.

Silica-supported cobalt catalysts were prepared by incipient wetness impregnation with a Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O aqueous solution, yielding 10\% cobalt loading after reduction. In several catalyst syntheses, sorbitol and/or ruthenium nitrosyl nitrate were added to the impregnating solutions. Thermal activation was performed with a ramping rate of 2°C.min\textsuperscript{-1} up to 400°C in presence of air, He or 5\%NO/He. The catalysts were characterized using ex-situ techniques: XRD, DSC-TGA, TPR, TEM. The in-situ QXAS combined with simultaneous Raman measurements was collected at the Co and Ru absorption K-edges in the transmission mode on the SAMBA beamline (SOLEIL synchrotron, France) with a time resolution of 500 ms. The FT performance of the catalysts activated in hydrogen was measured in a fixed bed reactor at 220°C and H\textsubscript{2}/CO=2.

Results and Discussion

It is uncovered that cobalt nitrate decomposition in air or helium proceeds via formation of dehydrated species at 140°C. These species convert into Co\textsubscript{3}O\textsubscript{4} crystallites below 200°C. In diluted NO, dehydration remains the first stage of Co(H\textsubscript{2}O)\textsubscript{6}(NO\textsubscript{3})\textsubscript{2} decomposition. However, in contrast to activation in air or He, an intermediate cobalt (II) hydroxynitrate phase is detected by both XANES and EXAFS above 110°C, before the formation of Co\textsubscript{3}O\textsubscript{4}. The quantitative identification of cobalt hydroxynitrates by QXAS was consistent with in-situ Raman data and ex-situ XAS and XRD measurements. The presence of cobalt (II)
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Hydroxynitrate was further confirmed using FEFF modelling. Cobalt (II) hydroxynitrate formation in diluted NO is explained by a reaction between partly hydrated cobalt (II) nitrate and NO below 100°C. The hydroxynitrate decomposition leads to the oxide nuclei which contribute to enhancement of the metal oxide dispersion. The effect of calcination atmosphere (air, He or NO) on cobalt dispersion was more significant when the catalysts were activated at lower temperatures. Enhancement of cobalt dispersion in calcined silica-supported catalysts was also observed when sorbitol has been used for catalyst preparation. A combination of characterisation techniques did not detect any complexes between sorbitol and cobalt ions in the impregnating solutions and in the impregnated catalysts. The in-situ XANES/EXAFS data are indicative of higher temperature of cobalt nitrate decomposition in the presence of sorbitol. It seems that organic acids produced during sorbitol oxidation interact with cobalt ions and stabilize cobalt precursor. The in-situ QXAS at Ru K-edge suggests incorporation of Ru ions into mixed CoRu oxides in the calcined catalysts, better catalyst reducibility and formation of CuRu bimetallic particles in the reduced catalysts. The FT catalytic performance data of the catalysts activated in diluted NO or prepared with sorbitol addition were consistent with cobalt dispersion data. The highest hydrocarbon productivity was observed with Ru promoted catalysts which combine both higher cobalt dispersion and reducibility.

Conclusions

In-situ time-resolved QXAS allowed identification of intermediates of cobalt nitrate decomposition in silica supported FT catalysts. Addition of sorbitol during catalyst impregnation or calcination in diluted NO introduced additional sites for cobalt oxide nucleation and led to higher cobalt dispersion in the resulting catalysts. A strong impact on cobalt reducibility and catalytic performance in FT synthesis was observed.

References

Operando IR Measurements of CO Oxidation over Bifunctional Catalysts: Microwave vs. Conventional Heating

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Introduction and Objectives

Microwave heating has been known for some time for its benefits in organic syntheses [1]. More recently, the use of microwave heating in heterogeneous catalysis has attracted much interest, with several publications reporting an enhancement of the reaction yields, changes in selectivity, as well as reduction of the bulk reaction temperature compared to conventional heating [2]. Possible explanations were attributed to the creation of different temperature regimes in the reaction system, with the formation of hot-spots due to selective heating by microwaves [2,3]. Surface phenomena in heterogeneous catalysts during microwave irradiation still need clarification. Infrared operando spectroscopy is a useful technique for the study of the dynamic behaviour of the catalytic system under real working conditions [4,5]. In the present work, a reaction cell was developed coupling microwave heating with IR analysis. Such association is interesting since it can introduce a very sudden change in the reactional system by means of a temperature pulse, which can provide new insights into the influence of microwaves on reaction mechanisms and selectivities.

Experimental

A microwave cavity was constructed for in situ IR spectroscopy studies performed while the sample is irradiated with microwaves at a frequency of 5.8 GHz. The microwave cavity is connected to the microwave generator through a waveguide and is then placed inside the spectrometer. The reactant flow gases fed to the reactor cross the sample, in the form of a self supported wafer placed in the middle of the microwave cavity, and are then analyzed in an IR gas cell. The reaction cell was tested using the CO oxidation reaction with a bifunctional catalyst of 1 wt.% Pt on a BEA zeolite (Si/Al ratio of 12.5).

Results and Discussion

CO oxidation was first performed using conventional heating in an operando cell as developed by Saussey et al.[6]. Total CO conversion was achieved by 150°C, evidenced by the decrease of the band corresponding to the CO in the gas phase at the expense of the CO₂ band. When analyzing the catalyst surface spectra during the course of the reaction, the peak at 2078 cm⁻¹ assigned to linearly adsorbed CO on metallic Pt decreases with increasing temperature, until its complete disappearance. In the ν(OH) region, the 3745 cm⁻¹ band, Si-OH groups, shifts to lower wavenumbers in a linear correlation with respect to the variation in the catalyst temperature. When using the same flow conditions (GHSV) under microwave irradiation, total CO oxidation was achieved after an irradiation time of 1.5 min (100 W), as evidenced by the disappearance of the CO-Pt band on the sample spectra. Moreover, when suspending microwave irradiation, this band was recovered, meaning that the sample was in fact rapidly heated without
major modifications such as metal sintering or framework destruction. Determination of the local temperature under microwave conditions was performed using the modifications observed in specific IR bands, since the use of conventional thermocouples is avoided due to interferences with the electromagnetic field. Given that heating the sample causes the redshift of the 3745 cm⁻¹ band, the correlation obtained under conventional heating was used for the determination of the temperature achieved during microwave irradiation. In these conditions, a 2 cm⁻¹ shift was obtained which is consistent with a catalyst temperature of about 230°C.

These results confirm the ability of microwaves to induce rapid variations in the sample and, consequently, in the reaction temperature and furthermore the suitability of this reactor for performing operando studies of catalytic systems. Experimental setup will be dedicated to the study of more complex reactions, such as hydrocarbon cracking and isomerisation, in order to investigate possible differences in reaction mechanisms when using microwaves instead of conventional heating.

Figure 1: Sample spectra in the ν(CO) region and redshift of the 3745 cm⁻¹ band in the ν(OH) region.

References
Tip-Enhanced Raman Spectroscopy, a Novel Approach to Study a Catalytic Reaction In-Situ

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Introduction and Objectives

Tip-Enhanced Raman Spectroscopy (TERS) is a very promising technique in the field of catalysis. The optical resolution of TERS is limited by the tip-apex rather than the wavelength-dependent optical diffraction limit, which makes it possible to study catalytic reaction on a molecular level. We describe the first time-resolved investigations of TERS for use in heterogeneous catalysis by using the photo-catalytic reduction of p-nitrothiophenol in a self-assembled monolayer (SAM) as a probe reaction. [1]

Results and Discussion

The photo-reduction of p-nitrothiophenol is well studied in the field of Surface-Enhanced Raman Spectroscopy (SERS). It occurs only in the presence of both a SERS-active silver catalyst and excitation with a green laser. [2,3] In its adaption to a TERS experiment, a silver-coated tip acts simultaneously as both the catalyst and the means of observation (or enhancement) of the molecules on the sample surface.

Conclusions

By employing TERS rather than SERS, the observation area is scaled down to an area with 10-20 nm in diameter. [4] This extremely small observation area has enabled us to observe molecular dynamics within the SAM, and can potentially be used to study e.g. molecular processes on a single catalytic particle.

References

In-situ DRIFT Study of Formic Acid Decomposition on Bulk Metal Catalysts

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Introduction and Objectives

The trends in catalytic reactivity for varying pure metals have been used in the design of bimetallic catalysts for the purpose of optimizing the activity of related reactions.¹ For example, the seminal work of Sachter-Fahrenfort reveals a volcano curve for the plot of reactivity of metals for formic acid decomposition vs. the stability of reaction intermediates (i.e. the bulk heat of formation of the formate²). This seminal study, however, employed non-specific reaction rates and bulk properties to develop the volcano curve. It is, thus, critical to revisit this classical reaction system with a modern approach where the overall reaction rates are normalized as turnover frequency (TOF-1/s) and the stability of the surface reaction intermediates are employed in developing a volcano curve.

In this modern study, the specific overall reaction rates for formic acid decomposition (TOF) were correlated with the thermal stability of the surface reaction intermediates over a series of metal catalysts with the assistance of (1) thermal gravimetric analysis (TGA) for quantifying the number of surface catalytic active sites, (2) in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to determine the nature of the surface species (3) temperature programmed surface reaction (TPSR) spectroscopy and in situ DRIFTS to determine the thermal stability of the surface reaction intermediates, and (4) specific overall reaction rates.

Results and Discussion

The unsupported metal catalysts investigated were the same ones employed in the classical Sachter-Fahrenfort study (Cu, Co, Fe, W, Ag, Ni, Au, Pt, Pd and Ru)² and formed via reduction of their respective metal oxides. Formic acid was obtained from GT& S INC as 2000 ppm in He and the chemisorption temperature varied from 40-100 °C and physisorbed HCOOH was removed by flushing in He for 20 mins. The number of surface metal sites was quantitatively determined with formic acid chemisorption in a TGA (Cahn Model TG-131). The HCOOH-TPSR spectroscopy experiments were performed on an Altamira temperature programmed system (AMI-200) equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). The thermal stability and decomposition rates for the surface reaction intermediates were determined with HCOOH-TPSR and in situ DRIFTS. The in situ DRIFTS measurements were conducted with a Thermo Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis accessory (model DRA-2) and a Harrick reaction chamber HT-100. The IR spectra were recorded during formic acid chemisorption and thermal decomposition of the surface species. The catalysts were heated at the rate of 10 °C/min and the IR spectra were recorded every 1-2 minutes (15-20 °C).

The in situ DRIFTS studies reveal that surface reaction intermediates are present as bridged surface formates on Fe, Ru, Pt, and Au; monodentate surface formates on Pd, Co and Ni form; and monodentate surface formates initially form on Cu and Ag, but convert to bridged surface formates at higher temperatures.³⁴ No relationship was found between the surface formate decomposition temperatures and the bulk M-OOCH heats of formation indicating that bulk M-OOCH heats of formation are not the proper metrics.
to attempt to correlate with surface reactions. In addition, no relationships exist between the nature of the surface formates, monodentate or bridged, and their surface decomposition temperatures. An inverse relationship, however, was found to exist between the TOF values for formic acid decomposition and the thermal stability of the surface formates.

**Conclusions**

These modern results demonstrate that a volcano-type relationship does not exist for HCOOH decomposition on metals when the proper metrics of TOF and surface formate thermal stability values are employed in constructing the classical volcano plot. Thus, the classical formic acid decomposition volcano curve is just a consequence of the incorrect metrics employed for the specific activities for formic acid decomposition and bulk M-OOCH heats of formation.

**References**


**In situ XAS and APPES Characterization of Bimetallic LaNi$_{1-x}$Co$_x$O$_3$ Perovskite Catalysts Active for CH$_4$ Reforming Reactions**

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The recent discoveries of natural gas (as shale gas and others) have renewed the interest in the reforming of methane. As an endothermic reaction, high temperatures are required, being the coke formation and the deactivation of catalysts the main problems for industrial practices. Although nickel or cobalt as active phases are the best candidates, these metals present also some disadvantages: the Ni produces an important coke deposit; while the Co is less resistant to oxidation under reaction conditions [1]. We have focused the study to bimetallic Ni-Co systems supported on La$_2$O$_3$ prepared by reduction of a LaNi$_{1-x}$Co$_x$O$_3$ perovskite.

**Experimental**

The LaNi$_{1-x}$Co$_x$O$_3$ perovskites were prepared by the spray pyrolysis method [2], using a solution of La(NO$_3$)$_3$ and Ni(NO$_3$)$_2$/Co(NO$_3$)$_2$, which is passed through two on-line furnaces at 250°C and 600°C respectively, producing a powder that was later calcined in air at 600°C. The physicochemical state of the powders was characterized by means of SEM, XRD, TPR, XPS, etc. The measurements of the catalytic performance in the DRM/SRM reactions were accomplished using an atmospheric flow reactor. The feed gas was a methane/carbon dioxide (or water)/helium mixture with a space velocity of 300000 ml/hg. XAS spectra were collected in transmission mode at the BM25 station of the ESRF (Grenoble, France), while the Ambient Pressure Photoemission Spectroscopy (APPES) experiments were performed at beam line U49/2-PGM1 at BESSY II (Berlin, Germany).

**Results/Discussion**

The nickel phase in the reduced LaNiO$_3$ and LaNi$_{0.5}$Co$_{0.5}$O$_3$ samples, analyzed by operando XAS, evolves from a mixture of Ni$^{3+}$ and Ni$^{2+}$ to metallic Ni0 under both, hydrogen reduction treatment and DRM reaction. This behavior contrasts with the partial oxidation of nickel observed under SRM reaction [3]. The results obtained by in situ XAS for Co phase for DRM and SRM in the LaCoO$_3$ and LaNi$_{0.5}$Co$_{0.5}$O$_3$ reveal that in both cases the cobalt phase is partially oxidized, remaining visibly less oxidized in the LaNi$_{0.5}$Co$_{0.5}$O$_3$ than in the monometallic catalysts. These results could be explained considering the formation of a NiCo bimetallic alloy after hydrogen reduction of the original Ni-Co perovskite.
The APPES spectra obtained for the LaNi$_{0.5}$Co$_{0.5}$O$_3$ sample submitted to a hydrogen reduction treatment agree with the XAS results. The differences observed in the spectra obtained for the LaNi$_{0.5}$Co$_{0.5}$O$_3$ sample during a treatment with H$_2$ at 600°C with two different photon energies (200 and 600 eV, related respectively with the surface and bulk composition of the metallic particles), allow us to propose a structure for the bimetallic particles, where the metals are arranged as a “pseudo core-shell” Ni@Co.

References
Study of the Oxidation by Water of Au/CeGaO$_x$ Catalysts Active in the WGS Reaction

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Introduction and Objectives

We have investigated the synthesis and catalytic activity of catalysts supported on CeGaO$_x$ mixed oxides, which show an improved reducibility as compared with pure ceria. Gold supported catalysts on both CeO$_2$ and CeGaO$_x$ show activity towards the water gas shift (WGS) reaction [1,2]. It has been suggested in the literature that the WGS reaction on gold based catalysts proceeds via a redox mechanism. CO initially adsorbs on the metal sites and from there reduces the oxide support. The support is then re-oxidized by water [3], being this the rate limiting step. Thus, we studied the reoxidation by water of the Au/CeO$_2$ and Au/CeGaO$_x$ catalysts (Ce/Ga = 75/25, 80/20, and 95/5 mol/mol, coded Ce$_{75}$Ga$_{25}$, Ce$_{80}$Ga$_{20}$ and Ce$_{95}$Ga$_{05}$, respectively) by time-resolved X-ray diffraction (XRD) and infrared spectroscopy (DRIFT) coupled with Mass Spectrometry (MS). Preliminary results for the WGS reaction on these catalysts during operando conditions obtained by DRIFTS, XRD and XAS will be presented.

Results and Discussion

Oxygen storage capacity (OSC) and XPS measurements on CeGaO$_x$ indicate that at 300 °C no less than 10% of the Ce$^{4+}$ was reduced to Ce$^{3+}$, which is 10-fold higher than the amount obtained for pure ceria. Furthermore, the addition of Au improves the reducibility of the supports, this increase being more remarkable in the case of the Ce-Ga mixed oxide. This redox property of CeGaO$_x$ was verified by in-situ time-resolved XRD: the lattice constant of the Ce$_{75}$Ga$_{25}$ sample increase from 0.029 to 0.088 Å (at 500 °C) under H$_2$. Exposure to O$_2$ fully re-oxidized both reduced CeO$_2$ and CeGaO$_x$ supports at room temperature. However, the temperature-programmed oxidation with water, followed by XRD, showed that H$_2$O was able to re-oxidized 40 and 70 % of Ce$^{3+}$ on CeO$_2$ and Ce$_{75}$Ga$_{25}$, respectively, at 450 °C. Re-oxidation by water was also tested by DRIFT and MS studies at 250°C. Fig. 1 shows the IR spectra of the Ce$^{3+}$ signal ($^3$F$_{5/2}$ $\rightarrow$ $^3$F$_{7/2}$) before and after exposing the gold-based catalyst to water (2% v/v, 100ml/min), and the evolution of this IR integrated signal (inset). Thus, similar to the case of the supports, H$_2$O was unable to fully re-oxidize the Ce$^{3+}$ cations. However the extension of re-oxidation is greater on Au/Ce$_{90}$Ga$_{20}$ than on Au/CeO$_2$ (50% vs. 30%, respectively). The evolution of H$_2$, followed by MS at 250°C (Fig. 2), also showed a higher capacity of Ce$^{3+}$ re-oxidation on the CeGaO$_x$ gold-supported catalyst than on Au/CeO$_2$. Moreover, the H$_2$ concentration decreases more rapidly on Au/Ce$_{90}$Ga$_{20}$ as compared to Au/CeO$_2$, indicating that the replacement of oxygen vacancies by water is faster in the first case than in the last one.
Fig. 1. IR spectrum of Au/CeO$_2$ and Au/Ce$_{80}$Ga$_{20}$ at 250°C recorded during the isothermal oxidation by H$_2$O (DRIFTS): Reduced (solid) vs. oxidized samples (dashed) in H$_2$ or H$_2$O. Inset: evolution of the IR signal of Ce$^{3+}$.

