8th Annual Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS-2021) Virtual Workshop

December 7-10, 2021
Scientific Advisory Committee

- Luca Artiglia (Paul Scherrer Institute, Switzerland)
- Hendrik Bluhm (Fritz-Haber-Institut der MPG, Germany)
- Georg Held (University of Reading, UK)
- Axel Knop-Gericke (Fritz-Haber-Institut der MPG, Germany)
- Hiroshi Kondoh (Keio University, Japan)
- Zhi Liu (Shanghai Tech University, The People's Republic of China)
- Bongjin Simon Mun (Gwangju Inst. of Science & Technology, South Korea)
- Slavomir Nemsak (Advanced Light Source, USA)
- Virginia Perez-Dieste (ALBA Synchrotron, Spain)
- François Rochet (Sorbonne Université, France)
- Joachim Schnadt (Lund University, Sweden)
- Sven L. M. Schroeder (University of Leeds, UK)
- Ira Waluyo (Brookhaven National Laboratory, USA)
- Yaw-Wen Yang (NSRRC, Taiwan)

Local Organizing Committee

- Ira Waluyo (chair)
- Ashley Head
- Adrian Hunt
- Sanjaya Senanayake
Plenary Speakers:
- Markus Ammann (Paul Scherrer Institut, Switzerland)
- Jose Rodriguez (Brookhaven National Laboratory, USA)
- Junko Yano (Lawrence Berkeley National Laboratory, USA)

Invited Speakers:
- Heather Allen (Ohio State University, USA)
- Sara Blomberg (Lund University, Sweden)
- Fabrice Bournel (Sorbonne University, France)
- Baran Eren (Weizmann Institute of Science, Israel)
- David Grinter (Diamond Light Source, UK)
- Beomgyun Jeong (Korea Basic Science Institute, South Korea)
- Rik Mom (Leiden University, Netherlands)
- Jeunghee Park (Korea University, South Korea)
- David Starr (Helmholtz-Zentrum Berlin, Germany)
- Jason Weaver (University of Florida, USA)
- Susumu Yamamoto (Tohoku University, Japan)
- Lada Yashina (Lomonosov Moscow State University, Russia)
# Workshop Agenda

<table>
<thead>
<tr>
<th>Time (Eastern Standard Time, UTC-05:00)</th>
<th>Tue, 12/7 Topic: Heterogeneous Catalysis</th>
<th>Wed, 12/8 Topic: Electrochemistry and Battery</th>
<th>Thu, 12/9 Topic: Materials and Interfaces</th>
<th>Fri, 12/10</th>
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<tbody>
<tr>
<td>10:00 AM</td>
<td>Welcome</td>
<td>Overview of the day</td>
<td>Overview of the day</td>
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<tr>
<td>10:10 AM</td>
<td>Plenary 1 - Rodriguez</td>
<td>Invited 5 - Jeong</td>
<td>Invited 9 - Yamamoto</td>
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<tr>
<td>10:20 AM</td>
<td>Plenary 1 - Rodriguez</td>
<td>Invited 6 - Park</td>
<td>Plenary 3 - Ammann</td>
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<tr>
<td>10:30 AM</td>
<td>Invited 1 - Blomberg</td>
<td></td>
<td>Technical session</td>
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<tr>
<td>10:40 AM</td>
<td>Invited 2 - Grinter</td>
<td>Plenary 2 - Yano</td>
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<tr>
<td>10:50 AM</td>
<td>Contributed 1 - Garcia Martinez</td>
<td>Contributed 4 - Chaveanghong</td>
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<tr>
<td>11:00 AM</td>
<td>Contributed 5 - Källquist</td>
<td>Contributed 7 - J. Wang</td>
<td>Contributed 10 - Goodwin</td>
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<tr>
<td>11:10 AM</td>
<td>Break</td>
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<td>2:00 PM</td>
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All times are in Eastern Standard Time/UTC-05:00
## Day 1: Tuesday, December 7, 2021

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>10:00 am – 10:10 am</td>
<td><strong>Welcoming remarks – John Hill (NSLS-II Director)</strong></td>
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<tr>
<td>10:10 am – 10:50 am</td>
<td><strong>Plenary 1 – Jose Rodriguez (Brookhaven National Laboratory)</strong></td>
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<tr>
<td></td>
<td>“APXPS and C1 Catalysis: Fundamental Studies on the Conversion of CO₂ and CH₄”</td>
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<tr>
<td>10:50 am – 11:20 am</td>
<td><strong>Invited 1 – Sara Blomberg (Lund University)</strong></td>
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<tr>
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<td>“In situ APXPS applied to catalysis for renewables”</td>
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<tr>
<td>11:20 am – 11:50 am</td>
<td><strong>Invited 2 – David Grinter (Diamond Light Source)</strong></td>
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<td>“Ambient Pressure NEXAFS at VerSoX B07-B”</td>
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<tr>
<td>11:50 am – 12:10 pm</td>
<td><strong>Contributed 1 – Fernando Garcia-Martinez (Centro de Física de Materiales (CSIC - UPV/EHU))</strong></td>
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<td></td>
<td>“Asymmetric CO ignition on Rh stepped surfaces studied with a curved sample”</td>
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<tr>
<td>12:10 pm – 12:30 pm</td>
<td><strong>Break</strong></td>
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<tr>
<td>12:30 pm – 1:00 pm</td>
<td><strong>Invited 3 – Baran Eren (Weizmann Institute of Science)</strong></td>
</tr>
<tr>
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<td>“The interaction of methanol vapor with copper surfaces”</td>
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<tr>
<td>1:00 pm – 1:30 pm</td>
<td><strong>Invited 4 – Jason Weaver (University of Florida)</strong></td>
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<td></td>
<td>“Methane Oxidation on IrO₂(110) Thin Films”</td>
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<tr>
<td>1:30 pm – 1:50 pm</td>
<td><strong>Contributed 2 - Jessica Jenkins (Oregon State University)</strong></td>
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<tr>
<td></td>
<td>“Reaction of 2-Propanol on SnO₂(101) and SnO₂(110) Studied using Ambient-Pressure X-ray Photoelectron Spectroscopy”</td>
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<tr>
<td>1:50 pm – 2:10 pm</td>
<td><strong>Contributed 3 - Bar Mosevitzky Lis (Lehigh University)</strong></td>
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<td>“Surface-bulk dynamics of bulk mixed oxide and supported metal oxide catalysts under reaction conditions: an in situ NAP-XPS study”</td>
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## Day 2: Wednesday, December 8, 2021