Fig. 2. Evolution of H$_2$ concentration during isothermal oxidation by H$_2$O at 250°C on Au/CeO$_2$ and Au/Ce$_{80}$Ga$_{20}$.

Conclusions

The results obtained by combining XRD, DRIFT and MS techniques suggest that the support re-oxidation by water may not be the rate limiting step for the WGS reaction on cerium-based gold-supported catalysts. Results from current experiments under *operando* conditions obtained by DRIFTS, XRD and XAS will help us to detect intermediate species and the state of the CeGaO$_x$ gold-supported catalysts during the WGS reaction.

References

Applications of Light Element X-ray Raman Spectroscopy and Hard X-ray Emission Spectroscopy to the Electronic Structure of Energy Storage Materials under In-situ Conditions

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Introduction and Objectives

In situ conditions for energy related science applications -and beyond- require the development and implementation of demanding characterization techniques. Hard x-ray based spectroscopies exhibit some unique advantageous properties for providing structural and electronic information under in situ environments. Modern high brilliance beamlines in synchrotron radiation facilities and developments in hard-x-ray optics render high energy-resolution x-ray spectroscopy as a state-of-the-art analytical tool.

Recently, we have designed and built a high-resolution and large solid angle spectroscopy end-station at beamline 6-2 at Stanford Synchrotron Radiation Lightsource. Three multicrystal high energy-resolution x-ray spectrometers (a 40-crystal low-q x-ray Raman spectrometer, a 14-crystal high-q x-ray Raman spectrometer and a 7-crystal x-ray emission spectrometer) coupled on a single end-station provide non resonant and resonant inelastic x-ray scattering, as well as x-ray emission and high resolution x-ray absorption (XANES) and extended x-ray absorption fine structure (EXAFS) capabilities.
Both the energy resolution and the high throughput of the instruments enables the real-time characterization of in-situ processes towards addressing outstanding scientific questions for a wide range of scientific cases.

**Results and Discussion**

Here, we present the applicability of x-ray Raman spectroscopy of light elements and hard x-ray emission to probe the electronic structure of energy storage materials under *in-situ* conditions. In particular, the recent advances in resolution and throughput of x-ray raman spectroscopy (XRS) offer the capability to measure 1s x-ray absorption profiles of light elements such as lithium, boron, carbon, nitrogen and oxygen with less than 0.3eV resolution in the order of 10s of minutes. Initial results from the Spectroscopy program at SSRL and collaborations with groups in various energy storage fields will be presented, with an emphasis on Lithium Ion/Air Batteries and Hydrogen Storage applications.

**Conclusions**

The instrumental capabilities and the first scientific results indicate prospects towards developing new directions on the systematic applicability of these hard x-ray photon-in/photon-out techniques on various aspects of energy related science and catalysis.

**References**

**Surface Chemistry of Oxygenated Molecules on CeO\(_2\)(111) by RAIRS**

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**Introduction and Objectives**

The study of adsorption and reactivity of oxygenated molecules on model oxide catalysts is of great interest to gain a better understanding of the mechanism of industrial reactions. Cerium oxide is commonly used in three-way auto exhaust and WGS catalysts. Our experimental design is intended to find the conditions where UHV experiments could mimic the real catalytic processes and from these results explain the reaction pathway from the atomistic level. Reflection Absorption Infrared Spectroscopy (RAIRS) is a very important and useful technique that studies the structure of adsorbed species on surfaces and two examples of its capabilities are presented here.

**Results and Discussion**

We have examined these adsorption and decomposition pathways for two ethers, diethyl ether (DEE) and dimethyl ether (DME). Both ethers adsorb on fully oxidized CeO\(_2\)(111) and highly reduced CeO\(_x\)(111) under UHV conditions at low temperature without showing decomposition. If the catalyst surface is pre-covered by hydroxyls, then the adsorption geometry of the ethers on this hydroxylated surface changes, indicating interaction with OH groups. Regarding their reactivity towards decomposition, the two ethers behave differently when exposed to hydroxylated CeO\(_{2-x}\)(111) at 300-400 K. DEE promptly reacts by breaking the C-O bond presenting a very interesting chemistry. By using RAIRS and XPS, we could detect ethoxide and possibly carboxylate species as adsorbed intermediates for the reaction. However, when the hydroxylated CeO\(_{2-x}\)(111) is exposed to DME at same conditions, the ether shows no reactivity, indicating the importance of H on a carbon atom β to oxygen. [1]

RAIRS was coupled with density functional theory (DFT) to study the adsorption of acetaldehyde, the simplest C2 aldehyde. The molecule adsorbs weakly on the fully oxidized surface at low temperatures, and desorbs without further reaction near 215 K, by bonding to Ce\(^{4+}\) cations through the oxygen lone pair electrons in the carbonyl group with its C-C bond perpendicular to the surface plane and the acyl hydrogen tilted slightly towards one of the lattice oxygen anions of the first layer. On the reduced surfaces, acetaldehyde interacts more strongly with the surface upon adsorption at low temperatures by losing its carbonyl bond character and adsorbing as diacetal species by dimerization of two acetaldehyde molecules forming an ether linkage between the two. Heating the surface to 400 K leads to desorption of some amount of di-acetal adsorbed species as acetaldehyde and the appearance of hydroxyl and enolate species (CH\(_2\)=CHO-Ce). The identities and structures of the different intermediates on the CeO\(_2\) and CeO\(_{2-x}\) surfaces have been determined by their characteristic signatures in RAIRS and by DFT calculations.[2] The assignment of the enolate species is furthermore consistent with C1s XPS and C k-edge NEXAFS results.[3]
Conclusions

UHV-RAIRS studies of adsorbates on ceria films gives great insights into the chemistry of oxygenated molecules to further understand their chemistry in heterogeneous catalytic processes. This technique can provide IR characterization of adsorbates and reaction intermediates geometry and their interaction with the surface. These results coupled to other surface science techniques and specially with DFT calculations can explain reactivity pathways and the role of co-adsorbates (vacancies and hydroxyls) on the catalytic surface.

References

COSMO-RS Based Predictions for the Extraction of Lignin From Lignocellulosic Biomass using Ionic Liquids: Effect of Cation and Anion Combination

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A total of 34 cations belonging to 6 classes and 34 anions resulting in 1156 possible combinations were screened via Quantum chemical based COSMO-RS (Conductor Like Screening Model for Real Solvents) model. The Hildebrand solubility parameter (δH) was calculated using the predicted infinite dilution activity coefficient (γ∞) of lignin in ionic liquids at temperature (303.15 K). Initially benchmarking was performed to predict the Hildebrand solubility parameter of lignin in ionic liquids. Comparison with literature values involving 12 ILs gave the average root mean square deviation (RMS) to be 10.15%. In case of Imidazolium, Pyridinium, Pyrrolidinium, Ammonium, Phosphonium and other cations such as octylquinolinium, 1,2,4-Trimethylpyrazolium, 1-ethyl-1-methylpiperidinium, 4-ethyl-4-methylmorpholinium, Choline, except for anions based on [PF6], [BOB], [B(CN)4] and [BTA] all the cations anion combination indicated that the solubility parameter value was equal to that of lignin at temperature of 303.15 K, thus showing high solubility for lignin.

Keywords: Biomass, ionic liquids, COSMO-RS, solubility

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Supported Rhenium Catalysts for the Methanol Conversion to Methylal: 
*Operando* Spectroscopies Supported by DFT Calculations Lift the Veil on an 
Unexpected Ingredient for Catalytic Activity: Water

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Introduction and Objectives

As affordable from biomass degradation, alcohols are top choice starting compounds for producing chemicals through a green chemistry pathway. The direct conversion of methanol to dimethoxymethane (methylal, or DMM) involves two steps: (i) the oxidation of methanol to formaldehyde over a redox function and (ii) the condensation of formaldehyde with two methanol molecules over an acidic function. This pathway makes the reaction a relevant model for testing redox/acidic bifunctional catalysts. Among the possible materials, supported or bulk rhenium oxide-based materials are recognized as efficient catalysts for the direct conversion of methanol to DMM. Indeed, ReOₓ oxides possess the right redox/Lewis acidity balance to perform the direct conversion of methanol to DMM under mild conditions without needing further modification.

On the base of a wide-ranging series of complementary approach involving (i) catalysts preparation, (ii) Raman and Qu-EXAFS spectroscopies collected according to the *operando* approach, (iii) model *in situ* experiments and (iv) DFT modelling, the present work aims at giving unprecedented insights on the reactivity of rhenium containing materials.

Results and Discussion

A series of supported oxorhenate catalysts was prepared using two opposite strategies. The first one is based on the calcination of a mix containing a given amount of metal rhenium thoroughly grinded with the support material. The second one involves the gelification of a silica sol containing perrhenic acid. The structure of the as-prepared catalysts under ambient conditions as a function of the rhenium loading, the support and the preparation route has been compared using conventional techniques such as elementary analysis, temperature-programmed reduction under hydrogen, conventional catalytic tests and ambient spectroscopies. In comparison with conventional cata-

![Figure 1: Operando Raman spectra of Re/SiO₂ sol-gel catalyst a) after calcination, dehydrated conditions, b) operating methanol conversion to methylal at 200°C and c) flushed under pure He and O₂ for 20 min](image-url)
lys, the Re/SiO₂ material prepared using the sol-gel route was found to exhibit both an unexpected structure and an outstanding activity in the direct conversion of methanol to methylal [1]. Moreover, contrary to what is generally reported, the Re coverage was found to exert a strong influence on both the conversion level and the selectivity.

The structure of the operating catalysts was investigated using operando Raman spectroscopy in order to shed light on the structural similarities and differences detected when varying (i) the catalyst formulation and (ii) the preparation pathway.

The Raman spectra of the most active catalyst, shown in Figure 1 make it clear that an unprecedented structure clearly plays an active role in the catalyst activity.

On the base of a comprehensive investigation involving model reaction with H₂O and D₂O, DFT modeling, molecular dynamics and EXAFS refinement, we propose that this original structure could involve a Si-O-ReOₓₙH₂O adduct in line with the structure of the model bis-aquo compound Re₂O₇.2H₂O.

In order to collect information on the redox activity of the oxorhenate phase, we have designed and adapted an original set up devoted to combined X-Ray absorption/Raman operando experiments. The recent implementation of Qu-EXAFS at SOLEIL has made it possible to record simultaneously the L₄,III edges of Re with an acquisition time of 100 ms. As a result, we have evidenced an apparent Re⁷⁺/Re⁴⁺ equilibrium in absence of oxygen, as suggested by the presence of quasi-isosbestic points in Figure 2.

Conclusions

The investigation we propose here gathers several pieces of the puzzle which were actual prerequisite for understanding the reactivity of rhenium oxides. We intend to review in detail all the step that were required and the way we have built up an integrated approach centred on operando spectroscopies, model experiments, theoretical modelling and the use of complimentary techniques.

References

Determination of Diffusion Coefficients in Liquid Polymers with ATR Spectroscopy

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Introduction and Objectives

The application of highly viscous media in the chemical industry is steadily increasing, because fossil feedstock is replaced by renewable materials like fats, lignin and cellulose. Another reason is the use of new solvents like ionic liquids. In these highly viscous media transport processes become more important, because diffusion is the rate-limiting factor for example in two phase extraction. Therefore, it is necessary to study the transport parameters in the system, especially the diffusion coefficient. Already, there are many ways to determine diffusion coefficients. One method is the time-resolved FTIR-ATR (Fourier Transform Infrared Attenuated Total Reflectance) spectroscopy. FTIR-ATR spectroscopy is a non-invasive in situ method, which provides reliable data. This method has already been used to determine diffusion coefficients in solid polymer films.\textsuperscript{[1]} The objective of this study is to analyse the diffusion of small molecules in liquid polymers.

Experimental design

For measuring diffusion coefficients of small tracer molecules in polymer solutions, an ALPHA FT-IR spectrometer from Bruker was used. The polymer layer was about 0.5 cm. The small tracer molecules were layered on top of the polymer (Fig. 1 left). To monitor diffusion of CO\textsubscript{2} in highly viscous media, a steel autoclave was used with IR probes at the bottom and at the top of the autoclave (Fig. 1 right). It was pressurized with CO\textsubscript{2} and both phases could be monitored.

Results and Discussion

For the analysis of IR data the equation of J. Crank\textsuperscript{[2]} was used. This equation is based on the Fickian diffusion and on various assumptions. The transient absorbance only depends on the polymer thickness (which is known) and the diffusion coefficient. The equation predicts a sigmoidal curve shape. The diffusion coefficient can hence be obtained by parameter estimation. Figure 2 shows the measured absorbance profile (red dots) and the values calculated with parameter estimation (black line). The initial mismatch (between 50 min and 150 min) may be related to the assumption of a “thin film”. This is not fulfilled.
sidering that the whole profile is taken into account to determine the diffusion coefficient, the small deviation of the two curves is neglected.

In the other setup, diffusion coefficients of CO₂ in polymers were measured. With the covered IR probe at the bottom of the autoclave the diffusion of CO₂ could be monitored. In solvents with higher viscosities the diffusion of CO₂ takes longer. The diffusion coefficient of the first measurements for the water/CO₂-system was in the same order of magnitude ($D=2.3\cdot10^{-5} - 2.7\cdot10^{-5}$ cm²/s) as the diffusion coefficient from literature ($D=1.9\cdot10^{-5}$ cm²/s).[3] It could be shown that this method to determine diffusion coefficients in highly viscous media is promising.

**Conclusions**

Measurements have shown that the diffusion coefficient in liquid polymers can be determined with FTIR-ATR spectroscopy. It is also possible to monitor the diffusion of CO₂ in water and different polymers. The diffusion coefficient which was determined for the water/CO₂-system was in the same order of magnitude as the literature value. To further enhance the method, the setup will be improved.

**Acknowledgement**

This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

**References**

In situ Studies of Structural and Electronic Properties of Pt Nanoparticles Supported Catalysts During Steam Reforming of Methane

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Introduction and Objectives

Steam reforming of methane (SRM) or ethanol (SRE) can be pointed out as some of the main alternatives for hydrogen production from hydrocarbons and alcohols \[1\]. One of the common factors that are behind these reactions is the influence of the metal-support interface. Understanding how to tune the metal-support interaction and how it can modify the reaction pathway is an important step in the development of more efficient catalysts \[2\]. In this work, we used colloidal platinum nanoparticles (Pt-NPs) supported on Al\textsubscript{2}O\textsubscript{3} (PtAl) and CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (PtCeAl) in SRM to investigate the electronic and structural properties of the metallic phase using \textit{in situ} XAFS.

Experimental

Pt-NPs were prepared according Song \textit{et al.}\[3\] but using a PVP/Pt ratio of 10. Pt-NPs solution (1.5\% Pt w/w) was incorporated to Al\textsubscript{2}O\textsubscript{3} prepared by sol-gel method \[4\]. CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} was prepared adding cerium nitrate to Al\textsubscript{2}O\textsubscript{3} synthesis (12\% Ce w/w). The precursors were treated in synthetic air at 500 °C for 4h.

XAFS measurements at the Pt L\textsubscript{3}-edge were carried out at the D08B-XAFS2 beam line of the LNLS (Campinas-SP, Brazil) at transmission mode using a tubular quartz furnace. The samples were first reduced at 500 °C and then submitted to SRM reaction up to 760 °C. XANES spectra were measure during the heating ramp (10 °C/min) with time intervals of about 5 min while EXAFS measurements were done at two steps (500, 760 °C).

Results and Discussion

Before reduction, both samples are oxidized being the PtCeAl more oxidized than PtAl. The reduction under H\textsubscript{2} start at lower temperature for the PtAl sample but at the end of the process, both samples are similarly reduced (Figure 1A). Under SRM conditions the samples partially re-oxidize at low temperature (< 300 °C), and this effect was more pronounced in the PtCeAl sample (Figure 1B). These results suggest that the support has a larger effect in the PtCeAl sample. This was corroborated by the EXAFS analysis that pointed out smaller coordination numbers for PtCeAl sample in all cases, after reduction, under SRM at 500 and 760 °C, despite using the same batch of colloidal Pt-NPs. Figure 1C shows the Fourier transform of the EXAFS oscillations and best fits. An encapsulation phenomena caused by Ce may be occur-
ring, affecting particle morphology and contributing to diminish the surface energy. It has been proposed that the formation of Pt-CeOₓ may help to stabilize the Pt particles and to increase the catalytic activity [2]. As a consequence, the morphology changes of the Pt-NPs in the PtCeAl and the sensitivity to oxidation state could be related with the formation of these species.

**Figure 1.** Quantification of Pt L₃-edge XANES considering a linear combination of Pt⁰ and PtO₂ standards under (A) 5%H₂/He and (B) SRM atmospheres. (C) Magnitudes of the Fourier transform of the EXAFS oscillations at 25 °C after reduction process and for SRM at 760 °C. Under temperature are the coordination numbers obtained from the fits.

**Conclusions**

The use of colloidal Pt-NPs to study support effects in SRM shows morphology and electronic changes of the Pt-NPs that was more pronounced in the PtCeAl sample, suggesting partial encapsulation by CeOₓ species. The presence of Pt-CeOₓ species could indirectly promote the cleaning of the surface and enhance the catalytic activity in this system.

**References**

Stabilization of Subnanometric Gold Oxide Nanoparticles on Multiwalled Carbon Nanotubes

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Introduction and Objectives

The use of molecular oxygen replacing inorganic oxidants used in industrial oxidation processes is an actual task from the point of view of green chemistry. In these processes, one important point is the knowledge about the reaction mechanism, i.e. oxygen activation mechanism, since the nature of the oxygen species has a strong influence on the selectivity of the process. Gold, when in form of small nanoparticles, becomes an active and selective catalyst for oxidation reactions using molecular oxygen, such as CO oxidation, and the oxidation of olefin, alkanes and alcohols (1). Particle size and shape, metal oxide support, and the metal-support interface play an important role in how oxygen is activated on the gold catalyst (2). Moreover partial oxidation of small Au nanoparticles (~1.7 nm size) supported on Al\textsubscript{2}O\textsubscript{3} has been evidenced by EXAFS-XANES studies (3). According to this, it appears to us that if very small gold nanoparticles (≤1 nm) within a very narrow crystallite size distribution were synthesized, a surface oxide-like layer would be easily formed in the presence of oxygen, which would be the interface in where the catalytic oxidation process would occur.

Results and Discussion

Small gold nanoparticles presenting a very narrow size distribution (1.1±0.5 nm) have been synthesized supported on multiwalled carbon nanotubes (MWCNT). By combining spectroscopic, kinetic and theoretical studies, oxidised gold nanoparticles have been determined. DFT calculations indicate that small Au\textsubscript{38} nanoparticles can dissociate at least twelve O\textsubscript{2} molecules with low activation barriers producing stable Au\textsubscript{38}O\textsubscript{16} and Au\textsubscript{38}O\textsubscript{24} oxidized particles (fig.1), being this finding experimentally supported by XPS spectroscopy.

![Figure 1: DFT optimized structures of oxidized gold nanoparticles.](image)

Moreover \textsuperscript{16}O\textsubscript{2}/\textsuperscript{18}O\textsubscript{2} isotopic exchange experiments confirm that small (0.9-1.5 nm) gold nanoparticles are able to dissociate O\textsubscript{2} at room temperature being oxidised, while O\textsubscript{2} dissociation does not occur on larger...
gold particles (4nm). In this case no oxidation of the gold nanoparticle has been found in agreement with their XPS data. On the other hand, the surface oxide layer has been titrated with CO (fig.2a) leading to CO$_2$ formation. A lower reactivity is observed at decreasing oxygen coverages according to the required higher CO titration temperatures (fig.2b). Repeated cycles of CO titration followed by O$_2$ reoxidation have shown that these oxidised gold nanoparticles undergo reversible reduction - oxidation cycles. In this sense an additional oxidation pathway on very small gold nanoparticles has been inferred that could be assimilated to a Mars van Krevelen (MVK) mechanism. This behaviour makes oxidized gold nanoparticles interesting catalysts in oxidation processes, like for instance styrene epoxidation and alcohol oxidation.

Figure 2: CO titration followed by FTIR. A) CO$_2$ evolution with time at 25ºC, and B) CO$_2$ evolution with time and at increasing temperature.

References
Spectroscopic Observation of Active Sites at Work on a Au/TiO₂ Catalyst

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Catalytic reactions are of central importance to today’s industrial development and productivity, especially when a metal that is normally unreactive becomes active. Gold nanoparticles supported on TiO₂ powder have been found to be an outstanding catalyst for various reactions, while neither the Au nanoparticles nor the TiO₂ powder by themselves have shown such property.¹ We used the oxidation of H₂ by O₂ and the oxidation of CO by O₂ over the Au/TiO₂ catalyst as our model to look for the active sites during the reaction.²,³ It is found that the dual catalytic sites at the perimeter of 3 nm Au particles supported on TiO₂ are the active sites where the oxidation occurs.

Low temperature IR experiments showed that the Au/TiO₂ catalyst are extremely active for CO oxidation, even at 110 K.² The measured apparent activation energy for the entire oxidation process is 0.16 eV. A sequential consumption of reactant is observed, with the CO/TiO₂ species reacting first, followed by the CO/Au species. This is because the CO/TiO₂ species experiences a lower diffusion barrier compared to the CO/Au species. Combined with density functional theory (DFT) simulations, we found that the O₂ is captured and activated at the dual perimeter site located at the Au/TiO₂ interface. The initial oxidation reaction takes place when a CO molecule diffuses over TiO₂ into the dual perimeter site adjacent to an adsorbed O₂ molecule and forms a CO-O₂ intermediate.

A set of separate experiments following the H₂ and O₂ reaction on the same Au/TiO₂ catalyst by transmission IR and DFT calculations also showed that the reaction “hot zone” is at the dual perimeter sites on the Au/TiO₂ catalyst.³ Oxygen molecules are adsorbed and dissociated at there sites via the formation of a Ti-OOH hydroperoxy intermediate. The measured apparent activation energy is 0.22 eV, in very good agreement with the DFT calculated barrier of 0.25 eV. A deuterium kinetic isotope effect, kH/kD=7, matches the theoretical ratio of 5 indicating that the reaction takes place via an early transition state.

*Work supported by DOE-BES under grant DE-FG02-09ER16080

References
Thermal and Composition Effects on the Structure and Dynamics of Pt$_n$Sn$_m$/γAl$_2$O$_3$ from ab initio Molecular Dynamics and X-ray Absorption Spectra*

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Introduction and Objectives

Supported metal clusters are key ingredients in many industrial applications, especially in the heterogeneous catalysis of petroleum refining processes. Their durability and activity are determined by their composition, internal structure and their interaction with the support at high temperature conditions. We have previously shown that their dynamical properties are of crucial importance, and that a combination of ab initio density-functional theory molecular dynamics (DFT/MD) and x-ray absorption spectroscopy simulations can provide a deep understanding of the behavior of these systems.[1,2] In particular, we have shown that unusual phenomena such as large structural disorder and negative thermal expansion in supported Pt clusters arise from their dynamic behavior and the interplay between charge transfer and entropic effects. In particular we find that these phenomena are driven by large, non-equilibrium dynamical fluctuations in the structure of the cluster.[1] Here we have extended these methods to treat nano-scale alloy clusters of Pt and Sn on γAl$_2$O$_3$. Alloy clusters are especially appealing since they are cheaper than pure noble metal ones and their catalytic properties can be tuned through changes in their composition.

Results and Discussion

To understand these effects in detail, we have studied the effects of variations in temperature and Pt/Sn ratio (50%Pt-50%Sn or Pt$_{10}$Sn$_{10}$ and 75%Pt-25%Sn or Pt$_{15}$Sn$_{5}$). By simulating these models under realistic (operand) conditions, an overall picture emerges in which the concentration of Sn atoms has huge effects on the atomic and electronic structure and behavior of these nanoparticles. For instance, lowering the Sn concentration from 50 to 25% modifies the interaction between the Pt atoms, shrinking the Pt-Pt coordination shell from 2.72 Å to 2.66 Å (Figure 1). The Sn atoms also have a striking effect on the interaction between the Pt atoms and the γAl$_2$O$_3$, effectively shielding them from the O atoms in the surface. This has the added effect of changing their oxidation state, and thus directly changes their catalytic properties. This is clearly seen in the increase in the average number of Pt-O bonds per Pt atom, which goes from 0.2 in the 50-50 clusters to 0.5 in the 75-25 ones. Interestingly, the Sn atoms tend to reside on the surface of the cluster and are very mobile (Figure 2). This change results in very broad Sn-Sn coordination shells, and a distinct Pt-Sn coordination shell at 2.69 Å which is independent of concentration. The Pt L$_3$ XANES spectra show a small 0.2 eV edge blueshift for lower Sn concentrations, indicative of a net change in Pt charge. More importantly, we observe that the composition also has a large effect on the average charge of the Pt atoms, which varies from -0.5e at 50-50 to -0.1e at 75-25. We also discuss implications of these effects for their catalytic properties. For example, we show how this differential charging affects the adsorption energy of simple molecules on these clusters.

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Conclusions

In conclusion, we have applied a combination of theory and experiment to explore thermal and composition effects on the structure and dynamics of supported PtSn alloy nanoclusters. The DFT/MD approach tackles the non-equilibrium nature of the nanostructures from a simulated real-time point of view, and provides a wealth of information about the clusters. Given the close connection between atomic and electronic structure, and catalytic function, our results lead to a new level of understanding of the nature of these catalysts.

*Supported in part by NSF Grant PHY-0835543 (FDV, JJR), by UOP LLC, a Honeywell Company and with computer support from NERSC.

References
Ab initio Modeling of EXAFS Spectra of Nanoparticles

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Introduction and Objectives

The three dimensional structure of nanoparticles in the 1-3 nm-range is often investigated using extended x-ray adsorption fine structure (EXAFS). Structural information for nanoparticles is typically determined from the fits to EXAFS data using the bulk structure for theoretical calculations. The average coordination numbers, interatomic distances, and their mean squared disorder can be found. The coordination numbers for the first few coordination shells are then interpreted in terms of the particle size, shape and, often - morphology. This method has proven powerful in particles with a high degree of atomic order that can be stabilized, for example, by passivating ligands. The applicability of this procedure is less obvious when the particles are strongly disordered and/or the disorder is asymmetric (non-Gaussian), i.e., when there are significant structural differences between the nanoparticles and the corresponding bulk structure. We use molecular dynamics (MD) simulations of 2 nm nanoparticles to construct EXAFS spectra ab initio, with the atom-by-atom approach, averaged over the time of the MD run.

Results and Discussion

We obtain that the analysis of this "data" done by conventional procedures reveals significant differences between the actual (time- and configuration- average) structure of the simulated nanoparticles and what was determined from data analysis using a bulk reference. Furthermore, we obtained significant differences in bond vibration dynamics between the two calculations.

Conclusions

Combined, these two observations point to the new method of refining experimental data in the nanoparticles by comparing them with ab initio simulations that include strongly disordered contributions (both static and dynamic). We demonstrate that EXAFS spectra calculated for a variety of theoretical models of nanoparticles can be directly compared to the experiment and thus used to determine the best-fit structure.
SO$_2$ Adsorption Products on Pt Nanoparticles as a Function of Electrode Potential and Oxidative Properties of Carrier Gas: in-situ Sulfur K-edge XANES Approach

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Introduction and Objectives

The electrocatalytic activity of platinum nanoparticles employed in the cathodes of H$_2$/air proton exchange membrane fuel cells (PEMFCs) can be severely affected by adsorbed species such as SO$_2$ originating as “airborne impurities”. Adsorption of SO$_2$ molecules on Pt is complicated by the fact that they can be easily oxidized/reduced by changing electrode potential. Here we use in-situ sulfur K-edge XANES (X-Ray adsorption near-edge structure) spectroscopy in combination with electrochemical techniques to directly identify the adsorbed SO$_2$ species on carbon-Pt nanoparticles incorporated in commercial catalyst coated membranes (CCMs) employed in PEMFC. SO$_2$ adsorption was carried out from a SO$_2$/N$_2$ gas mixture, while holding the working electrode (WE) potential at 0.1, 0.5, 0.7 and 0.9 V vs. reversible hydrogen electrode (RHE). For additional insight into the role of O$_2$ in the SO$_2$ electrochemistry, we compare products of SO$_2$ adsorption from a SO$_2$/N$_2$ gas mixture at four electrode potentials to those determined for SO$_2$ adsorption from a SO$_2$/O$_2$ gas mixture. The identity of adsorbed SO$_2$ species on Pt nanoparticles is verified by FEFF8 and combination-fit modeling.

Results and Discussion

Figure 1 shows pre-edge background corrected XANES spectra measured after exposure of the WE to SO$_2$ in N$_2$ while holding the WE at 0.1 (black), 0.5 (red) and 0.7 V (blue). Each spectrum shown in Figure 1 has a strong sharp peak at ~2480 eV and one or two smaller peaks at lower energies. As SO$_2$ exposure potential increases from 0.1 to 0.7 V, the intensities of the peaks at 2471 and 2476 eV decrease, while the peak at 2480.5eV shifts to higher energies by ~2 eV. The strong peak at 2480.5±0.2 eV in the 0.1 and 0.5 V measurements is assigned to S$^{2+}$ from Nafion sulfonic groups present in the catalyst layer, while the other peaks are due to SO$_2$ oxidation/reduction on Pt nanoparticles. Based on comparison of our experimental spectra with XANES spectra for sulfur standards and FEFF8 modeling, the peaks at 2471, 2476 and 2482 eV are assigned to adsorbed sulfur adatoms (S$^{0}_{ads}$), SO$_2$ molecules (SO$_2$$_{ads}$) and (bi)sulfate ions, respectively [1]. Interestingly, the nature of SO$_2$ adsorption products do not change upon switching from SO$_2$ adsorption from N$_2$ to that from O$_2$ for all the potentials except when measured at 0.1 V. Figure 2 shows XANES spectra for SO$_2$ adsorbed from SO$_2$/O$_2$ gas mixture vs. SO$_2$/N$_2$ while holding the WE at 0.1 V. The major difference between the two spectra is a 2 eV positive shift for the peak centered at 2480 eV for SO$_2$/N$_2$ vs. SO$_2$/O$_2$ gas mixtures. We assign this shift to formation of (bi)sulfate ions from the chemical reaction between SO$_2$ and H$_2$O$_2$, a byproduct of the oxygen reduction reaction in the hydrogen adsorption region.
We identified SO$_2$ adsorption products on Pt nanoparticles incorporated in the CCMs at 0.1-0.9 V using a combination of sulphur K-edge XANES and electrochemistry. The nature of SO$_2$ adsorption products is found to be essentially identical both for SO$_2$ adsorption from nitrogen and oxygen. The major difference is the generation of (bi)sulfate ions on Pt nanoparticles held at 0.1 V when the SO$_2$ is adsorbed from SO$_2$/O$_2$ mixture. This suggests that SO$_2$ may act as a peroxide radical scavenger that diminishes the detrimental effect of SO$_2$ at the FC cathode.

Acknowledgements. The authors are grateful to the Office of Naval Research for financial support of this project. Beamline X15B at NSLS is supported and operated by a multi-institutional consortium of scientists coordinated by Stony Brook University. The NSLS is supported by the Department of Energy.

References
**Introduction and Objectives**

Fuel cells afford a competent route to environmentally friendly energy production. They require hydrogen-rich gas, which is beneficially produced by methanol steam reforming (SR). Iridium catalysts have shown promising activities and selectivities for MeOH SR reactions [1, 2]. Nevertheless, commercial use of iridium catalysts has been rare [3].

Methanol is also a well-established surface probe. Infrared spectroscopy gives information about the surface species derived from methanol. [4, 5] IR-characterizations on iridium catalysts have not been commonly performed.

The aim of this study was to investigate the effect of support on MeOH adsorbed species on Ir-catalysts using in-situ DRIFTS and the relation to catalyst performance during MeOH SR.

**Results and Discussion**

MeOH steam reforming activity tests were carried out in a tubular quartz reactor at 300-500 °C. The activity and H2-selectivity was in the order Ir/β-zeolite < Ir/Al2O3 < Ir/SiO2. Coking was observed on Ir/Al2O3 and Ir/β-zeolite whereas on Ir/SiO2 it was minor.

The interaction of methanol with Ir/Al2O3, Ir/SiO2, and Ir/β-zeolite (prepared by ALD as reported in ref. 3) was studied by in situ DRIFTS combined with mass spectrometry (MS) as a function of temperature (100 to 500 °C). Methanol (2000 ppm MeOH in N2, AGA) was fed continuously during the temperature increase. Spectra were taken after each 100 °C after nitrogen flush to obtain spectra without the contribution of gas-phase MeOH. Gaseous products were analyzed on-line by MS.

MeOH adsorbed dissociatively forming methoxy species on Ir/Al2O3 at 100 °C as indicated by the peaks in Fig. 1, left, whereas the Ir/SiO2 showed no peaks.