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Presenters</th>
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<tbody>
<tr>
<td>10:00 am – 10:10 am</td>
<td>Overview of the day</td>
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</tr>
<tr>
<td>10:10 am – 10:40 am</td>
<td>Invited 5 – Beomgyun Jeong (Korea Basic Science Institute)</td>
<td>“Ongoing APXPS studies in Korea Basic Science Institute”</td>
</tr>
<tr>
<td>10:40 am – 11:10 am</td>
<td>Invited 6 – Jeunghee Park (Korea University)</td>
<td>“Two-Dimensional Transition Metal Dichalcogenide Alloy Nanosheets to Enhance Electrocatalytic Performance”</td>
</tr>
<tr>
<td>11:50 am – 12:10 pm</td>
<td>Contributed 4 – Suwilai Chaveanghong (Institute for Molecular Science, Japan)</td>
<td>“Sulfur poisoning Pt and PtCo anode and cathode catalysts in polymer electrolyte fuel cells studied by Operando near ambient pressure hard X-ray photoelectron spectroscopy”</td>
</tr>
<tr>
<td>12:10 pm – 12:30 pm</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>12:30 pm – 1:00 pm</td>
<td>Invited 7 – Lada Yashina (Lomonosov Moscow State University)</td>
<td>“Photoemission studies of Li-O₂ batteries”</td>
</tr>
<tr>
<td>1:00 pm – 1:30 pm</td>
<td>Invited 8 – Rik Mom (Leiden University)</td>
<td>“Modeling of Fuel Cell and Electrolyzer processes using Electrochemical XPS and XAS data”</td>
</tr>
<tr>
<td>1:30 pm – 1:50 pm</td>
<td>Contributed 5 – Ida Källquist (Uppsala University)</td>
<td>“Potentials in Li-ion batteries probed by operando APPES”</td>
</tr>
<tr>
<td>1:50 pm – 2:10 pm</td>
<td>Contributed 6 – Hassan Javed (Leiden University)</td>
<td>“Platinum electrocatalyst oxidation under steady state and transient conditions examined by in situ XPS and XAS”</td>
</tr>
</tbody>
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# Day 3: Thursday, December 9, 2021

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>10:00 am – 10:10 am</td>
<td>Overview of the day</td>
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</tbody>
</table>
| 10:10 am – 10:40 am | **Invited 9 – Susumu Yamamoto (Tohoku University)**  
“Operando observation of photo-excited carriers and molecules at solid surfaces using time-resolved XPS” |
| 10:40 am – 11:20 am | **Plenary 3 – Markus Ammann (Paul Scherrer Institut)**  
“Surface Science in the Atmosphere”                                                                 |
| 11:20 am – 11:50 am | **Invited 10 – Heather Allen (Ohio State University)**  
“Iterfacial Aqueous Organization and Electric Fields Generated from Chemical Composition: Environmental and Material Surfaces” |
| 11:50 am – 12:10 pm | **Contributed 7 – Jiayue Wang (Massachusetts Institute of Technology)**  
“Quantifying the strain-dependent surface defect equilibria of perovskites”  |
| 12:10 pm – 12:30 pm | Break                                                                                                 |
| 12:30 pm – 1:00 pm | **Invited 11 – Fabrice Bournel (Sorbonne University and Synchrotron SOLEIL)**  
“Real time NAP-XPS study of dry silicon oxidation”                                                                 |
| 1:00 pm – 1:30 pm | **Invited 12 – David Starr (Helmholtz-Zentrum Berlin)**  
“Solid-liquid interfaces studied with synchrotron-based ambient pressure X-ray photoelectron spectroscopy” |
| 1:30 pm – 1:50 pm | **Contributed 8 – Adam Gross (University of California, Davis)**  
“Copper migration in intercalated topological insulator Cu$_x$Bi$_2$Se$_3$”  |
| 1:50 pm – 2:10 pm | **Contributed 9 – Burcu Karagoz (Brookhaven National Laboratory)**  
“Surface Chemistry of NO$_2$ and CO on a Cu$_2$O(111) Surface”  |

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# Day 4: Friday, December 10, 2021

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tr>
<td>10:00 am – 10:05 am</td>
<td><strong>Overview of technical session</strong>&lt;br&gt;“Streamlining and Enabling Automated/Remotely-Controlled AP-XPS Experiments”&lt;br&gt;Contributions from:</td>
</tr>
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<td>• <strong>Ignacio Villar</strong> (ALBA Synchrotron, Spain)&lt;br&gt;“Remote experiments at the CIRCE-NAPP station in ALBA”&lt;br&gt;• <strong>Patrick Zeller</strong> (BESSY, Germany)&lt;br&gt;“NAP-XPS remote operation capabilities at BESSY II”&lt;br&gt;• <strong>Luca Artiglia</strong> (Swiss Light Source/PSI, Switzerland)&lt;br&gt;“PShell software implementations to control the In Situ Spectroscopy beamline at SLS”&lt;br&gt;• <strong>Robert Temperton</strong> (MAX IV, Sweden)&lt;br&gt;“Enabling remote AP-XPS measurements at the HIPPIE and SPECIES beamlines at MAX IV”&lt;br&gt;• <strong>Georg Held</strong> (Diamond Light Source, UK)&lt;br&gt;“Remote Operation at the VerSoX beamline of Diamond Light Source”&lt;br&gt;• <strong>Slavomir Nemsak</strong> (Advanced Light Source, USA)&lt;br&gt;“Semi-automated remote APXPS experiments at the ALS”</td>
</tr>
<tr>
<td>10:05 am – 10:20 am</td>
<td>Break&lt;br&gt;Contributed 10 - Christopher Goodwin (Stockholm University)&lt;br&gt;“In situ observations of ammonia synthesis”</td>
</tr>
<tr>
<td>10:20 am – 10:35 am</td>
<td>Contributed 11 - Anthony Boucly (Paul Scherrer Institut)&lt;br&gt;“Water inhibition effect and highly cationic Pd species detected by AP-XPS on Pd/Al\textsubscript{2}O\textsubscript{3} catalysts for methane oxidation reaction”</td>
</tr>
<tr>
<td>10:35 am – 10:50 am</td>
<td>Contributed 12 - Rosemary Jones (Lund University)&lt;br&gt;“AP-XPS study of the adsorption of ethanol on rutile TiO\textsubscript{2} (110)”</td>
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<tr>
<td>10:50 am – 11:05 am</td>
<td>Next APXPS workshop and Closeout</td>
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### Pre-Recorded Contributed Talks