Fig. 1, right shows the effect of temperature on the surface species on Ir/Al2O3. Bands observed at 2945, 2845, and 2819 cm⁻¹ indicate formation of different types of methoxy groups. Methoxies started to disappear at 300 °C and at 500°C they were no longer seen. Hydroxyl groups were affected suggesting reaction with adsorbing MeOH (not shown). Same trends were observed on Ir/β-zeolite. Formates (1593, 1393 cm⁻¹) [4] appeared on Ir/Al2O3 at 100°C and above with increasing intensity until 400°C (Fig. 1, right) indicative of the reaction of methoxies to formates. This was not observed on other catalysts. Methyl formate has been considered in the reaction mechanism of MeOH SR [1].
On Ir/SiO₂ small peaks indicating the formation of methoxies at 2959 and 2858 cm⁻¹ were only observed at 300-500 °C. However, on Ir/SiO₂ CO was formed (2048-2038 cm⁻¹) [6] at 100-500 °C (not shown). MeOH adsorption on Ir/SiO₂ is considered to be minor, which is consistent with the low methanol conversion during activity tests.

H₂ formed on all the catalysts (MS-results, not shown) indicative of the decomposition of methoxies. Dimethyl ether formed mostly on Ir/Al₂O₃, some on Ir/β-zeolite, and not on Ir/SiO₂ suggesting acidity order of Ir/Al₂O₃ < Ir/β-zeolite < Ir/SiO₂ [5]. Higher acidity of Ir/Al₂O₃ and Ir/β-zeolite also partly explains coke formation during activity tests.

![Fig. 1. Left: Methanol adsorption at 100 °C on the studied catalysts. Right: In situ DRIFT spectra measured for Ir/Al₂O₃ during temperature-programmed experiment with methanol. All spectra were measured after N₂ flush.](image)

**Conclusions**

It is concluded that the support has a considerable effect on the surface species formed upon MeOH adsorption on Ir-supported catalysts. On Ir/β-zeolite, which showed the highest selectivity to H₂ during activity tests, the decomposition of MeOH proceeded through methoxy species. On Ir/Al₂O₃ methoxies reacted to formates and further to gaseous products. It was also found to be the most acidic catalyst, which didn’t prove beneficial for MeOH SR (medium H₂-selectivity). Ir/SiO₂ was considered to be fairly inert based on MeOH-DRIFTS study, which was reflected as inactivity (poor MeOH conversion and H₂-selectivity) during MeOH SR.

**References**

**In situ X-ray Absorption Spectroscopy for Solid Oxide Fuel Cell Composite Cathodes**

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**Introduction and Objectives**

In the effort to create a more effective solid oxide fuel cell cathode, a composite cathode was synthesized by the infiltration of La\textsubscript{0.85}Sr\textsubscript{0.15}MnO\textsubscript{3} (LSM), a cathode material with good catalytic activity but poor conductivity, into a porous backbone of La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ} (LSCF), a cathode material with high conductivity. The resulting LSM-coated LSCF composite cathode demonstrated improved performance and stability compared to its constituent materials [1]. The objective of this experiment is to explain the cause of the improved performance on a fundamental level by probing the electronic and local structures of the composite cathode material with a combination of soft and hard x-ray absorption spectroscopy techniques. X-ray absorption spectroscopy techniques were employed to understand the charge compensating roles of transition metal dopants as oxygen vacancy concentrations change under reducing and oxidizing environments at operating temperatures of 750°C. Additionally, extended X-ray absorption spectroscopy was used to track the changes in the local environment of Sr cations for studying Sr segregation.

**Results and Discussion**

A baseline study first confirmed the influence of reducing and oxidizing atmospheres on the oxidation states of Mn and Co in LSM and LSCF, respectively. After the LSM-coated LSCF was annealed 850°C for 120 hours, soft x-ray absorption near-edge structure (XANES) indicated insignificant changes in Mn valence. Meanwhile, the Co cation in LSM-coated LSCF becomes responsible for charge compensating the oxygen vacancies generated and consumed under reducing and oxidizing conditions at 750°C, after annealing at 850°C for 120 or more hours, as illustrated in the left figure below. The hard x-ray Co K-edge XANES agrees with and further supports this assertion. In the Fourier transformed (FT) extended x-ray absorption fine structure (EXAFS), the LSM-coated LSCF tends to favor a single Co-O bond length, compared to a bimodal distribution of Co-O bond lengths in LSCF, which is likely a product of long-term annealing.

The Sr FT EXAFS indicates that there are three major groups of bond lengths for Sr cations in LSM-coated LSCF with finer features that are only observable at room temperature, since the Debye-Waller factor at higher temperatures becomes significant. These have been correlated to the bond lengths of nearest neighbors of various degrees and compared to the Sr-O bond length observed in SrO, the predominant phase resulting from Sr segregation. The overall Sr FT EXAFS, shown in the right figure below, maintained a stable local structure after annealing in contrast pure LSCF, particularly at the 4 Å distance from the Sr cation, which suggests that the LSM-coated LSCF promotes local stability in the structure during long thermal treatments and may in turn inhibit Sr segregation that is detrimental to the stability of LSCF.
Conclusions

A series of soft and hard x-ray spectroscopies were performed in situ on a novel LSM-infiltrated LSCF cathode under reducing or oxidizing conditions at operating temperatures for the purpose of developing an understanding of the chemical and electronic states of transition metal dopants and Sr cations, a key point of interest in the study of LSCF’s chemical stability. When LSM and LSCF are combined in such a way, Co takes the sole role of charge compensation for oxygen vacancies without the local structural instability of the cations which is otherwise observable in LSCF. Although the LSM coating is not observed to participate electrochemically by change of valence, LSM improves both the performance and Sr cation stability, resulting in an enhanced solid oxide fuel cell cathode.

References

Formic Acid Electrooxidation at Platinum-modified Gold Surface: A Combined Study by Electrochemistry and Surface Enhanced Raman Spectroscopy

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Introduction and Objectives

Present fuel cell technology is limited by low kinetics at the anode indicating the need for effective catalysts to improve formic acid oxidation.\(^1\) As a prerequisite, we need to investigate the nature of adsorbed species and specifically the intermediates in this process. Current work focuses on electrooxidation of formic acid and the study of the nature of intermediates, especially formate at platinum-modified gold surface by combination of electrochemistry and in situ surface enhanced raman spectroscopy (SERS).\(^2\)

We have examined the potential dependant vibrational properties of HCOO\(^-\) stretching mode in the wide potential range of 0 to 1.1 V using electrochemical in situ SERS. Furthermore, we studied dependence of the chemisorbate vibrational frequency on the electrode potential known as stark effect. The results provide a new insight into the behavior of the formate adsorbate generated in the electro oxidation process on Pt (Au) catalyst surface. A detailed study of the electrochemical behavior of formic acid oxidation on Pt (Au) catalyst surface was also performed.

Results and Discussion

The platinum was deposited spontaneously on gold surface (Pt@Au).\(^3\) This Pt@Au surface assists in oxidizing formic acid at potentials as low as 0.1 V vs. Ag/Ag/Cl as compared to that on plain gold ca. 0.4 & 1.0 V. Also, the oxidation currents obtained on Pt/Au electrode is higher than that on bare Pt surface and 200 times higher than that on bare Au surface.\(^4\) (Figure a). The electrochemical results affirm the enhanced catalytic activity of Pt@Au for formic acid oxidation. Furthermore, formate was observed as an intermediate in the oxidation process on Pt@Au by SERS (Figure b). This formate peak which appears at 300 cm\(^{-1}\) showed a higher stark slope as compared to that on plain gold surface.\(^4\) Figure b inset shows the comparison of the SERS intensity of the formate peak with the cyclic voltammetric currents. It is interesting to observe that formation of gold oxide was necessary for the attraction of the formate on Pt@Au. Further in the cathodic scan, the formate shows a high SERS intensity, which is not unexpected and is attributed to the low activity of platinum oxide for formic acid oxidation. Finally as the reduction potential of platinum was reached, the reduced platinum immediately catalyzes the oxidation process causing the drop in the SERS peak. Thus a unique relationship was observed between the formic acid oxidation currents and the SERS intensity of the formate adsorbate on Pt @Au.
Figure a) Cyclic voltammograms on the plain Au (in blue) and Pt@Au (in red) at 10 mins, bare Pt electrode (black) in 0.125M HClO₄. b) SERS of electroxidation of 0.5 M HCOOH in 0.125 M HClO₄ on Au@Pt 10mins (cathodic scan). Inset shows comparison of the SERS intensity of HCOO⁻ adsorbate (●) with cyclic voltammogram.

Conclusions

Pt@Au showed high catalytic activity for formic acid electroxidation in the potential range of 0.2-0.4 V, critical for fuel cell applications. By electrochemical experiments, we were able to see that formic acid was oxidized by the dehydrogenation pathway till the concentration of 0.5 M. By SERS, we were able to corroborate the electrochemical data and study the vibrational spectroscopic behavior of the formate adsorbate at 300 cm⁻¹. This adsorbate plays the role of an intermediate in this formic acid oxidation process on Pt@Au.

References

Operando Studies of CeO₂-supported Pt, Ru and Pt-Ru Alloy Catalysts for the Water-Gas Shift Reaction

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Introduction and Objectives

Noble metal-based catalysts can be used to provide the pure hydrogen feed necessary for the operation of fuel cells through the water-gas shift reaction (WGSR)¹. Pt on CeO₂ is one of the most active catalysts². The catalytic property can be potentially enhanced by alloying Pt with other metals such as Re³ or Cu⁴. Substituting a single noble metal with metal alloys is a valid approach to develop WGS catalysts and deserves more research. In the current study, three CeO₂-supported Pt/Ru catalysts (Pt-CeO₂, Ru-CeO₂ and Pt-Ru alloy-CeO₂) were examined with X-ray diffraction (XRD), X-ray absorption near edge spectroscopy (XANES) and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) during the WGSR. The operando spectroscopic methods revealed bulk and surface changes of these catalysts during the WGSR, which helped to understand the performance of the Pt-Ru alloy, as well as the WGSR reaction mechanism on noble metal catalysts, which is still under debate⁵.

Results and Discussion

All the three systems investigated displayed a high WGS activity. The Pt-Ru alloy does not have a clearly improved activity with respect to Pt-CeO₂, but the alloy does have a reduced generation of methane under WGSR conditions compared to Ru-CeO₂. DRIFTS spectra shown in Figure 1 revealed the formation of a substantial amount of formate (HCOO⁻) on Pt-CeO₂ during the WGSR, while formate on PtRu-CeO₂ and Ru-CeO₂ was at a much lower level. The inhibition of formate formation on PtRu-CeO₂ points to a modification of the chemical property of Pt by alloying with Ru. The fact that the inhibition of Pt-bound formate does not affect catalytic activity implies that formate is merely a spectator on Pt, or at least not involved in the main reaction pathway. DRIFTS spectra also show the formation of Pt/Ru-bound CO at 50 to 100 °C on all the three catalysts prior to the start of the WGSR, which indicates that a Pt/Ru reduced state which can bond CO is a prerequisite for the WGSR. Indeed, operando XANES data confirmed the reduction of Pt in both Pt-CeO₂ and PtRu-CeO₂ during heating in the WGSR environment. We also studied reduction of these catalysts in 5% CO by XRD. The results show an extra expansion of the CeO₂ crystal lattice at 100 to 200 °C in all the catalysts. The extra expansion is due to oxygen removal from CeO₂, which is promoted by the deposited metals.
Fig. 1 DRIFTS profiles of the three catalysts in a heating series under the WGSR condition (1% CO, 3% H₂O balanced by He). Notice the strong bands of formate (2940, 2840 and 2710 cm⁻¹) on Pt-CeO₂ are rarely seen on Ru-CeO₂ and PtRu-CeO₂.

Conclusions

A series of operando spectroscopic methods were used to study the activation and function of Pt-CeO₂, Ru-CeO₂ and Pt-Ru alloy-CeO₂ catalysts under WGSR conditions. The Pt-Ru alloy has a unique ability of suppressing formation of methane and formate while displaying high activity for the WGSR. Formate is perhaps only a spectator in the WGSR.

References

In-situ FTIR Spectroscopic Investigation of Au/TiO₂/Si Anode at Temperatures up to 450 °C.

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Abstract

Recent work on the electrochemical behaviour of novel Au/TiO₂/Si composite anodes has suggested their potential application in fuel cell technology [1], particularly with respect to “fuel cell-on-a-chip” and high temperature fuel cell technologies. The composite anodes consist of a 120 nm TiO₂ layer sputtered onto a 300 μm n-doped Si wafer, onto which is deposited a 100 nm metal (gold) grid. Holes thermally, and/or photochemically, generated near the Si/TiO₂ interface in the Si are able to reach the surface of the TiO₂ and oxidise gas or liquid phase species. Hole transport across the TiO₂ is facilitated by the application of a bias voltage across the silicon and metal grid.

In-situ FTIR spectroscopy was employed to provide essential molecular information on the behavior and potential catalytic activity of the composite anodes as a function of temperature in the presence and absence of carbon monoxide (CO). The effect of CO concentration in the gas phase was also studied. These (non electrochemical) studies were carried out to provide essential baseline data. Data will also be presented on the effect of temperature and concentration of CO, as well as a model describing the chemistry taking place at the Si/TiO₂ and TiO₂/gas interfaces. Additionally, data will also be presented on the behaviour of the anode under potentiostatic control as a function of temperature using a home-made electrochemical cell operated within the high pressure/high temperature chamber.

Typical spectra obtained during heating of the anode up to 450 °C and subsequent cooling back to room temperature in CO/N₂ are shown in fig. 1. Bands due to the loss of gas phase CO (ca. 2120 and 2170 cm⁻¹) and the gain of CO₂ (double peak near 2350 cm⁻¹) can be seen, due to the oxidation of the former, presumably by oxygen from the TiO₂ substrate. Interestingly, the marked effect of temperature on the extinction coefficient of CO is clearly visible in the figure (ε decreases as temperature increases). The large loss feature which develops between 1000 and 1200 cm⁻¹ as the temperature is increased (and is also lost on cooling) may be attributed to Si-O-Si bands [2–4], suggesting marked changes at the Si/TiO₂ interface.
Figure 1. Spectra obtained during the heating of a composite anode sample to 450 °C, followed by cooling to room temperature again

References
Innovative *Operando* Characterisation by DRX-DRIFT-GC of Various Cobalt Fischer-Tropsch Catalysts

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**Introduction and Objectives**

Global energy trends tend to go nowadays towards an energy resource diversification. This context gives rise to an increasing interest in the Fischer-Tropsch (FT) process that allows the catalytic hydrogenation of CO into linear hydrocarbons. Cobalt catalysts are mostly used to produce heavy waxes that are later easily upgraded into diesel/kerosene cuts. Their catalytic properties, i.e. selectivity and activity, strongly depend on the structural and morphological properties of the catalysts themselves [1-3].

In this study, we focus on the *operando* characterisation of alumina and silica supported cobalt catalysts with various crystallite sizes. Before performing the Fischer-Tropsch synthesis under realistic conditions, the cristallographic structure of metallic cobalt is oriented towards either a mainly hexagonal or a mainly cubic phase. The selectivity towards heavy paraffins as well as the catalytic activity will be further described with respect to time on stream and the catalyst morphology and structure.

**Results and Discussion**

To better understand the impact of the catalysts’ properties on the catalytic activity and selectivity, a new innovative *operando* system has been developed. It consists of associating a X-Ray Diffraction (XRD) system to an IR spectrometer. Each analysis can be performed simultaneously thanks to the use of a dedicated reaction cell able to support pressure up to 18bar and temperature up to 600°C inside the catalyst bed (figure 1). An online GC allows the characterisation of the reaction products.

During the activation process, the majority of metallic cobalt of a cobalt silica catalyst \((D_{\text{CoO}_4}=12\text{nm})\) is tuned into a hexagonal structure with a dedicated procedure. The Fischer-Tropsch synthesis is performed with the tuned metallic cobalt catalyst under atmospheric pressure, 230°C, \(H_2/CO = 4\) for 24 hours. During the reaction the crystallographic phase of the cobalt is followed by XRD while the reactants adsorption and products formation on the surface are observed by Diffuse Reflectance IR Spectroscopy (DRIFTS). The CO conversion and the selectivity towards methane and light hydrocarbons are obtained from on line GC analysis.

As shown in the diffractograms of figure 2, the crystalline phase of cobalt remains unchanged: metallic cobalt is mainly hexagonal. Cobalt oxidation was not observed. Since Co phase changes do not operate
during FT start-up period, other causes like sinterin or carbidisation during catalysts aging have to be found.

Meanwhile, the formation of methane and light alkanes was followed by DRIFT spectroscopy (figure 3). IR spectra also revealed that there was no CO₂ formation.

![Figure 3: XRD pattern during the Fischer Tropsch synthesis](image)

The gaseous effluent analysis carried out online by GC showed that the CO conversion was low, which can be explained by the low reaction temperature and the low porosity of the silica support (dₚ=6nm). Concerning the product selectivity, light hydrocarbons were preferentially produced regarding the high H₂/CO ratio.

**Conclusions**

FT synthesis was performed on a hexagonal cobalt silica catalyst. *Operando* characterisations showed no structural modification though a small activity and hydrocarbons formation were observed. By extending this study to another support (alumina) and with various particle size, metallic cobalt crystalline structures and realistic conditions, it will be possible to link the catalytic properties to the structure and morphology of model cobalt FT catalysts. These results will be presented during the Operando IV meeting.