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<tr>
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<th>Affiliation</th>
<th>Title</th>
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<tbody>
<tr>
<td>RT-01</td>
<td>Peter Amann</td>
<td>The State of Zn under Methanol Synthesis Conditions over Zn/ZnO/Cu(211) Catalyst</td>
</tr>
<tr>
<td>RT-02</td>
<td>Hao Chen</td>
<td>Resolving the Nature of SMSI among Au-CoOₓ Model Catalyst</td>
</tr>
<tr>
<td>RT-03</td>
<td>David Degerman</td>
<td>Pressure hopping: Investigating CO and CO₂ hydrogenation on Rh in the borderlands between operando and post-mortem</td>
</tr>
<tr>
<td>RT-04</td>
<td>Pedro Alzaga</td>
<td>Oxidation of amorphous metal alloy surfaces studied using ambient pressure X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>RT-05</td>
<td>Heath Kersell</td>
<td>In-situ evolution of structure and chemical state during nanoparticle exsolution from perovskite hosts by reduction in H₂</td>
</tr>
<tr>
<td>RT-06</td>
<td>Esko Kokkonen</td>
<td>Using Ambient Pressure XPS to study ALD in real-time</td>
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<tr>
<td>RT-07</td>
<td>Withdrawed</td>
<td>Withdrawed</td>
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<tr>
<td>RT-07</td>
<td>Xiangrui Kong</td>
<td>A Surface-Promoted Redox Reaction Occurs Spontaneously on Solvating Inorganic Aerosol Surfaces</td>
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<tr>
<td>RT-08</td>
<td>Alexander Large</td>
<td>Anodized aluminium as a model catalyst support material in the complete oxidation of methane</td>
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<tr>
<td>RT-09</td>
<td>Patrick Lömker</td>
<td>Single crystalline Co(0001) Fischer-Tropsch observations at 550mbar (and above) using a virtual cell approach and hard X-rays</td>
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<tr>
<td>RT-10</td>
<td>Withdrawed</td>
<td>Withdrawed</td>
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<tr>
<td>RT-11</td>
<td>Richard Oleksak</td>
<td>In situ study of alloy degradation in high temperature CO₂</td>
</tr>
<tr>
<td>RT-12</td>
<td>Christoph Rameshan</td>
<td>Tailoring of Catalyst Surfaces for Energy Conversion – In-situ Studies of Electrochemical driven Nanoparticle Exsolution</td>
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<td>RT-13</td>
<td>Joachim Schnadt</td>
<td>Lund University</td>
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<td>RT-14</td>
<td>Markus Soldemo</td>
<td>Stockholm University</td>
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<td>RT-15</td>
<td>Andreas Thissen</td>
<td>SPECS Surface Nano Analysis GmbH</td>
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<td>RT-16</td>
<td>Ryan Thorpe</td>
<td>Lehigh University</td>
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<td>RT-17</td>
<td>Ryo Toyoshima</td>
<td>Keio University</td>
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<td>RT-18</td>
<td>Matthijs Van Spronsen</td>
<td>Diamond Light Source</td>
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<td>RT-19</td>
<td>Mykhailo Vorokhta</td>
<td>Charles University</td>
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<td>RT-20</td>
<td>Haiko Wittkämper</td>
<td>FAU Erlangen-Nürnberg - Physikalische Chemie II</td>
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<td>RT-21</td>
<td>Rito Yanagi</td>
<td>Yale University</td>
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<td>RT-22</td>
<td>Youngseok Yu</td>
<td>KBSI</td>
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<tr>
<td>RT-23</td>
<td>Xueqiang Zhang</td>
<td>Beijing Institute of Technology</td>
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# Pre-Recorded Poster Presentations

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<tr>
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<tbody>
<tr>
<td>PP-01</td>
<td>Luca Artiglia</td>
<td>The In Situ Spectroscopy beamline at the Swiss light source</td>
</tr>
<tr>
<td>PP-02</td>
<td>Sheng Yuan Chen</td>
<td>APXPS investigation of photocatalytic nitrogen reduction reaction in Bi₅O₂Br₀.₅I₀.₅: the critical role played by oxygen vacancy</td>
</tr>
<tr>
<td>PP-03</td>
<td>Sabrina Gericke</td>
<td>An in situ APXPS characterization of Al₂O₃ supported NiMo catalyst</td>
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<tr>
<td>PP-04</td>
<td>Withdrawn</td>
<td>Withdrawed</td>
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<tr>
<td>PP-05</td>
<td>Man Gu</td>
<td>Unveiling the active oxygen species in ethylene epoxidation over silver by ambient pressure X-ray photoelectron spectroscopy</td>
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<tr>
<td>PP-06</td>
<td>Tianhao Hu</td>
<td>In situ Spectroscopy Studies of Anisole Adsorption in NiMoO₄ Catalysts</td>
</tr>
<tr>
<td>PP-07</td>
<td>Nuria J. Divins</td>
<td>Investigation of ball-milled Pd/CeO₂ catalysts under operando methane combustion conditions</td>
</tr>
<tr>
<td>PP-08</td>
<td>Moonjung Jung</td>
<td>Exploring chemical/electronic change of environment of platinum atom on Pt₃M (M=Ti,V) alloy surface under oxidation process</td>
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<tr>
<td>PP-09</td>
<td>Geonhwa Kim</td>
<td>Catalytic reactivity stud on an atomically modified glassy carbon surface</td>
</tr>
<tr>
<td>PP-10</td>
<td>Xiansheng Li</td>
<td>Structure-activity evolution of platinum species supported on ceria during Water-Gas Shift Reaction</td>
</tr>
<tr>
<td>PP-11</td>
<td>Hojoon Lim</td>
<td>Nature of the surface space charge layer on undoped SrTiO₃ (001)</td>
</tr>
<tr>
<td>PP-12</td>
<td>Bo-Hong Liu</td>
<td>Ambient Pressure X-ray Photoelectron Spectroscopy Study of Room-Temperature Oxygen Adsorption on Cu(100) and Cu(111)</td>
</tr>
<tr>
<td>PP-13</td>
<td>Carlos Morales</td>
<td>Induced reduction by H₂ exposure at room temperature of ceria ultrathin films grown by atomic layer deposition</td>
</tr>
<tr>
<td>PP-14</td>
<td>Andreas Nenning</td>
<td>Voltage dependent kinetics and surface chemistry of solid oxide cell electrodes</td>
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<table>
<thead>
<tr>
<th>PP</th>
<th>Author</th>
<th>Institution</th>
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<tbody>
<tr>
<td>PP-15</td>
<td>Philip Petzoldt</td>
<td>Technical University of Munich</td>
<td>Monitoring the Behavior of Pt Loaded TiO$_2$(110) under Oxidizing and Reducing Conditions</td>
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<tr>
<td>PP-16</td>
<td>Ina Schmidt-Hanke</td>
<td>InProcess Instruments GmbH</td>
<td>Tailored Mass Spectrometry Solutions for the Gas Analysis of APXPS Systems at Different Pressure Ranges</td>
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<tr>
<td>PP-17</td>
<td>Minsik Seo</td>
<td>Gwangju Institute of Science and Technology</td>
<td>Investigation of surface oxidation on Pt3V alloys using ambient pressure XPS</td>
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<tr>
<td>PP-18</td>
<td>Stefan Van Vliet</td>
<td>ARCNL</td>
<td>Oxidation kinetics of Ru(0001) studied by NAP-XPS</td>
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<tr>
<td>PP-19</td>
<td>Withdrawn</td>
<td>Withdrawn</td>
<td>Withdrawn</td>
</tr>
<tr>
<td>PP-20</td>
<td>Chia-Hsin Wang</td>
<td>NSRRC</td>
<td>Ambient pressure/ UHV X-ray Photoelectron Spectroscopy End Stations at TPS BL43A</td>
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<tr>
<td>PP-21</td>
<td>Chueh Cheng Yang</td>
<td>National Yang Ming Chiao Tung University</td>
<td>Investigation of Redox Reaction of Platinum during Electrochemical Catalysis Reaction by Ambient Pressure XPS</td>
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<td>Youngseok Yu</td>
<td>KBSI</td>
<td>Surface chemical states of carbon-steel utilizing near ambient pressure XPS</td>
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The transformation of carbon dioxide and methane into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of these molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task have usually trouble binding CO$_2$ and CH$_4$, thus, they exhibit low catalytic activity. In this talk, a series of APXPS studies focused on the activation of C-O and C-H bonds on metal-oxide interfaces will be discussed [1-5]. In the case of CO$_2$, CeO$_x$/Cu(111), ZnO/Cu(111) and Cu/CsOx/ZnO(000\bar{1}) exhibit an activity for the CO$_2$ + 3H$_2$ $\rightarrow$ CH$_3$OH + H$_2$O conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Cu-ZnO interfaces, the combination of metal and oxide centers affords complementary chemical properties that lead to special reaction pathways for methanol synthesis [1,4,5]. Metal-oxide interfaces also can be tuned for the activation and conversion of CH$_4$ [2,3]. On CeO$_x$/Cu$_2$O/Cu(111) and ZnO/Cu$_2$O/Cu(111), methane is activated at room temperature and the CH$_4$ + 0.5O$_2$ $\rightarrow$ CH$_3$OH reaction takes place at moderate temperatures (450-500 K). APXPS has been used to study the cleavage of C-H bonds in methane and the formation of CH$_3$O groups on the catalyst surfaces. The addition of water to the reaction feed changes the main reaction mechanism, enhancing the formation of CH$_3$O species and favoring their extraction as CH$_3$OH [2,3].

References
Plenary Talk 2

Application of X-ray Techniques for Studying Artificial Photosynthetic Systems

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Artificial photosynthesis capable of the CO₂ reduction reaction (CO₂RR), with solar energy as external excitation energy and water (H₂O) as the electron and proton source, has been considered an attractive method to achieve a sustainable energy cycle, since it allows direct solar-to-chemical energy conversion. To design such systems, X-ray techniques play an important role for gaining the fundamental understanding needed to tailor its components and assemblies, by providing their chemical and structural information [1-3]. We have utilized surface-sensitive soft and hard X-ray techniques to investigate the interaction of metal catalytic surfaces with electrolytes and/or gases (H₂O and/or CO₂) under in situ/operando conditions. Among those, Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) probes CO₂ adsorption on catalyst surfaces, providing the information of the initial atomic level events for CO₂ electroreduction on the metal catalysts. We discuss current challenges of studying artificial photosynthetic systems.

References
Plenary Talk 3

Surface Science in the Atmosphere

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The atmospheric environment hosts a multitude of materials in solid, liquid or gaseous states, on the ground and in the air. The atmosphere is a dynamic medium, both in the physical and chemical sense, driven by the continuous exchange between these materials and ensuing chemical interactions. Many important atmospheric processes occur at the interface between the phases, such as gas-liquid, gas-solid, or solid liquid. Nucleation of cloud droplets, nucleation of ice particles, surface reactions driving ozone depleting chemistry, dissolution of metals from minerals later feeding the ocean or driving health impacts, or reactions proceeding faster at surfaces than in bulk materials are just a few examples. Water vapor is one of the main driving forces to control the physical conditions at interfaces and is the main host of chemical reactions. X-ray photoelectron spectroscopy (XPS) provides chemical composition information, and electron yield near edge X-ray absorption fine structure (NEXAFS) spectroscopy gives insight into the structure of the local molecular environment at interfaces with a probe depth ideally covering the scales relevant for the atmosphere. The development of ambient pressure electron analyzers has offered tremendous opportunities for molecular understanding of environmentally relevant aqueous solution surfaces, ice surfaces, and mineral oxides, all in presence or absence of reactive trace gases and in or out of equilibrium with water vapor. Applications involving the characterization of interfacial structure at mineral oxides and ice, the protonation state of acids or the direct observation of reaction intermediates at the surface of liquid water will be presented.