**References**

X-ray Absorption Spectroscopy and Heterogeneous Catalysis: Unique Performances at the SOLEIL’s SAMBA Beamline

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Introduction and Objectives

Due to its atomic selectivity and high sensitivity, X-ray Absorption Spectroscopy (XAS) is recognized as a tool of prime importance for the study of heterogeneous catalysts. With the development of third generation synchrotron radiation sources, like SOLEIL, sub-second analysis are now accessible using the so-called Quick-EXAFS technique, allowing time-resolved characterizations of catalytic materials under working conditions. This technique is based on the sequential data acquisition, where a double crystal monochromator is continuously swung from high to low Bragg angles and the absorption spectrum is measured on the fly. At the SAMBA (Spectroscopies Applied to Materials Based on Absorption) beamline [1], specific efforts were undertaken in the past three years in order to propose a unique setup composed of two complementary and permanently installed Quick-EXAFS monochromators and state-of-the-art catalytic cells usable for experiments in both transmission and fluorescence mode. The Quick-EXAFS approach coupled with time-resolved Raman spectroscopy offers tremendous knowledge for cutting edge research in the field of catalysis for a broad spectrum of reactions (RT-600°C, pressure: 1-20 bar) involving bulk, supported or diluted active species [1-3].

Results and Discussion

The SAMBA Quick-EXAFS monochromators are equipped with Si(111) and Si(311) channel-cut crystals mounted on two independent cam driven tilt tables that oscillate around a selected central Bragg angle, $\theta$, with a user selectable angular amplitude, $\Delta \theta$, up to 4° [1]. The time-resolution accessible with these monochromators can be as fast as 25 ms. Even with such short data acquisition times, the wide oscillation amplitude allows recording EXAFS data with a spectral range of 1000 eV or more at any edges covered by the beamline (from the Ti to Cs K edges). The wide energy range available with the 4° angular amplitude available at SAMBA can be used for the simultaneous recording of L edges of 5d catalysts (Figure 1) providing access both to the structural (L$_3$) and electronic (L$_1$) states of the catalyst. Moreover, the most powerful capability of this new design is the easy, fast (< 1 min) and remote change of the channel-cut crystals from Si(111) to Si(311) allowing the simultaneous study of two active metals of a bimetallic catalyst during the same catalytic reaction undergone on the same sample.

![Figure 1: Quick-EXAFS spectrum of the Re L edges of NaReO$_4$ (10 acq x 0.5 s).](image-url)
Conclusions

Mass spectrometry and Raman spectroscopy, used to monitor the chemicals produced by the catalytic reactions, provide the necessary quantitative information for accessing to the activity or the selectivity of the catalysts in real catalytic conditions, simultaneously with the collection of EXAFS data. Both technical and methodological developments allow for accessing the so-called *operando* spectroscopic approach in a time scale suitable for unraveling complex mechanisms of catalyst transformation with, in particular, the identification of intermediate species.

The *operando* approach available on the SAMBA beamline is illustrated by examples of important industrial processes in relation with the energy feedstocks: the Fischer-Tropsch reaction carried out at 20 bar under syngas and the hydrodesulfurization process of petroleum with a special emphasis on the simultaneous time-resolved characterization of molybdenum and 3d promoter local order changes during activation under H$_2$S/H$_2$ (Figure 2).

![Figure 2: Simultaneous Quick-EXAFS study at the Ni and Mo K edges of the activation of a NiMo based catalyst under H$_2$S/H$_2$ (heating ramp 2°C/min).](image)

References


A Combined Magnetometer / Raman Device for Studies of Catalysts at Industrial Conditions

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Introduction and Objectives

The paper describes the development of the second in-situ magnetometer at the University of Cape Town and its use for characterisation of ferro-magnetic catalysts at industrial conditions. This set-up is based on the original design, which allows reaction conditions of up to 500°C and more than 50 bar (see figure, [1]) and it has now been coupled with an in-situ Raman option which makes use of two different laser wavelengths.

The system allows to monitor catalyst phase changes (oxidation, reduction, carbiding) as well as effects of sintering as magnetic behaviour of nano-material is strictly crystallite size dependent [2]. Importantly, the design of the reactor allows ideal plug-flow behaviour and therefore kinetically fully relevant information regarding the catalyst performance can be obtained setting it apart from many other catalyst characterisation devices.

Results and Discussion

The set-up has been used to characterise various Fischer-Tropsch catalysts, cobalt and iron-based, during catalyst pre-treatment, and during Fischer-Tropsch synthesis. Examples of these studies will be given in the paper. Inter alia, the size dependent oxidation of cobalt crystallites could be studied as function of synthesis gas conversion [3], which resulted in preferred deactivation of very small cobalt crystallites.

Conclusions

The novel magnetometer provides a unique new tool for in-situ characterization of ferromagnetic catalysts and ferro-magnetic material in general. Information on phase changes (e.g. degree of reduction), crystallite size changes (sintering) and even crystallite size distribution can be obtained at fully relevant reaction conditions.

References

Effect of Calcination Temperature and in situ Reduction in the Synthesis of Some Supported Cobalt Catalysts

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Introduction and Objectives

Supported cobalt catalysts are important catalytic materials for the hydrogenation and hydro treating reactions [1-4]. The active phase in these catalysts is the cobalt metal phase. Proper synthesis of these supported cobalt catalysts is important since it is often possible that the active cobalt phase is ill formed or reacts with the support to form compounds. Specifically, some synthesis methods require calcination of the cobalt precursor-impregnated support at elevated temperatures. During this calcination step cobalt is oxidized, which necessitates reduction so that the active site is formed. Sometimes cobalt-support compounds are formed during the calcination step. Instead, by removing the calcination step the supported cobalt catalysts may be directly reduced after impregnation of the precursor to the support.

Based on the above, the objective of the present study is to study the effect of the calcination step during the synthesis of some supported cobalt catalysts. To achieve the objectives supported catalysts containing 15 weight percent cobalt were synthesized using three different supports, alumina, silica and magnesia and then characterized by: (i) XRD, (ii) UV-vis-NIR spectroscopy under ambient and in situ conditions, and (iii) in situ DRIFTS with simultaneous activity measurements during the CO2 hydrogenation reaction. It was expected that the information provided by a combination of these characterization techniques would assist in a better understanding of the synthesis of an active supported cobalt catalyst.

Results and Discussion

The XRD pattern of the unsupported cobalt sample and the alumina and silica supported cobalt catalysts, calcined at 383, 473, 573, 673 and 773 K, and reduced at 823 K for 4 hours, revealed the evolution of the cobalt metal peak. The intensity of the cobalt peak, however, depends on the specific synthesise condition. For the magnesia supported cobalt catalyst the features of the support dominates the XRD pattern.

The UV-vis-NIR spectra of the three dessicator-dried supported catalysts at increasing calcination temperatures revealed the formation of Co3O4 at temperatures above 473 K on the alumina and silica supported cobalt samples. At temperatures below 473 K, precursor related bands were observed. A temperature of 673 K was, however, required for the magnesia supported cobalt catalyst to observe Co3O4. Below 673 and above 473 K, the cobalt oxide bands were weak and different from Co3O4. At calcination temperatures above 973 K, cobalt aluminate and cobalt-magnesia compounds were formed in the alumina and magnesia supported cobalt samples, respectively; the silica supported cobalt sample, however, retained the features of Co3O4.

Based on the above observations, the DRIFT spectra of the three supported cobalt catalysts during the CO2 hydrogenation reaction and the corresponding conversion and methane yield data were obtained. The catalysts were exposed to different in situ treatment conditions. Infrared bands due to formate and carbon monoxide were observed on the reduced alumina and magnesia supported cobalt catalyst. The intensity of
these bands, however, varied depending on the specific in situ treatment. These IR bands were absent for the reduced silica supported cobalt catalyst. It was also observed that for the three supported cobalt catalysts, calcination at 473 K followed by reduction at 823 K was ideal. Higher calcination temperatures followed by reduction at 873 K were detrimental to the reactivity of the alumina and magnesia supported catalyst. For the silica supported cobalt catalysts that have been finally reduced at 873 K, however, the reactivity initially decreased with an increase in calcination temperature above 473 K and then increased with a further increase in calcination temperature. Lower calcination temperatures were also not as effective.

Conclusions

Thus, it appears that calcination at 473 K followed by reduction at 823 K is required to form the most active supported cobalt catalyst. At 473 K, the cobalt precursor is decomposed and the active cobalt sites are formed after reduction at 823 K. Calcination of the supported cobalt samples at 773 K prior to reduction at 823 K is not required and is in fact detrimental to the reactivity. Furthermore, calcination of alumina and magnesia supported cobalt catalyst at temperatures in excess of 973 K is undesirable due to the formation of cobalt-support compounds.

References

Continuous Flow NMR Studies of Probe Molecule Adsorption

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'MASCAT', a continuous flow magic angle spinning (MAS) NMR probehead has been developed, which enables simultaneously the observation of NMR spectra in the presence of sorbate or reactants, in flow mode and possibly in reaction conditions. The understanding of events occurring on catalyst surfaces, such as in zeolitic materials or more generally in nanoporous materials, is of primary importance to improve the performance of these materials. Our main interest is focused on the study and the development of methanol conversion to hydrocarbons (MTH), a catalytic process which is currently attracting a renewed attention due to worldwide energy concerns. For this purpose, the first steps controlling the absorption, diffusion and desorption of water and methanol have been investigated, with a particular interest on the interaction of these molecules with the structural defects and acidic sites in zeolites such as silicalites (micro and nanosized cristals) and ZSM-5. In this poster, the preliminary results will be presented and discussed.
Operando XAS-MS Studies of Alumina Supported Pt Catalysts Promoted with Ce for Methane Reactions

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Introduction and Objectives

Several studies for methane reforming catalysts have been extensively reported on literature and have raised important features to understand the role of supports effects on their activity and stability: i) the reaction is structural sensitive \cite{1} and ii) carbon formation and metal particle agglomeration are the principal mechanisms for catalysts deactivation \cite{2,3}. Factors able to affect these mechanisms may modify the catalytic performance: noble metals as a promoter were found to modify electronic properties of metal and avoid carbon formation \cite{2}; rare earths were found to modify thermal stability of the supports and to anchor metal particle avoiding his size increasing \cite{3,4}. However structural and electronic aspects of the catalysts promoters could not be understood due to the techniques limitations and the complexity of these systems. Since catalysts are dynamics and sensible to atmospheres and temperature, in situ and operando studies become very useful to clarify these aspects, specially using XAS spectroscopy, which is able to obtain oxidation state, geometry, particle size and organization structural information. The aim of this work is to advance at understanding of supported Pt catalysts for methane reactions by operando XAS-MS spectroscopy, confirming Ce promoter effects and explaining methane reaction mechanism.

Results and Discussion

The results show that the properties conferred to the alumina and Pt catalysts by CeO\textsubscript{2} and the effect of metal-support interaction became improved when materials were prepared by sol-gel method. PA and PCA catalysts were prepared by impregnation of alumina and ceria-alumina (12% wt. of CeO\textsubscript{2}) obtained by sol-gel method with Pt solution (1% wt. of Pt). After calcination in air at 1223 K, their showed higher specific area, lower apparent Pt crystallites and higher thermal stability against alumina and ceria segregation after oxidizing conditions at high temperature than respective PA and PCA conventional catalysts, reported before \cite{5}. Oxygen-reducing properties are also favored. TPR profiles of PCA show superficial ceria is also reduced at low temperature (473 K) with Pt oxide; by re-oxidizing in air at 773 K to reduce again, the peak is moved to 500 K where ca. 50 % of ceria was kept reduced compared to previous reduction and all Pt was re-oxidized; by re-oxidizing in air at 1073 K to reduce again, ca. 50 % of ceria was also kept reduced, the peak was moved to 532 K and a shoulder at 650 K appeared, indicating higher Pt-support interaction. PA show much less intense reduction peak and just
kept some reduction after re-oxidations, suggestion Pt agglomeration. EXAFS parameters obtained during heating up to 773 K under hydrogen atmosphere present overall first-shell coordination numbers with important contribution of Pt-O scattering for PCA meanly and suggest changes in Pt cluster morphology with increasing temperature. PCA catalyst exhibits higher activity (conversion about 73%) and stability for methane reactions than the PA one (conversion about 40%). However the stability of the catalysts in the partial oxidation of methane (POM) is much improved than conventional catalysts [5]. FTIR of adsorbed CO and dehydrogenation of cyclohexane experiments show Pt sites are very covered by the support, principally by CA, and the catalysts present higher frequency of reaction (TOF). The hypothesis of [CePtO]Ptø species formation in the interface [4] is a possible mechanism to transfer O* to C* adsorbed on Pt surface from the dissociation of methane, that removes coke and makes Pt sites accessible to CH₄ again. Operando XAS-MS experiments under conditions of oxi-reductive and POM (Fig. 1) reveal the presence of vacancies in the reduced Pt 5d orbital and the interaction between Pt and ceria, which prevents the migration and coalescence of Pt nanoparticles by balancing PtOₓ ↔ Pt⁰ dispersa at high temperatures and variables atmospheres. At 1073 K under POM, Pt and Ce are in their reduced forms, confirming that Ce probably provides oxygen to reoxidize carbon on reduced Pt sites, cleaning the surface and keeping the catalyst active.

Conclusions
Sol-gel method preparation improved the properties of alumina and Pt catalysts modified by CeO₂. EXAFS parameters showed more impressive interface metal-support when Ce is present. Ce promoter structural effects were confirmed by operando XAS-MS studies and ceria may improve Pt catalysts performance by a possible mechanism to transfer O* to C* adsorbed on Pt surface, that oxidizes coke.

References
Operando and in situ Characterization of Inverse Copper Ceria Catalysts with Combined XRD and XAS and with Simultaneous PDF and DRIFTS

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Introduction and Objectives

It has been show that an “inverse catalyst” with nanoceria (<6nm) deposited on large particles of copper oxide (>20nm) have improved performance for preferential oxidation of CO (CO-PROX) \cite{1}. This catalyst has also been studied in operando with X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) under water gas shift (WGS) reaction conditions.\cite{2}. This inverse CeO\textsubscript{2}/CuO-Cu catalyst exhibits significantly higher WGS activity than standard Cu/CeO\textsubscript{2} catalysts. We have performed operando studies that combine different techniques (XRD, pair distribution function (PDF), XAS, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)) to explore possible correlations among the structural and catalytic properties of the inverse CeO\textsubscript{2}/CuO-Cu catalyst.

Results and Discussion

Time-resolved X-ray diffraction experiments under WGS conditions on the inverse catalyst showed the transformation of CuO to metallic Cu via a Cu\textsubscript{2}O intermediate as a crystalline material. X-ray absorption spectroscopy also revealed oxidation state changes from Cu\textsuperscript{2+} to Cu\textsuperscript{0} and the partial reduction of CeO\textsubscript{x} nanoparticles\cite{2}.

To further characterize the catalyst we have performed in situ combined XRD/XAS studies under oxidizing and reducing conditions \cite{3}. From XRD the reduced catalyst mostly has metallic copper, but the linear combination analysis (LCA) analysis of the XAS data indicated that the product is 70\%Cu\textsuperscript{0}, 17\%Cu\textsuperscript{1+}, and 13\%Cu\textsuperscript{2+}. During partial re-oxidation the XRD analysis shows no metallic copper while the LCA analysis shows that the material is a mixture of Cu\textsuperscript{0}, Cu\textsuperscript{1+}, and Cu\textsuperscript{2+}. These data suggest that poorly crystalline phases are present under these conditions.

Measurements of PDF during operando studies provide another way to obtain information about amorphous phases and catalyst surface interactions\cite{4, 5}. Short-order structural changes were followed by pair distribution function analysis and corroborated the results obtained by diffraction. Recently a setup (similar to the one at the ESRF \cite{6}) which combines PDF measurement with DRIFTS measurement has been built at beamline 11ID-B of the APS. We have used this instrument to characterize the inverse copper ceria catalyst under WGS conditions and during oxidation and reduction cycles. We have correlated the DRIFTS spectra of adsorbed CO with the Cu-containing phases as determined by simultaneous XRD measurements.
Conclusions

The activity data obtained by mass spectrometry revealed that hydrogen production through the WGS on CeO$_2$/CuO-Cu starts once the copper has been fully reduced. The strong interaction of ceria and copper enhanced the catalytic performance of the sample. The active phases of the inverse CeO$_2$/CuO-Cu catalyst are partially reduced ceria nanoparticles strongly interacting with metallic copper.

The combined XRD/XAS data suggest that poorly crystalline phases are present under oxidizing and reducing conditions. The combined XRD/DRIFTS studies showed that the catalyst transformed from CuO to metallic Cu via a Cu$_2$O intermediate during ramping in CO. More importantly, the Cu$_2$O phase, which was “invisible” in XRD patterns, has been demonstrated by Cu(I)-CO peak at 2,100 cm$^{-1}$ in the DRIFTS. It also indicates that the Cu$_2$O intermediate structure is either amorphous or a poorly crystalline layer on the surface of the catalyst.