References
Invited Talk 1

**In situ APXPS applied to catalysis for renewables**

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There is an urgent need for a transition from fossil-based feedstock to the use of more sustainable feedstocks. An increased number of possible candidates for renewable resources has been proposed over the last decades, where lignin is one of the most promising alternatives [1]. Conventional pulp and paper industries generate a large amount of lignin as a byproduct that is mainly used as low-quality fuel but can be converted to biofuel by the use of heterogeneous catalysis. One interesting pathway is via co-processing of renewable and traditional hydrocarbons in hydrotreating processes in petroleum refineries. For this purpose, a tailored, large-pore NiMo-catalyst has been developed, which recently also showed successful results in the catalytic hydrotreatment process, which efficiently reduces the high oxygen content in lignin to produce high-quality biofuel. To develop the tailored catalyst further a deeper understanding is needed. The interaction between the NiMo catalysts and H\(_2\) is highly interesting both for the activation process in the transition from oxide to sulfide and also in the catalytic hydrotreatment application [2]. APXPS has therefore been used to characterize the alumina-supported NiMo catalysts in situ during H\(_2\) reduction. To achieve a fundamental understanding of Ni as promoters in the material the ratio of the Ni to Mo in the catalysts has been varied systematically. The detailed understanding of the industrial catalysts has made it possible to design a model system of engineered 20 nm NiMo nanoparticles with the same Ni to Mo ratio as the industrial catalysts. The APXPS study of the nanoparticles has provided insights into the role of the alumina support but also the size of the active NiMo nanoparticles. The parallel APXPS studies of industrial catalysts and model catalysts provide a detailed understanding on atomistic level making it possible to tailor the catalysts for conversion of renewables.

**References**

Invited Talk 2

Ambient Pressure NEXAFS at VerSoX B07-B

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VerSoX B07-B is a newly-operational beamline at Diamond Light Source, dedicated to soft X-ray spectroscopy under varied experimental conditions. Since May 2021 we have been accepting science commissioning user groups from diverse fields including heterogeneous catalysis, organic electronics, advanced functional materials for CO₂ capture, paints and coatings, batteries (including in-situ electrochemical cells) and enzyme polymer degradation. In this talk we will discuss some highlights of the science commissioning and optimisation processes and present the experimental opportunities available at the beamline and endstations.

B07-B has a shared bending magnet source with the Ambient Pressure XPS beamline (VerSoX B07-C)[1] and completely separate optics and control systems allowing simultaneous independent operation of the two beamlines. It consists of two user endstations: ES-1 for high-throughput UHV XPS measurements with full sample preparation facilities and automated sample transfer; and ES-2 for ambient X-ray absorption spectroscopy of gas, liquid and solid samples. The beamline covers a wide photon energy range from 40-2200 eV, and has demonstrated a resolving power >30000 during commissioning, with a beam size ~200 x 200 μm².

Figure 1. C K edge NEXAFS spectra of polymers, ES-2 experimental chamber, Gas phase XAS used to calibrate the beamline resolution

References

Invited Talk 3

The interaction of methanol vapor with copper surfaces

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Cu-based materials are currently our best option as catalysts for all methanol-to-hydrogen reactions, which makes the interface between Cu and methanol vapor exceedingly important; yet, only a handful of spectroscopic and microscopic studies are available in the literature.

In the past few years, we scrutinized the interface between various faces of Cu with methanol vapor using a variety of techniques including ambient pressure scanning tunneling microscopy, ambient pressure x-ray photoelectron spectroscopy (APXPS), and polarization modulation infrared reflection absorption spectroscopy PM-IRRAS. Methanol adsorbs dissociately as methoxy on both Cu(111), Cu(100), and Cu(110) surfaces when present in the mbar range at room temperature and above, as evidenced by all three techniques. Formate formation, as often observed with APXPS by us and other authors originate from impurities in the measurements chambers. IR spectroscopy provides a more detailed information on the adsorption behavior as both C=O and C-H stretching frequencies are accessible. Methoxy adlayer gradually reaches a lower equilibrium coverage by further dehydrogenation into formaldehyde and carbon monoxide, the latter observed as a relatively short-lived species with IR spectroscopy. Kinetics analysis based on the shifts in the C=O stretching frequency of methoxy suggests that the structural transformation is faster on the Cu(110) surface compared to Cu(111) and Cu(100) surfaces. We also think that APXPS, the most commonly used technique in the field, overestimates coverage of dissociated species because of enhanced surface activity due to secondary electron generation.

The observed coverage evolution kinetics and our proposed model for methanol dissociative adsorption on Cu surfaces are different from the classical kinetic models of chemisorption. Commonly used models, such as Langmuir kinetic model for dissociative adsorption, predict that the surface coverage monotonically increases with time towards equilibrium. We propose a new model to explain this unusual behavior.
Interest in the surface chemistry of late transition-metal (TM) oxides was originally stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this talk, I will discuss our investigations of the facile activation and subsequent oxidation of methane on IrO$_2$(110) films grown on Ir(100). Experiments in ultrahigh vacuum (UHV) demonstrate that the C-H activation of methane is highly efficient on IrO$_2$(110) at 100 K and that the resulting CH$_x$ groups remain stable to about 400 K but thereafter tend to oxidize to gaseous CO and CO$_2$. These characteristics establish a wide temperature range over which methane-derived intermediates can be produced on IrO$_2$(110) and potentially transformed to more valuable products. The possibility for achieving selective oxidation provides substantial motivation for investigating the reactivity of methane on IrO$_2$(110) under catalytically-relevant conditions. My talk will focus mainly on recent in situ x-ray photoelectron spectroscopy investigations of CH$_4$ oxidation on IrO$_2$(110) films and the relation between these results and the chemical behavior identified from UHV surface science experiments and molecular simulations. These studies demonstrate that IrO$_2$(110) films are catalytically active for CH$_4$ oxidation and provide insights about the surface intermediates which form and elementary processes that influence the reaction over a range of conditions. Overall, the exceptional activity of IrO$_2$(110) toward alkane C-H bond cleavage, along with the ability to manipulate the subsequent oxidation pathways, may provide new opportunities for developing IrO$_2$-based catalysts that are capable of directly and efficiently transforming light alkanes to value-added products.
Invited Talk 5

**Ongoing APXPS studies in Korea Basic Science Institute**

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KBSI and PAL constructed APXPS end-station at Pohang light source (PLS) 8A2 beamline in 2019, and they keep collaborating for user support. By leveraging around 45 days of annual beamtime for the institutes and the auxiliary Al Ka lab-sourced APXPS, we are conducting independent studies on various subjects we are interested in. In this talk, we would like to present ongoing researches and plans with the APXPS beamline at PLS. In addition, I would like to introduce the project for building a 4\(^{\text{th}}\)-generation synchrotron light source in Korea.