The use of the NSLS was supported by U.S. DOE contract No. DE-AC02-98CH10886, and in part by the Synchrotron Catalysis Consortium with U.S. DOE Grant No DE-FG02-05ER15688. Use of the Advanced Photon Source was supported by the U. S. DOE contract No. DE-AC02-06CH11357.

References

Operando Studies of the Thermal Decomposition of Copper and Manganese Acetate and the Formation of Metal Oxide Phases


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Introduction and Objectives

Hopcalite (Cu-Mn-O phases) is a well known catalyst for ambient CO oxidation, the water-gas shift reaction and total oxidation of volatile organic compounds [1-3]. In an effort to avoid nitrate waste effluent the use of acetate salt precursors, as opposed to nitrate salts, has been investigated [4]. The thermal decomposition of acetate salts is known to result in the formation of a reducing atmosphere and consequently the formation of metals or metal oxides with lower oxidation number than the initial salt [5]. With the use of Operando XRD studies and XPS we have investigated the effect of the thermal decomposition of a copper and manganese acetate mixture. It was found that the two metal phases interacted during heat treatment and altered the reduction process relative to that seen for the single metal acetates. In addition, the oxygen content of the atmosphere during heat treatment was shown to dictate the final metal oxide phase present after acetate decomposition. This variance in oxide phase formation was then used to elucidate information on the active phases for ambient CO oxidation.

Results and Discussion

The decomposition of the metal salts under an inert atmosphere results in the formation of metallic Cu and MnO, when heat treated separately. The Cu phases showed an observable reduction from CuO →
Cu₂O → Cu while the only phase observed in the Mn system was that of MnO (Figure 1.a). The decomposition of a 2:1 Mn:Cu mixture of acetate salts (Figure 1.b) under an inert atmosphere provided similar phases to the separate experiments. However, it was noted that Mn₃O₄ phases were present, which indicates a partial oxidation of Mn phases. This was attributed to a spill over mechanism with Cu species, where oxygen is donated to the Mn phase at the interface between Cu and Mn phases. Furthermore, it was observed that a greater proportion of Cu₂O was present at 400 °C in the mixed system than in the Cu only. This suggests that the kinetics of the Cu₂O reduction was retarded by the presence of the Mn phases, with a redox system occurring at Cu-Mn phase boundaries.

Under an oxygen containing atmosphere the Cu phases still showed an observable reduction pattern, but with a rapid re-oxidation to form CuO. The Mn:Cu mixture of acetate salts showed the formation of discrete oxide phases prior to migration of metal ions across the Cu-Mn interface to form a CuMn₂O₄ spinel phase. The flow rate of gas over the acetate mixture was shown to influence the rate of CuMn₂O₄ phase formation.

CO oxidation was performed on materials prepared under an inert atmosphere, flowing air and static air. It was shown that the CuMn₂O₄ spinel was required for activity, in line with the redox mechanism stipulated in the literature.

Conclusions

Operando studies have shown the evolution of copper and manganese oxide phases in the decomposition of their parent salts. Interaction between copper and manganese phases was observed. The effect of atmosphere was investigated, with an inert atmosphere producing separate Cu and Mn phase and an oxygen containing atmosphere producing a mixed metal spinel phase. It was demonstrated that the spinel phase is required for catalytic activity.

References

**In situ and Operando Raman/IR/UV-vis/MS Spectroscopic Studies During Propylene Metathesis by Supported WO\textsubscript{x}/SiO\textsubscript{2} Catalysts**

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**Introduction and Objectives**

Olefin metathesis is a very significant industrial reaction that finds applications in producing important petrochemicals, oleochemicals, polymers and specialty chemicals [1]. The SiO\textsubscript{2}-supported tungsten oxide catalysts are mainly used for high temperature (300-400 °C) metathesis of low molecular weight products such as propylene metathesis for the production of ethylene and butene and vice versa [2]. By relating the nature of the tungsten oxide species and reaction intermediates involved under realistic conditions to the desired metathesis products, rational design of olefin metathesis catalysts can be undertaken.

In this project, ultra-small (< 2 nm) tungsten oxide nanoparticles on a SiO\textsubscript{2} support (NP WO\textsubscript{x}/SiO\textsubscript{2}) were synthesized using a solvothermal reaction between ammonium metatungstate (AMT) and oleylamine. Even smaller (0.8-1.2 nm) nanoparticles (sNP WO\textsubscript{x}/SiO\textsubscript{2}) were obtained by controlling the precursor ammonium metatungstate (AMT) decomposition/reduction rate during synthesis using trimethylamine N-oxide (TANO). Their catalytic performance for propylene metathesis was compared with conventional supported WO\textsubscript{x}/SiO\textsubscript{2} catalysts prepared by incipient-wetness impregnation of AMT.

**Results and Discussion**

The *in situ* Raman and UV-vis spectra collected during propylene metathesis reaction conditions along with aberration corrected-STEM images showed that the concentration of surface monotungstate and polytungstate species was highest for the sNP WO\textsubscript{x}/SiO\textsubscript{2} series followed by the NP WO\textsubscript{x}/SiO\textsubscript{2} series and lowest for the conventional WO\textsubscript{x}/SiO\textsubscript{2} catalysts. At a surface density of 1.1 W/nm\textsuperscript{2}, both crystalline WO\textsubscript{3} NPs and surface tungsten oxide species coexist on the silica support, in accordance with previous observations [3]. No noticeable reduction in the UV-vis W\textsuperscript{6+} ligand-to-metal charge transfer (LMCT) band was observed during the reaction. *In situ* DRIFT-IR employed both C\textsubscript{3}H\textsubscript{6} and isotopically labeled C\textsubscript{3}D\textsubscript{6} to confirm band assignments and found that surface \(\pi\)-allyl species (CH\textsubscript{2}-CH*-CH\textsubscript{2}) were the most abundant reaction intermediates (mari) during propylene metathesis by the supported WO\textsubscript{x}/SiO\textsubscript{2} catalysts.
he nano catalysts (NP and sNP) were better metathesis catalysts than conventional samples due to better dispersion of surface WO₄ monomers and oligomers. The metathesis turnover rate (TOR and \( \frac{n\text{C}_2}{n\text{C}_4} \times \text{TOR} \)) was highest at the lowest tungsten oxide loading of 0.6 W/nm² for the sNP catalysts indicating that surface monotungstate WO₄ and surface polytungstate WO₅/WO₆ species are more active in this catalyst series. For the supported WOₓ/SiO₂ and NP WOₓ/SiO₂ series, however, the WO₃ crystals improved the catalytic performance as their metathesis TORs were highest at 1.1 W/nm².

Conclusions

Time-resolved operando Raman/IR/UV-vis spectroscopic measurements during the initial stages of the propylene metathesis reaction provide additional fundamental molecular level insights into the relationships between the different tungsten oxide catalytic active sites, surface reaction intermediates and olefin conversion/selectivity. Additional insights into the catalyst structure-activity relationships during propylene metathesis are also provided by transient isotopic switching experiments (C₃H₆ vs. C₃D₆). The above information will used in developing a molecular model for olefin metathesis by supported WOₓ/SiO₂ catalysts.

References

New Insights into the Influence of CO2 on the Storage Properties of Pt-Ba/Al2O3 NSR Catalyst Studied by Operando FT-IR and Pulse Reactor Experiments

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Introduction and Objectives

In our previous works, \textit{in situ} and \textit{operando} FT-IR spectroscopy and reactor experiments 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\textsubscript{2} mixture on Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalysts [1-3]. In particular, we have demonstrated the existence of two alternative pathways: \textit{i}) one, hereafter denoted as \textit{nitrates route}, where NO is at first oxidized by Pt to NO\textsubscript{2}, which is then stored onto alkali-earth metal compound in the form of nitrates according to a dismutation reaction (3 NO\textsubscript{2} + O\textsuperscript{−} → 2 NO\textsubscript{3}\textsuperscript{−} + NO), without formation of nitrites as stable intermediates; \textit{ii}) another one, hereafter denoted as \textit{nitrites route}, where NO is first adsorbed and oxidized leading to the formation of nitrites as stable intermediates (2 NO + \frac{1}{2} O\textsubscript{2} + O\textsuperscript{−} → 2 NO\textsubscript{2}\textsuperscript{−}), the stored nitrites might be further oxidized to nitrates as consecutive reaction.

As for the relevance of the \textit{nitrite} and \textit{nitrates} routes, studies in a wide temperature range showed that at low temperatures (150-250 °C) the \textit{nitrite} pathway is the prevalent route, since nitrates are not observed (at 150 °C) or only observed after long contact times; at variance, at 350 °C the nitrate formation is relevant, while nitrites are seen in the preliminary stages of the storage.

In this work, we combine FT-IR spectroscopy of the adsorbed species under \textit{operando} conditions with on-line analysis of the gas phase to investigate the influence of CO\textsubscript{2} on the NO\textsubscript{x} storage mechanism. Actually, we already investigated the influence of CO\textsubscript{2} on the NO\textsubscript{x} storage mechanism at 350 °C by \textit{in situ} FT-IR spectroscopy and pulse reactor experiments [4]. With the present study we will confirm the results obtained in the past with \textit{in situ} FT-IR spectroscopy and we will provide new insights, analyzing the influence of CO\textsubscript{2} at lower temperature down to 150 °C.

Results and Discussion

Homemade Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalyst (Pt 1%, Ba 16% w/w) were prepared by impregnation of \textgamma-alumina with Ba(CH\textsubscript{3}COO)\textsubscript{2} and Pt(NH\textsubscript{3})\textsubscript{2}(NO\textsubscript{2})\textsubscript{2} precursors. The gas phase composition and the nature, time evolution and relative amounts of NO\textsubscript{x} surface species were investigated by imposing rectangular step feed of NO (1000 ppm) in Ar + 3% v/v O\textsubscript{2} and in Ar + 3% v/v O\textsubscript{2} + 0.3 v/v of CO\textsubscript{2} in the range 150-350 °C.

Gas phase analysis showed that at saturation the NO\textsubscript{x} storage capacity is not significantly affected by CO\textsubscript{2} at 350 °C, although the dead time in the NO\textsubscript{x} detection is lower in the presence of CO\textsubscript{2}. At 250 °C and 200 °C the presence of CO\textsubscript{2} decreases both the amounts of stored NO\textsubscript{x} and the NO\textsubscript{x} breakthrough as well;
at 150 °C the NO\textsubscript{x} breakthrough is nihil both in the presence and in the absence of CO\textsubscript{2}.

FT-IR spectra recorded at the same temperatures upon NO\textsubscript{x} adsorption pointed out that at 150 °C CO\textsubscript{2} does not significantly influence the nature, time evolution and saturation amount of surface nitrites, the only species formed at this temperature. On the other hand at higher temperatures the presence of CO\textsubscript{2} significantly decreases the maximum intensity reached by the nitrites. This effect increases upon increasing the temperature, so that at 350 °C the CO\textsubscript{2} in the feed strongly inhibits the formation of nitrites. Nitrates are also formed starting from 200 °C, but their nature and surface amounts can be hardly detected in view of the strong superposition of the carbonate bands. At all the temperatures studied, when CO\textsubscript{2} is present in the feed, the NO\textsubscript{x} storage occurs with the simultaneous partial displacement of surface carbonate species.

Conclusions

The results attained at 350 °C confirm our previous results obtained by in situ FT-IR spectroscopy, i.e. at this temperature nitrite route is inhibited by the presence of CO\textsubscript{2}. The inhibition effect decreases on decreasing temperature. This is reasonably related to the different thermal stability of nitrites and carbonates, as demonstrated by desorption experiments performed in the range 150-350 °C. At 350 °C the nitrite route is strongly inhibited but the storage capacity is not significantly affected thank to nitrate route, whose occurrence increases with temperature starting from 200 °C.

References

The Reduction of Stored NOₓ by Heptane on Pt-Ba/Al₂O₃ NSR Catalyst: Combined in situ FT-IR and Temperature-programmed Reactor Experiments


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Introduction and Objectives

In previous studies of our group devoted to the analysis of the regeneration step on Pt-Ba/Al₂O₃ NSR catalysts, it has been found that the reduction of the stored NOₓ by H₂ and CO under nearly isothermal conditions occurs via a Pt-catalyzed pathway which does not involve, as preliminary step, the thermal decomposition of the stored NOₓ. Based on in situ FT-IR analysis, a pathway for the reduction of the stored NOₓ species has been suggested [1,2]. In this work, our earlier investigations have been extended considering the reactivity of a hydrocarbon (n-heptane) as reductant: for this purpose we combine in situ FT-IR spectroscopy and flow microreactor experiments to obtain the simultaneous qualitative and quantitative analysis of the adsorbed and gaseous species involved in the process.

Results and Discussion

The reduction by heptane of NOₓ species stored on a model Pt-Ba/Al₂O₃ catalyst sample (Pt 1%, Ba 16% w/w) has been studied by in situ FT-IR spectroscopy and flow microreactor experiments such as temperature programmed surface reaction (TPSR) and isothermal step concentration (ISC) experiments. FT-IR analysis pointed out that, with pure heptane, bands related to surface nitrate species (formed in the previous storage phase at 350 °C with NO/O₂) start to decrease at 200-250 °C, i.e. well below the onset of nitrate thermal decomposition (350 °C). Hence also in the case of heptane the reduction of the stored NOₓ does not require the preliminary thermal decomposition of the NOₓ adsorbed species. Contemporary to NOₓ reduction, band related to hydroxyl groups increases on increasing temperature along with bands related to carbonates, these last well visible only at 400 °C when the NOₓ reduction is complete. No bands assignable to other surface species have been observed.

TPSR experiments pointed out under dry conditions that heptane reacts with stored NOₓ species at temperatures near 220-250 °C. The reduction of the stored nitrates is accompanied by the initial evolution of NO and N₂O (few ppm), followed by N₂ formation. Formation of CO₂ and H₂O is also observed; complete nitrate reduction is attained at 400 °C. All these data are in well agreement with FT-IR results. Experiments have also been carried out with heptane in the presence of water vapor. FT-IR data showed results very similar to those obtained under dry conditions. Preliminary heptane steam-reforming (SR) reactor experiments pointed out that heptane is converted to H₂ and CO₂ above 250 °C, although with poor reactivity (less than 10% conversion at 400 °C). During the TPSR run, the onset of the nitrate reduction is observed at a temperature very close to that measured under dry conditions, i.e. the reaction is
not significantly affected by the presence of water, in agreement with FT-IR data. This fact, along with
the observation that the rate of H₂ production via the heptane SR reaction is well below that of N₂
production according to the stoichiometry Ba(NO₃)₂ + 5 H₂ → N₂ + H₂O + Ba(OH)₂, points out that the
heptane steam-reforming route is not able to account for the major amount of nitrate reduction. Besides,
the lack of any detectable N-containing surface species (and in particular isocyanate adspecies) which
have been observed by several authors during the HC-SCR (i.e. the reduction of gas-phase NO with HCs),
suggests that the reduction of the stored nitrates may involve a different route if compared to the HC-SCR
pathway.

On the basis of these and previous results regarding the use of H₂ and CO as reductants, it seems
reasonable to propose a pathway which involves the surface migration of the stored NOₓ species towards
the Pt sites kept in a reduced state by the hydrocarbon. The NOₓ ad-species are then decomposed at the Pt
sites leading to very reactive N- and O-adspecies, The N-adspecies recombine between them to give N₂,
while O-adspecies readily oxidize hydrocarbon to CO₂ and H₂O.

Conclusions

The reduction by heptane of NOₓ species stored on a model Pt-Ba/Al₂O₃ has been studied by in situ FT-
IR spectroscopy and flow microreactor experiments. The results obtained both in dry and wet conditions
point out that nor heptane steam-reforming route nor a pathway similar to the HC-SCR one are able to
account for the nitrate reduction. Reasonably heptane reduces the Pt sites on which NOₓ adspecies
migrate and decompose giving very reactive N-adspecies and O-adspecies, the ones combining to give
N₂, the other ones oxidizing the heptane.

References

Reduction of CuO-CeO$_2$/Al$_2$O$_3$ and CeO$_2$/Al$_2$O$_3$ Catalysts Studied by Operando XAS and XRD

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Introduction and Objectives

Supported metal oxides are frequently used in heterogeneous catalysis as alternative to noble metal catalysts. In particular, copper oxide catalysts are reported to be efficient and environmentally benign for a wide range of reactions, including volatile organic compound (VOC) elimination [1]. CeO$_2$ is often added as promoter to CuO/γ-Al$_2$O$_3$ to enhance reducibility and improve activity compared to unpromoted CuO/Al$_2$O$_3$ [2-3].

In view of determining the role of the CeO$_2$ promoter in the reducibility of a (11wt%)CuO-(6wt%)CeO$_2$/γ-Al$_2$O$_3$ catalyst, a combined operando X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) study was performed under reduction in C$_3$H$_8$ and H$_2$, and thermal reduction in He up to 1073K. In XRD, the crystalline phases CuO and CeO$_2$ are followed, while XAS focuses on the local Ce structure. Experiments are repeated for CeO$_2$/Al$_2$O$_3$ to assess the CeO$_2$ behaviour with and without CuO.