References

Invited Talk 6

Two-Dimensional Transition Metal Dichalcogenide Alloy Nanosheets to Enhance Electrocatalytic Performance

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Semiconductor two dimensional nanostructures (nanosheets) have recently attracted considerable attention for many applications including electrochemical catalysts and flexible optoelectronic nanodevices. Phase control of nanosheets using alloy is challenging because of the band gap tunability as well as electronic structure modulation. We developed solution reaction method to synthesize alloy phase of group VI-VII and V-VI transition metal dichalcogenide (TMD) nanosheets. The electronic structures were thoroughly examined using atomic resolution scanning transmission electron microscopy and X-photoelectron spectroscopy. We observed the enhanced the electrocatalytic performance toward water-splitting hydrogen evolution reaction (HER). Extensive spin-polarized density functional theory calculations consistently predicted the phase transition, in agreement with the experimental results. The Gibbs free energy along the pathway of HER indicates that this enhance HER performance is mainly due to the vacancy sites. Understanding the catalytic reaction at the atomic level would provide deep insight into the design of phase control systems.

References

Invited Talk 7

Photoemission studies of Li-O₂ batteries

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Operation of Li-O₂ batteries which are associated now with future high-energy storage devices includes reactions of molecular oxygen. In this case AP XPS is rather relevant tool to probe reaction mechanisms and to reveal the reasons of the current capacity and cyclability of the Li-O₂ batteries.

First, we have developed model electrochemical cell for operando studies with solid electrolyte to exclude influence of electrolyte. As a positive electrode transferred graphene was used. This approach enables to observe electrochemical reactions and side chemical reactions separately using different discharge and charge regimes. We observed directly in O 1s spectra short-living superoxide radical species (oxygen reduction intermediate) and their reactions with electrode materials. In addition, different electrode materials were tested.

Using the same cell, we find the way to evaluate solid electrolyte instability towards metallic lithium negative electrode and trace the formation of SEI.

Second, we have studies side reactions with electrolyte by admitting solvent vapor. This approach allows us to reveal some reactivity even for relative stable solvents such as acetonitrile. Unfortunately, this kind of studies is technically limited for many solvents since they are not safe for the spectrometer.

Third, in our experiments with liquid nonaqueous electrolytes we used approach with graphene window. We were able to observe EDL formation, however the lifetime of the corresponding cell is rather limiter from of radical attack of the species formed by radiolysis and final destruction of graphene. The radiolysis was not detectable in free liquid probably due to fast mixing with the bulk, and becomes rather critical in the case of small electrochemical cell.

All in all, AP XPS enables important findings for Li-O₂ batteries especially in the case when adequate model system is used. At the same time the approaching to the realistic operation conditions requires additional efforts including technical issues.
Modeling of Fuel Cell and Electrolyzer processes using Electrochemical XPS and XAS data

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Most industrial electrochemical devices make use of membrane-electrode assemblies, where the electrode material is loaded onto a solid polymer electrolyte. During operation, water or liquid electrolyte is also present, creating a complex mix of electrode, polymer and liquid. Understanding the dynamics of such a complex system is a major task, requiring a characterization technique that can separately address the various components. The element-specific nature of XPS and XAS make these techniques excellent for this task, although care has to be taken to maintain a realistic electrochemical environment in the vacuum of the spectrometer. An approach to do this was recently developed at ISISS/BESSY II [1,2], in which the membrane-electrode assembly is covered with a graphene window to minimize the evaporation of the water.

We have used this approach to unravel the chemistry of two processes: 1) the oxidation of platinum under fuel cell start-up conditions, and 2) the dynamics of the surface structure of iridium oxide under electrolyzer anode operation conditions. Based on a combination of XPS and XAS data, we have derived models for the surface reactions that occur. By comparing to electrochemical measurements or molecular dynamics simulations, we show that the models can quantitatively describe the surface electrochemistry of the electrodes.

References

Operando observation of photo-excited carriers and molecules at solid surfaces using time-resolved XPS

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Solid surfaces are important reaction fields in energy and material conversion processes such as catalysis/photocatalysis, fuel cell, and solar cell. For example, photocatalytic reactions consist of several elementary processes, such as photoexcitation in semiconductors, separation and transport of photoexcited carriers (electrons and holes), and redox reactions on metal co-catalyst surfaces. These elementary processes occur in a very wide range of time scales, from femtosecond to more than a second. Therefore, a comprehensive understanding of the dynamics of photo-excited carriers and molecules at solid surfaces is necessary to improve the efficiency of energy conversion processes.

X-ray photoelectron spectroscopy (XPS) is a powerful experimental technique that enables direct observation of solid surfaces with elemental and chemical sensitivity. The extension of XPS to time-domain, or time-resolved XPS, has been realized by the use of brilliant X-ray short pulses (several tens ps) available at the state-of-the-art synchrotron radiation facilities [1]. We have developed two operando XPS systems (time-resolved XPS [2] and ambient pressure XPS [3, 4]) at a soft X-ray undulator beamline BL07LSU at SPring-8 [5], which can monitor photoexcited carriers and molecules on solid surfaces in real time [6-11].

In this presentation, I would like to introduce our results on real-time observation of carrier dynamics at oxide surfaces (TiO₂) [12] and at the interface of plasmonic nanoparticles and oxides (Au/TiO₂) using time-resolved XPS. In addition, I will explain the recent development of time-resolved AP-XPS system at SPring-8 BL07LSU.