Results and Discussion

In H$_2$ reduction, the CuO phase in CuO-CeO$_2$/γ-Al$_2$O$_3$ is reduced to metal Cu, around 473K. In both samples CeO$_2$/Al$_2$O$_3$ and CuO-CeO$_2$/γ-Al$_2$O$_3$, CeO$_2$ diffraction peaks remain present under H$_2$ throughout the whole temperature range and reduced Ce$_2$O$_3$ or alloyed CeAlO$_3$ are never observed. However, the CeO$_2$ peaks move to lower 2θ angle with higher temperature (Fig. 1). This shift is larger than from pure lattice expansion and is accounted for by partial reduction of the CeO$_2$ phase, loosing lattice O by reaction

**Fig. 1:** CeO$_2$(111) position versus temperature during isothermal H$_2$ reduction for CuO-CeO$_2$/Al$_2$O$_3$ (green) and CeO$_2$/Al$_2$O$_3$ (blue).

**Fig. 2:** $k^3$ weighed χ function for CeO$_2$/Al$_2$O$_3$ versus temperature during stepwise isothermal H$_2$ reduction (2.5% H$_2$ in He, 40 ml/min).
with hydrogen. Since Ce$^{3+}$ ions occupy more space than Ce$^{4+}$, this reduction leads to lattice size increase, reflected in an additional downward shift of the peak position [4].

In Ce K edge XAS spectra and derived $\chi$ functions, small changes are observed during H$_2$ reduction for both samples at high temperatures (Fig. 2). A linear combination fit of the $\chi$ functions shows that the Ce$^{4+}$ content decreases with temperature, in an evolution similar to Fig. 1. Both XAS-LCF and XRD thus indicate that H$_2$ reduction has a stronger effect on CuO-CeO$_2$/γ-Al$_2$O$_3$ than on CeO$_2$/γ-Al$_2$O$_3$ (Fig. 1). Therefore, the presence of CuO near CeO$_2$ in CuO-CeO$_2$/γ-Al$_2$O$_3$ enhances the promoter’s reducibility.

C$_3$H$_8$ induces in CuO-CeO$_2$/γ-Al$_2$O$_3$ a two-step reduction pathway with the appearance of Cu$_2$O at 673K and Cu from 773K (Fig. 3). At similar temperatures where CuO is reduced, the CeO$_2$ XRD peaks shift more than from thermal expansion. Hence, C$_3$H$_8$ reduces CeO$_2$ at temperatures in the range of Cu formation. In CeO$_2$/γ-Al$_2$O$_3$, peak shifts are also observed. Likewise, Ce K edge XAS spectra show small changes in both samples.

Thermal treatment in He induces reduction of CuO to Cu$_2$O around 950K for CuO-CeO$_2$/γ-Al$_2$O$_3$, while the CeO$_2$ diffractions in both samples shift slightly to smaller angle. In the same temperature range, the Ce K edge XAS spectra show little change. Therefore, thermal reduction of CeO$_2$ is minimal and occurs only at high temperature.

**Conclusions**

Isothermal reduction of CuO-CeO$_2$/γ-Al$_2$O$_3$ induces parallel to CuO reduction a partial reduction of the CeO$_2$ promoter, as evidenced from both XRD and XAS. The temperature at which this occurs depends on the atmosphere and increases when going from H$_2$ to C$_3$H$_8$ to He. Oxygen removal from CeO$_2$ by reduction treatment equally occurs in CeO$_2$/γ-Al$_2$O$_3$, but at higher temperatures than for CuO-CeO$_2$/γ-Al$_2$O$_3$. The promoter’s reducibility in CuO-CeO$_2$/γ-Al$_2$O$_3$ is thus enhanced by the presence of CuO near CeO$_2$.

**References**

Operando and in situ Spectroscopic Studies of Platinum Nanoparticles Supported in Ceria-alumina under Water Gas Shift Reaction
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Introduction and Objectives
The water gas shift reaction (WGS) is an important reaction to produce hydrogen, from CO and steam, that is use in several processes, like in fuel cells [1,2]. In general, for this reaction, catalysts work in a bifunctional way whereas both metal and support participate in the mechanism [1]. One potential candidate as support is ceria, due to its redox properties, loaded with noble metals [1]. Besides their own catalytic role, the noble metals also help to promote the partial reduction of ceria via H$_2$ spillover, which can generate vacancies for water activation. In this work, we use pre-formed platinum nanoparticles (Pt-NPs) incorporated in cerium/aluminum oxides to study the catalyst structure during the WGS reaction, by fixing the dispersion of the metallic phase. Operando studies have been essential to gain insights about WGS reaction mechanism in this system.

Results and Discussion
Pt-NPs were synthesized according to Song et al.[3] but using a PVP/Pt ratio of 10. The colloidal solution (1.5% Pt w/w) was incorporated into alumina prepared by sol-gel method (Pt-NPs/Al) [4] and alumina promoted with 12% of CeO$_2$ (Pt-NPs/CeAl). The dried samples were calcined at 500°C for 4h. After a H$_2$ pre-treatment at 500°C the catalysts were characterized by operando and in situ techniques to obtain information about the catalyst structure under reaction conditions. Pt-NPs with average size of 2.8 nm and narrow size distribution ($\pm$ 0.1 nm) were incorporated on the supports and showed stability after the thermal treatments. XRD measurements after calcination confirmed the formation of $\gamma$-alumina and in the case of Pt-NPs/CeAl peaks of ceria were not identified, suggesting that ceria is highly dispersed. Operando XANES measurements at the Pt L3 edge (Fig. 1A) revealed that the Pt remains mostly reduced even under reaction atmosphere for both samples. Interestingly, changes in the oxidation state of ceria were observed as a function of temperature (Fig. 1B). While Pt-NPs/CeAl showed 50% of CO conversion at 300°C (Fig. 1C) the Pt-NPs/Al showed only 20% of conversion at the same conditions. These results suggest that the higher activity of Pt-NPs/CeAl catalyst may be associated to ceria-mediated redox mechanism in which Ce$^{3+}$ is oxidized by water to Ce$^{4+}$ at the first stages of the reaction. Increasing the temperature (>300°C) favours the reduction to Ce$^{3+}$. These results are in accordance with studies on Pd/CeO$_2$ catalysts [5] that indicated the oxidation of CO by oxygen transfer from ceria to the adsorbed CO on noble metal. An alternative mechanism involves the formation of formates, due the adsorption of CO in Ce$^{3+}$.
vacancies \[1\]. In situ FTIR studies (Fig 1D) confirmed a small concentration of formates by the presence of 2900, 1392 and 1375 cm\(^{-1}\) bands on the Pt-NPs/CeAl catalyst surface at 200 and 300\(^\circ\)C, although there is no consensus about their participation in the reaction mechanism \[6\]. These species are produced from CO reacting with the partially reduced ceria surface. Formates are decomposed to H\(_2\) and carbonates, prior to the liberation of CO\(_2\)\[1\]. In both mechanisms, the highly dispersed Pt leads to the partial reduction of the ceria possibly via H\(_2\) spillover, producing sites for water activation, considered the rate-limiting step.

Figure 1. Quantification of (A) Pt and (B) Ce species from XANES data, (C) mole fraction of products from mass spectrometer and (D) In situ FTIR of WGS on Pt-NPs/CeAl.

Conclusions

The use of the same Pt-NPs in both catalysts and the operando and in situ spectroscopic techniques allowed a better comprehension about the catalysts structure and consequence to the WGS reaction mechanism. The redox mechanism seems to be the main mechanism that occurs in the catalyst surface. In this way the ceria play a crucial role in oxygen transference for CO oxidation.

References

A Multi-technique Approach for Characterisation of Fischer-Tropsch Catalysts at Industrially Relevant Conditions

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Introduction and Objectives

Cobalt-based catalysts for the Fischer-Tropsch synthesis (FTS) have been studied at conditions close to what is commonly used in the industrial process. The catalysts have been examined by a multi-technique approach (XAS, XRD, ASAXS, RIXS, FT-IR, Raman) where also modulation enhanced XAS (ME-XAS) has been exploited to enhance the selectivity to the surface fraction which represents the active sites. Combining these techniques allows for probing both electronic and structural perturbations in the catalysts leading to changes in activity.

Initial deactivation in Fischer-Tropsch synthesis appears to be surface related. Probing the surface state during activation and deactivation would give better understanding of the mechanism of the Fischer-Tropsch reaction. X-ray absorption spectroscopy has been proven to be a valuable tool in monitoring changes in the coordination number of nanoparticles that may reflect surface reconstruction and shape changes. However, this is only the case for very small particles with a large surface fraction. However, in situ studies on model catalyst of smaller size distances the study from the industrial catalysts and hence questioning their sensitivity towards e.g. sintering at realistic reaction conditions. Changes in the surface configuration during FTS may be induced by adsorbed species including carbon containing intermediates and products. The detection of these phenomena is challenging and can only be done in situ at temperatures and pressures giving FT conditions.

A promising approach for enhancing the surface sensitivity of conventional bulk techniques such as XAFS and XRD is modulation enhanced experiments. In this type of experiments the system is periodically exited by an externally applied variation of a parameter (stimulation). The phase-domain spectra can be further analyzed by the so-called in-phase angle analysis. This analysis is of great help to gain insight into the dynamic behaviour and kinetics of a system; the signals having the same in-phase angle indicate that the species causing the signals appear at the same time of a period and, based on this information, reaction/transformation pathways can be investigated.

Results and Discussion

We have implemented a set-up at BM01 (SNBL) at the ESRF for combined in situ XAS/XRD/Raman catalyst characterisation able to operate at up to 20 bar pressure and high temperatures (Figure 1). This set-up has also been used for modulation enhanced XAS where the catalysts have been exposed to different reaction environments. The preliminary results indicate that the information which can be extracted goes far beyond the information content of conventional XAS experiments.
Figure 1: ME applied to in situ EXAFS on Co FT catalyst (T = 483 K, alternating between H₂ flow and CO flow). The XAS spectra and Fourier transforms are shown in time (upper) and phase domain (lower).

A similar set-up has also been used at HASYLAB for anomalous SAXS experiments and in our home laboratory for Raman and FT-IR studies. The information extracted from all these in situ techniques together with complimentary information from ex situ measurements (RIXS, TEM) will be discussed.

Conclusions

The combination of selected in situ techniques is necessary in order to obtain a complete overview of catalytic processes at reaction conditions. Collecting results from various techniques at similar conditions opens for the possibility to understand the interplay between electronic and structural phenomena, deconvolution of deactivation mechanisms and also surface sensitive information during the reaction.

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Profiling Metal Poisons and the Zeolite Phase within Individual FCC catalyst particle with synchrotron-based techniques

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Introduction and Objectives

Fluid catalytic cracking (FCC) is an important catalytic process to convert heavy oil fractions into more valuable chemicals, such as gasoline and olefins1. During the cracking process, the activity of the catalyst particles decreases due to deactivation. The detrimental effects of metals coming from the oil feedstock, especially Ni and V, on FCC catalysts have been widely recognized in the literature2-4. These metals deposit on the catalyst and act as poisons, damaging the zeolite structure, decreasing the accessibility and favouring dehydrogenation-hydrogenation reactions that subsequently lead to an increase in coke formation.

Herein we report the first application of a combination of \( \mu \)-XRF, \( \mu \)-XANES and \( \mu \)-XRD for the characterization of metal poisons and their detrimental effect on individual FCC catalyst particles. \( \mu \)-XRF and \( \mu \)-XANES spectra provide information on the distribution and chemistry of metal poisons, whereas \( \mu \)-XRD data reveal the distribution of the zeolitic material, the active phase, as well as its deactivation, i.e. dealumination, under real catalytic conditions.

Results and Discussion

Three-dimensional (3D) \( \mu \)-XRF images of the nickel and vanadium were recorded on the FCC catalysts. No traces of such metal elements were observed in the fresh sample. Interestingly, nickel and vanadium were present in the deactivated samples with a non-even spatial distribution. X-ray fluorescence images (Fig. 1 a and b) and the one dimensional analysis profiles of the fluorescence intensity (Fig. 1 c) reveal a very pronounced egg-shell distribution for nickel, while vanadium is more even across the FCC catalyst particle.

After the profiling of the metal poisons within the FCC catalyst particle, Ni and V K-edge XANES spectra were collected. This allowed unravelling chemical information of the metal poisons, since XANES spectra are sensitive to their electronic state and local structure. From the features of the Ni K-edge XANES spectra, it could be concluded that nickel is in its +2 oxidized state, forming NiO phases. In the case of the vanadium, XANES spectra show that this metal is in its +4-5 oxidation state.

\( \mu \)-XRD tomography was applied by using the most intense peak of the zeolitic component, at 7.22° (Fig. 1 f). The reconstruction of such a zeolitic component clearly differs for the fresh and deactivated FCC catalyst particles. The fresh catalyst particle displays a random distribution of the zeolitic component throughout the overall FCC particle, as il-
illustrated in Fig. 1 d. After deactivation, the zeolite undergoes changes in crystallinity and distribution, leading to a less ordered material with an egg-yolk distribution (Fig 1 e).

Figure 1. Nickel and vanadium $\mu$-XRF maps of the deactivated FCC catalyst particle. Orange lines illustrate the position where the fluorescence intensity profiles were taken. (c) One-dimensional fluorescence intensity profiles as a function of the position inside the FCC catalyst particle, derived from the 2D-images. Nickel is represented in green and vanadium in blue. $\mu$-XRD tomography reconstruction of the zeolitic phase for a (d) fresh and (e) deactivated FCC catalyst particle. (f) XRD powder patterns of the fresh (black line) and deactivates (blue line) samples.

Conclusions

The unique combination of $\mu$-XRF and $\mu$-XRD data reveals a relationship between metal deposition and zeolite destruction at the intra-particle level. The experimental approach presented herein offers potential for the 3-D characterization of other catalyst formulations containing metals and crystalline structures with micron-scale spatial resolution.

References

Investigating Crystallization Mechanism of Novel Nanoporous Materials with Combined in-situ X-ray Scattering/absorption Techniques

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Introduction and Objectives

Metal-organic frameworks (MOFs) are a novel class of microporous materials, consisting of metal ions linked by bridging organic ligands. The possibility of varying both the metal and the organic constituents has resulted in the vast number of different crystal architectures [1]. These new materials feature the largest pores and surface areas amongst crystalline compounds, high sorption capacities and complex sorption behaviour. In the past decades, promising applications of MOF in many interdisciplinary fields, most notably, catalysis and gas separation and storage have emerged. The variety of MOF structures reported so far presents with a question which is essential for rationally design new structures and improve upon existing ones, i.e., what are the major factors that impact the MOF crystallization process and how the resulting structures correlate with the variations in the synthetic conditions.

It has been demonstrated that synchrotron-based spectroscopy and scattering techniques could reveal the mechanism of the physicochemical processes associated with synthesis and function in microporous materials. Here, we will focus on recent examples of such applications of small/wide angle X-ray scattering (SAXS/WAXS) and X-ray absorption spectroscopy (XAS) of MOF crystallization process.

Results and Discussion

A combination of identical organic and inorganic precursors may result in a completely morphologically different MOF structures. It was shown that the choice of solvent is essential for driving the synthesis in a desired direction. In-situ SAXS/WAXS technique has shown that MOF crystallization is a complex, multi-step process [2]. When synthesis from aluminium salt and amino-terephthalate occurs in DMF, WAXS results indicate that initially a loose, disordered intermediate MOF phase (MOF-235) forms, which subsequently reconstructs into a 3D-porous MIL-101 structure [2]. Upon addition of water, hydrolysis of the intermediate phase leads to the formation of the more dense MIL-53 structure, which is characterized by one-dimensional...
pores. When DMF is replaced by water, slow dissolution of the precursors inhibits MOF-235 development, resulting in the direct synthesis of MIL-53. Analysis of the kinetics of the synthesis permits to differentiate between the nucleation and crystallization steps, as well as to determine the activation energies for the both processes. SAXS data points out at a fractal-type growth of the intermediate phase, whereas in the case of MIL-53 three dimensional growth results in particles with smooth surface. When catalytically active moieties, such as polyoxometalates are added to the synthetic mixture (which are encapsulated in the MOF cavities during synthesis), the recrystallization of MOF-235 phase slows down allowing for incorporation of Keggin polyanions into the structure. In-situ XAS studies of the iron-terephthalate system indicate that the initial coordination of the ion in solution is different at the initial steps of the synthesis as a function of the solvent composition (tetrahedral in DMF and octahedral in water and water/DMF mixtures) which is essential for directing the subsequent crystallization steps.

Conclusions

Our SAXS/WAXS/XAS results helped shedding light onto the complexity of the MOF synthetic mechanism. We interpret our findings in terms of thermodynamic vs. kinetic stability of various MOF structures. Depending on the properties of the desired MOF morphology, one can optimize the synthetic parameters to target the desired outcome. Moreover, introduction of the catalytic moieties into the structure appears to alter the crystallization process. Finally, based the comparison of results from different synchrotron facilities, beamline performance can be optimized to maximize the scientific output of future crystallization studies.