References
Interfacial Aqueous Organization and Electric Fields Generated from Chemical Composition: Environmental and Material Surfaces

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Studying aqueous interfaces presents challenges, and given that interfaces are ubiquitous in nature, their importance as a transition zone is clear. Ocean surfaces, atmospheric aerosol interfaces, bio-membranes, and material interfaces are examples of complex interfacial regions. Work in our group focuses on interfacial organization and the inherent electric field from aqueous solution surfaces. Alkaline earth, alkali metal and ferric halides, nitrates, and sulfates organize in the interfacial region distinctly differently and their respective surface potentials are reflective of the preference or non-preference for the aqueous surface. Soluble and insoluble organics also modify the interfacial electric field through organization to minimize the free energy of the surface. These effects impact binding of ions with organic molecules and thus modify the surface electric field. Experimental studies of sum frequency generation (SFG), second harmonic generation (SHG), infrared reflection absorption spectroscopy (IRRAS), ionizing surface potential and surface tension measurements will be presented for a unifying picture of aqueous salt and organic-rich interfaces.
Invited Talk 11

**Real time NAP-XPS study of dry silicon oxidation**

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During the last decades silicon oxidation has been the subject of numerous experimental and theoretical studies due to its technical importance to form the nano-dielectric layers in electronic devices. The initial steps of the oxidation of the Si(111)-7×7 surface has attracted a considerable attention as its complex surface exhibits a diversity of reactive sites (corner adatoms, center adatoms, and rest atoms) which offer an interesting model for the study of the oxidation process on semi-conductors.

We present here a real time XPS study of the Si(111)-7x7 surface oxidation by O$_2$ at room temperature in near ambient pressure conditions (to P(O$_2$) = 1 mbar) performed at TEMPO beamline, SOLEIL synchrotron.

An emphasis will be done on the changes of the surface work function and on the band bending variations with oxygen pressure and oxide thickness thanks to the Si2p level and to the electron cut-off measurements. Comparison with the low pressure silicon oxidation (P(O$_2$) = 10$^{-6}$ mbar) regime will be investigated and furthermore a pertinent comparison with the oxidation of metal, in this case, aluminum will be presented.
Solid-liquid interfaces studied with synchrotron-based ambient pressure X-ray photoelectron spectroscopy

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Ambient pressure X-ray photoelectron spectroscopy is a valuable tool for investigating surfaces and interfaces in elevated pressure conditions. We have recently constructed and commissioned a new end-station dedicated to Spectroscopic Analysis with Tender X-rays (SpAnTeX). The SpAnTeX end-station focuses on X-ray photoelectron spectroscopy measurements of solid-liquid interfaces. It is able to operate at pressures up to 30 mbar and photoelectron kinetic energies up to 10 keV. At the heart of the SpAnTeX end-station is a SPECS PHOIBOS 150 HV NAP electron spectrometer. This new spectrometer contains two additional features that allow for measurements with lateral resolution better than 30 μm and time resolved measurements with 100 ns or less time resolution. The SpAnTeX end-station is based on a modular concept which allows for the rapid exchange of sample environment modules. To date, we have constructed two modules. One module, the dip-and-pull module, is used for investigating solid-liquid interfaces under applied bias and illumination. The second module incorporates a droplet train which facilitates investigation of liquid phase processes with time resolution ranging from the μs to ms regimes. After a technical introduction to the SpAnTeX end-station and the experimental modules, results obtained using SpAnTeX will be presented. We will present results for Electrochemically Mediated Amine Regeneration (EMAR) for CO₂ capture and sequestration processes, and light induced changes at the bismuth vanadate- and silicon-aqueous electrolyte interfaces.

References
Contributed Talk 1

Asymmetric CO ignition on Rh stepped surfaces studied with a curved sample

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Tracking the active site of catalytic metallic nanoparticles in mandatory for tailoring new catalysts and promote a clean and green environment. The activity of each of the facets of the nanoparticle will differ depending on the orientation and coordination of surface atoms [1], yet isolating their individual activity is typically challenging. Within this context, curved crystals possess several different planes, hence they are ideal for selectively probing different types of undercoordinated atoms [2,3]. Using this methodology, we have studied the CO oxidation on Rh stepped surfaces using a curved Rh(111) crystal. This peculiar sample features the flat (111) surface at the center of the crystal, and an increasing density of either A- (square) and B- (triangular) steps as one approaches each of the edges of the sample.

Preliminary Planar Laser-Induce Fluorescence (PLIF) experiments reveal that the B-side of the crystal ignites earlier during the CO oxidation, mimicking the results obtained using an identical curved Pd(111) crystal [2b], and in clear contradiction with the symmetric ignition observed for a curved Pt(111) sample [3]. Near-ambient pressure X-ray photoemission measurements conducted on the same curved Rh(111) crystal show that prior to the ignition of the whole sample, which is marked by an abrupt CO desorption and CO₂ production, the B-steps are partially CO-depleted and oxidized, while the A-steps feature a CO-saturated situation. Therefore, such large asymmetry in the chemical composition of A- and B-steps points to be the reason of the early ignition of the B-steps observed by PLIF.

References

Contributed Talk 2

Reaction of 2-Propanol on SnO$_2$(101) and SnO$_2$(110) Studied using Ambient-Pressure X-ray Photoelectron Spectroscopy

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Tin dioxide (SnO$_2$) has been extensively studied due to its versatility in many areas of interest such as oxidation catalysis, transparent oxide conductors, and gas sensing. It has been shown that the crystal planes of SnO$_2$ play a critical role in the observed reduction properties and the resulting surface chemistries.[1][2] The dual valency of Sn enables the reduction of the SnO$_2$ surface and a transition from the Sn$^{4+}$ to the Sn$^{2+}$ state. For example, low energy ion scattering results indicated that SnO$_2$(110) begins to reduce above 350 K, compared to SnO$_2$(101) which begins to reduce above 550 K.[2] Furthermore, recent studies indicated that the Sn$^{2+}$/Sn$^{4+}$ ratio on SnO$_2$ nanomaterials strongly impact the activity of the oxidation of carbon monoxide.[3] SnO$_2$ has been demonstrated as an oxidation catalyst for volatile organic compounds (VOCs), where 2-propanol was used as a representative VOC.[4] The goal of our study is to better understand the role of surface structure and surface oxidation states on the reaction of 2-propanol on SnO$_2$.

For this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and low energy electron diffraction (LEED) to characterize the surface chemistry of 2-propanol on both SnO$_2$(110) and (101). Both surfaces were exposed to identical reaction conditions from UHV to 1 mbar of 2-propanol vapor at various temperatures. Using valence-band spectra, we find that surface reduction begins at 470 K and 410 K for the SnO$_2$(110) and (101) surfaces in UHV, respectively. We found that the transition of Sn$^{4+}$ to Sn$^{2+}$ in the presence of 2-propanol occurs at lower temperatures than in UHV for both surfaces. Furthermore, we used C 1s spectra to monitor the surface chemistries under identical reaction conditions for both the (110) and (101) surfaces. These results give insight into reaction mechanisms and advance our understanding of SnO$_2$ oxidation catalytic properties.