References

Phase Transformation of Iron Molybdate Catalysts in the Partial Oxidation of Decane

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Introduction and Objectives

Iron molybdates are known to be efficient catalysts for the oxidation of methanol to formaldehyde [1-3] and they comprise MoO\textsubscript{3} and Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} phases with different Mo:Fe bulk ratios. However, we recently extended the application of these materials, by employing MoO\textsubscript{3}/Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} for the partial oxidation of decane in the gas phase [4]. In particular, we identified that at low temperature (350 °C) the catalyst produced oxygenated aromatics, while at high temperature (460 °C) non-oxygenated products were obtained (Scheme 1). In order to explain this counterintuitive behaviour, operando XRD and a series of surface methods including diffuse reflectance UV-Vis spectroscopy, Raman spectroscopy, and SEM-EDX were used to determine the structural modifications of the catalyst under the reaction conditions. It was possible to identify the different reactivity associated with different iron molybdate phases, namely Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} and FeMoO\textsubscript{4}. In addition, the surface of the catalyst was extremely sensitive to the amount of oxygen present in the reaction atmosphere, thus allowing a switch from oxygenated to non oxygenated products.

![Scheme 1: Reactivity of MoO\textsubscript{3}/Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} at 350 °C and 460 °C in the partial oxidation of decane in aerobic conditions.](image)

![Figure 1: (A) Phase transformation of MoO\textsubscript{3}/Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} to FeMoO\textsubscript{4} in the presence of decane, N\textsubscript{2} and O\textsubscript{2} at 460 °C (olefinic products are obtained), (B) stability of Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} at 350 °C (oxygenated aromatic products are obtained).](image)
Results and Discussion

When decane was reacted under aerobic conditions over MoO$_3$/Fe$_2$(MoO$_4$)$_3$ at 460 °C, operando XRD revealed a phase transformation involving the reduction of Fe$_2$(MoO$_4$)$_3$ to FeMoO$_4$ (Figure 1A). In contrast, at 350 °C the Fe(MoO$_4$)$_3$ phase remained substantially unmodified (Figure 1B), thus explaining the absence and the presence of oxygenated products under these two different reaction regimes. However, the combined use of diffuse reflectance UV-Vis spectroscopy, Raman spectroscopy and SEM-EDX, showed that the catalyst had a surface sensitivity to the presence of oxygen, with structural changes at the surface level of MoO$_3$/Fe$_2$(MoO$_4$)$_3$ and involving the reduction of the Fe$_2$(MoO$_4$)$_3$ phase to FeMoO$_4$.

When oxygen was removed from the system, the reduction of Fe$_2$(MoO$_4$)$_3$ to FeMoO$_4$ occurred in inert atmosphere independently from the presence of the organic substrate. The reduced catalysts could be re-oxidized to their original form in air, and the kinetics of this process was estimated to be ca. 100 times faster than the reduction process. However, when the re-oxidation process was carried out at high temperature, a phase separation between MoO$_3$ and Fe(MoO$_4$)$_3$ occurred leading to the formation of independent MoO$_3$ crystallites (Figure 2).

Figure 2: SEM of the MoO$_3$/Fe$_2$(MoO$_4$)$_3$ catalyst (A) before and (B) after a reduction/re-oxidation cycle. (A) details of the Fe$_2$(MoO$_4$)$_3$ surface for the fresh catalyst, and (B) phase separation of MoO$_3$ and Fe$_2$(MoO$_4$)$_3$ after the high temperature re-oxidation.

Conclusions

MoO$_3$/Fe$_2$(MoO$_4$)$_3$ was capable of different reactivity at different temperatures. The oxygenated, and non-oxygenated products observed were the result of different catalyst structures forming under different regimes, which were dependent on the amount of oxygen present in the reaction atmosphere.

References

Revealing the Structure of Vanadium Oxide Supported on Ceria by 

in situ Multi-wavelength Raman Spectroscopy

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Introduction and Objectives

Supported vanadia (VOₓ) is among the most studied oxidation catalysts for variety of redox reactions such as dehydrogenation and oxidative dehydrogenation (ODH) of alkanes to olefins, oxidation of methanol to formaldehyde, and selective reduction of NOₓ. The development of more active and selective vanadia catalysts requires a full understanding of the structure of surface dispersed vanadia species under various conditions that are relevant to the storage, activation, usage and regeneration processes of the vanadia catalysts. To this end, a variety of techniques including Raman spectroscopy have been employed to investigate the structure of surface vanadia supported on various oxides including Al₂O₃, SiO₂, TiO₂, and MgO. Although CeO₂ has been extensively used as catalyst and catalyst support for oxidation reactions, it has been relatively less researched as a support for vanadia than other oxide supports. Recent studies have shown that ceria supported vanadia are very active and selective for the ODH of ethane, propane and methanol. In spite of existing efforts to understand the interaction between vanadia and ceria and the structure of surface vanadia species [1], the exact structure of surface dispersed vanadia species on ceria has not been completely identified yet. The objective of this paper is to reveal the detailed molecular structure of surface vanadia species dispersed on polycrystalline ceria under various conditions. To accomplish this, in situ multi-wavelength Raman spectroscopy was employed and complemented by UV-Vis diffuse reflectance spectroscopy (DRS), infrared spectroscopy, temperature-programmed reduction, and isotopic labeling techniques.

Results and Discussion

In this study, the evolution of the structure of surface vanadia species was investigated as a function of vanadia coverage and treatment conditions including dehydration (calcination), hydration, reduction and reoxidation.

Dehydrated VOₓ/CeO₂: For the first time, the detailed structure of dehydrated VOₓ species was revealed on the polycrystalline ceria support by Raman, UV-Vis-DRS and IR spectroscopy. By analogy to the structure-spectroscopy relationship obtained on VOₓ/CeO₂(111) model system [2], we suggest that VOₓ species can co-exist on ceria surface in the structure of monomer, dimer, trimer, polymer, crystalline V₂O₅ and CeVO₄ as a function of VOₓ loading. UV Raman, Raman-O₂ probe and IR results indicate that surface VOₓ species interact strongly with three types of surface sites on ceria surface, the defect sites, labile surface oxygen, and surface hydroxyl groups. The surface redox property of ceria is passivated by anchorage of VOₓ species.
**Hydrated VOₓ/ CeO₂** Under ambient condition, the dispersed VOₓ species are hydrated into polyvanadate species which can be reversibly dehydrated back to the original structure forms. When using H₂¹⁸O as the hydration source, the re-dehydration process showed that a very facile isotopic oxygen exchange happens between water (H₂¹⁸O) and V¹⁶Oₓ species even at room temperature, which is possibly facilitated by the defect sites present on the ceria support.

**Reduction and reoxidation of VOₓ/ CeO₂** During H₂ reduction, both the VOₓ species and the ceria support can be reduced with ceria surface being more reducible. The reducibility of various dispersed VOₓ species scales with their polymerization degree, i.e., polymer > trimer > dimer > monomer. The reoxidation of reduced VOₓ species is partially reversible on higher loading samples, which is found to proceed via ceria lattice oxygen instead of the gas phase oxygen where ceria acts as an oxygen buffer.

**Conclusions**

The study of VOₓ/ CeO₂ system through a combination of various in situ spectroscopic techniques has shown that the anchoring of surface VOₓ species greatly alters the redox behavior of ceria while at the same time, the unique surface property of the ceria support poses a profound effect on the structure evolution of surface VOₓ species under various conditions. The structural information obtained from this study would provide fundamental basis for understanding the vanadia-ceria catalysis [3].

**References**


**Acknowledgements:** This Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory, by the Office of Basic Energy Science, U. S. Department of Energy.
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BNL Map
Venue

Situated on a 5,250-acre campus, Brookhaven National Laboratory – in Upton, New York – is part of Long Island’s Central Pine Barrens region and home to 230 plant species, 15 animal species, and 85 species of birds. With innumerable restaurants, theaters, and internationally recognized sights of New York City 65 miles to the west, beautiful beaches stretching along the nearby coasts to the north and south, and an extensive array of vineyards and charming Hamptons towns to the east, Brookhaven offers visitors access to a little bit of everything.

"Do as You Please" in New York City
Sunday, April 29th

(Times are approximate) Excursion will be based on response of 50 or more persons.

9:30 a.m. Leave Brookhaven National Laboratory (BNL), Upton, New York
11:00 a.m. Arrive New York City (NYC) Bryant Park area
4:00 p.m. Leave Bryant Park, NYC, area
5:00 p.m. Arrive BNL
5:30 p.m. Reception at BNL

Cost is $15.00 US per person

Please be advised if we do not have enough people interested in the excursion, we may need to cancel the trip, and refund your payment. Decision will be made one week ahead.


The following links are provided for consideration on what you may want to do:

Boat Tour: Please note you should choose the 12:30 cruise only, so you have enough time to get back to the bus on time: http://www.circleline42.com/new-york-cruises/scheduling_pricing.aspx

Museums: Metropolitan Museum of Art: http://www.metmuseum.org
American Museum of Natural History: http://www.amnh.org/

Broadway Shows: Please be aware you will need to be back on the bus no later than 4 p.m., and most shows are at least two hours in length:
http://www.nytimes.com/Links/Broadway/listofcurrentshows.html
Operando IV Winery Tours and Conference Banquet
Wednesday, May 2, 2012

Winery Tours

The Long Island wine region encompasses Nassau and Suffolk Counties, with the majority of wineries and vineyards at the East End, on the North and South Forks. Here, age-old growing techniques are combined with state-of-the-art technology to produce a range of world-class wines from specific varietals and selected blends.

It has been said by many that Long Island is one of the country’s most exciting wine producing regions today, with great reviews and high praise found in major food and wine publications nationwide.

Schedule:
12:00 pm Lunch provided at Berkner Hall, Brookhaven National Laboratory (BNL)
1:30 pm Board tour busses
2:00 pm Arrival at Baiting Hollow Farm Vineyard (2:30 pm - Optional tour of horse barns at Baiting Hollow Farm Vineyard)
3:30 pm Board tour busses from Baiting Hollow Farm Vineyard
4:00 pm Arrival at Jason’s Vineyard
5:45 pm Board tour busses from Jason’s Vineyard
6:00 pm Dinner at “Vineyard Caterers,” 978 Main Road (Route 25), Aquebogue, NY 11931, (631) 722-3200
6:05 pm Bus returns to BNL for those not attending dinner
9:30 pm Busses leave The Vineyard Caterers to return to BNL
10:00 pm Hotel shuttles will be at BNL to return participants to hotels

Conference Banquet

Please join the International Organizing Committee, the Scientific Advisory Panel and the Local Organizing Committee for the 4th International Congress on Operando Conference Banquet! The banquet will be held at the scenic Vineyard Caterers, located at 978 Main Road, Aquebogue, New York. The Vineyard Caterers is a place of elegance, but yet it embraces the wine country flair of the North Shore of Long Island. The banquet will immediately follow the Winery Tour. The next stop will be the nearby Vineyard Caterers.

The evening will begin at 6:00 pm, with 1/2 hour Butler Service of Hors d’oeuvres and a Cocktail Hour featuring top-shelf brands and classic wines. Followed by a delicious buffet dinner and coffee, tea and dessert.

You can relax and enjoy the stunning ambiance of the Patio Overlooking the Private Vineyard Estate.

Banquet tickets cost 25 US$ and include transportation between Brookhaven National Laboratory and The Vineyard Caterers. All are welcome!
Accommodations

Accommodations on the BNL Site

Check-Out time is 3:00 p.m. Before leaving, return your keys to the Housing Office.

The Housing Office is open Monday through Friday, 8:00 a.m. to midnight, and also on Sunday from 4 p.m. to midnight. Those arriving or leaving at other times may pick up or drop off keys at Police Headquarters, Building 50.

Accommodations Offsite

Fairfield Inn - Marriott
When registering on line use the Group Code: BHK
Special Conference / BNL Rate - $89.00 - includes free continental breakfast, including Hot Breakfast Sandwiches and Hot Breakfast Quiche, free high speed wireless internet, indoor swimming pool and Jacuzzi, fitness center, free shuttle service to LI Islip Airport and Ronkonkoma Train Station and morning and afternoon shuttle service to and from BNL. Upon check-in, please be sure to inform the front desk that you will be requiring the shuttle service to/from BNL.

2695 Route 112
Medford, NY 11763
(631) 447-6200
 Exit 64 off the LIE
Est. Travel Time:18 minutes 9.1 Miles from BNL. The special room rate will be available until March 27, 2012.

Crown Plaza Hotel
Special Conference / BNL Rate - $112.00 plus tax
- includes free hot buffet breakfast, free high speed wireless internet, fitness center, free shuttle service to LI Islip Airport and Ronkonkoma Train Station and morning and afternoon shuttle service to and from BNL. Upon check-in, please be sure to inform the front desk that you will be requiring the shuttle service to/from BNL. This hotel also has Yogi’s Bar & Restaurant inside the hotel.

1730 North Ocean Avenue
Holtsville, NY 11742
(631) 758-2900
Exit 63 off Long Island Expressway (LIE)
Est. Travel Time:16 minutes 10.3 Miles from BNL
The special room rate will be available until March 27, 2012.

Hotel Indigo East End
Special Users’ Meeting / BNL Rate - $99 - includes free continental breakfast, free high speed wireless internet, business center, fitness center. Hotel restaurant - Bistro 72 - a casually elegant restaurant, lounge and patio. Tanger Outlets Riverhead is next door. Upon check-in, please be sure to inform the front desk that you will be requiring the shuttle service to/from BNL.

1830 Route 25
Riverhead, NY 11901
(631) 369-2200
Exit 72 off the LIE
Est. Travel Time: 10 mins / 8.24 miles from BNL
Est. Travel Time from Long Island MacArthur Airport to Hotel INDIGO: 34 mins / 24.97 miles

The special room rate will be available until April 14, 2012.

Hyatt Place Long Island East End
Special Conference / BNL Rate - $112 - includes free continental breakfast, free high speed wireless internet, fitness center. Upon check-in, please be sure to inform the front desk that you will be requiring the shuttle service to/from BNL.

451 E. Main Street
Riverhead, NY 11901
631-208-0002
Estimated travel Time:15 minutes 10.5 Miles from BNL
The special room rate will be available until April 15, 2012.
Offsite Transportation

Getting to Brookhaven National Laboratory

If you would like our assistance in arranging transportation between JFK International or Laguardia Airports and Brookhaven National Laboratory, please send your flight itinerary (arrival and departure times) to Corinne Messana (messana@bnl.gov). Ms. Messana will coordinate group transportation between destinations. Transportation fees will apply.

Both airports are approximately 60 mi / 96.54000 km (1.5 hours) from BNL. There may be some waiting time, but we will attempt to keep the waiting time to a minimum.

If you prefer to make arrangements on your own, you can find directions and information for car rentals as well as other modes of transportation:

Directions from area airports: http://www.bnl.gov/maps/#airports
Ground transportation services: http://www.bnl.gov/staffservices/othertransportation.php

Transportation between JFK International Airport and BNL

Car rental: http://www.panynj.gov/airports/jfk-car-rental.html

Long Island Railroad (LIRR) to BNL:

1. Take AirTrain from JFK to Jamaica Train Station (LIRR) $5 – it takes about 15 minutes to get to JFK from Jamaica or vice-versa
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Taxi from Ronkonkoma Train Station to BNL approximately $35 - 45 US$.

Ronkonkoma Train Station Shuttle to BNL (depends on your arrival time) - See information on next page.

If you are coming from LaGuardia International Airport (LGA)

LaGuardia Airport Homepage: http://www.panynj.gov/airports/laguardia.html

Long Island Railroad (LIRR) to BNL:

1. Take a Shuttle service from LGA to JFK ($10) : http://www.etsairportshuttle.com/
2. Take AirTrain from JFK to Jamaica Train Station (LIRR) $5 – it takes about 15 minutes to get to JFK from Jamaica or vice-versa
3. Take LIRR from Jamaica Train Station to Ronkonkoma Train Station: (Peak Time @ Station $12.50 - On Board $19.00 / Off Peak Time @ Station $9.00 / On Board $15.00. Long Island Rail Road Website: http://mta.info/lirr/index.html
Taxi from Ronkonkoma Train Station to BNL approximately 35 -45US$

Ronkonkoma Train Station Shuttle to BNL (depends on your arrival time)

- A Laboratory vehicle operates twice daily Monday through Friday with the exception of holidays and when BNL is officially closed, to transport visitors and guests of BNL to and from the Ronkonkoma Train Station.
- 8:30 AM - Vehicle departs from the rear main entrance of Building 400 on Bell Avenue to the Ronkonkoma Train Station. Vehicle will meet passengers on the 7:39 AM train from New York City/Penn Station arriving at Ronkonkoma at 8:59 AM.
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- This vehicle will only wait ten (10) minutes from the time the train arrives for any passengers going to BNL.
- 4:00 PM - Vehicle departs from the rear main entrance of Building 400 on Bell Avenue to the Ronkonkoma Train Station.
- Train departs Ronkonkoma at 4:46 PM, arriving in New York City/Penn Station at 6:08 PM.
- Due to limited seating, reservations are required for this service. Please call ext. 2535; reserve in person at the Transportation Counter located in Building 400A; or email transportation@bnl.gov.
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