References
Contributed Talk 3

**Surface-bulk dynamics of bulk mixed oxide and supported metal oxide catalysts under reaction conditions: an *in situ* NAP-XPS study**

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Valorization of hydrocarbons is commonly carried out with heterogenous bulk mixed oxide and supported metal oxide catalysts. Yet *in situ* surface characterization vital to establish molecular structure-activity relations under reaction conditions is still missing for many catalyst systems, especially under reaction conditions. Near ambient pressure - X-ray photoelectron spectroscopy (NAP-XPS) is uniquely capable of providing critical *in situ* information on the concentrations and oxidation states of constituent elements in the surface region (< 3 nm) of such catalyst systems under reaction conditions.

We will present results acquired using NAP-XPS as part of our studies of (a) propylene oxidation on bulk BiMoO\(_x\) and FeMoO\(_x\) mixed oxides, (b) methane aromatization on Li\(_2\)CO\(_3\) supported on a LaPrO\(_3\) bulk mixed oxide support, and (c) propane oxidative dehydrogenation on supported VO\(_x\)/In\(_2\)O\(_3\). The bulk mixed oxides exhibited surface enrichment of one countercation compared to bulk stoichiometry that further increased with temperature in some catalysts. This was corroborated by high sensitivity low energy ion scattering (HS-LEIS), which enables layer-by-layer atomic composition depth profiling. These techniques indicate that the surface of bulk mixed oxides is not an extension of the crystalline bulk phase, and that the surface region composition in such catalysts can change dramatically with temperature. While only one countercation participated in the redox reaction in some of the bulk mixed oxides, both countercations underwent redox in others. This suggests that countercations can play a promotional and/or active role in bulk mixed oxide redox catalysts. The incorporation of reduced surface VO\(_x\) sites into the In\(_2\)O\(_3\) support bulk phase during reaction was detected by NAP-XPS, indicating that not all of the supported VO\(_x\) stays on the In\(_2\)O\(_3\) surface during the propane oxidative dehydrogenation reaction. These surface-bulk dynamics demonstrate the vital need for *in situ* characterization of oxide catalysts under reaction conditions even in supported metal oxide catalysts.
Contributed Talk 4

Sulfur poisoning Pt and PtCo anode and cathode catalysts in polymer electrolyte fuel cells studied by Operando near ambient pressure hard X-ray photoelectron spectroscopy

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In present work, S adsorption behaviors on Pt-based anode and cathode electrode catalysts in polymer electrolyte fuel cells (PEFC) under working conditions for the fresh state just after aging and also the degraded state after accelerated degradation tests (ADT) were investigated by near ambient pressure hard X-ray photoelectron spectroscopy. All the S 1s HAXPES show not only the principal S species from the sulfonic acid group (-SO3H) in the Nafion electrolyte but also other characteristic S species such as zero-valent S (S⁰) adsorbed on the carbon support and anionic S (S²⁻) adsorbed on the Pt electrode. The S²⁻ species on Pt should be ascribed to S contamination poisoning the Pt catalyst electrode. The S²⁻ species on the cathode can be oxidatively removed by applying a high cathode-anode bias voltage (≥ 0.8 V) to form SO₃²⁻, while at the anode the S²⁻ species cannot be eliminated because of reductive environment in hydrogen gases. The important finding is the different S adsorption behavior between the Pt/C and Pt₃Co/C anode electrodes after ADT. The Pt/C (~2.6 nm) anode electrode after ADT exhibits much larger S²⁻ adsorption than the Pt₃Co/C (~3.0 nm) anode electrode after ADT. This indicates that the Pt₃Co/C anode is more desirable than the Pt/C one from the view point of S poisoning. The reason for more tolerance of the Pt₃Co/C anode catalyst against S poisoning after ADT can be ascribed to more negative charge of the surface Pt atoms in the Pt₃Co/C catalyst than the Pt/C one, this yielding weaker interaction between the surface Pt and the anionic S species as S²⁻, SO₃²⁻, and SO₄²⁻. A similar behaviour was observed also in the cathode catalyst. The present experimental findings will provide important information to design novel Pt-based PEFC electrodes with higher performance and longer durability.
Contributed Talk 5

Potentials in Li-ion batteries probed by operando APPES

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To further understand the kinetics of charge transfer over the solid/liquid interfaces in Li-ion batteries (LIBs), there is a need for techniques that can be performed during battery cycling, i.e., operando. Operando APPES is a suitable technique for the study of electrochemical interfaces, (including LIB interfaces) due to its sensitivity towards different chemical environments as well as local electrostatic potential differences. In recent studies performed by our group we have developed a methodology for studying LIB interfaces by operando APPES. In this presentation important practical considerations for these measurements will be highlighted [1, 2]. Results from recent operando APPES studies where a real LIB system is studied operando will also be presented [3]. A model for interpreting the data has also been suggested [3, 4]. According to this model and our methodology, the combination of electrochemistry (measuring voltage differences) and APPES (measuring shifts in kinetic energy) can be used to directly follow the electron electrochemical potential difference over the solid/liquid interface. A distinct difference in the behaviour of the potential differences over the interface is seen for charge transfer reactions compared to pure EDL-charging (see figure). Further, even without direct access to the solid/liquid interface (which is practically challenging to measure), the kinetic energy shifts of the electrolyte photoelectron peaks can be used to evaluate the change in Li chemical potential of the WE during Li-ion equilibrium. This information can be used to gain further insights regarding the kinetics of the (de)lithiation reactions occurring at the solid/liquid interface in a LIB.

References
Contributed Talk 6

Platinum electrocatalyst oxidation under steady state and transient conditions examined by in situ XPS and XAS

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Potential spikes during the start-up (SU) and shutdown (SD) of fuel cells are a major cause of platinum (Pt) electrocatalyst degradation, which limits the lifetime of the device[1]. The electrochemical oxidation of Pt that occurs on the cathode during the potential spikes plays a key role in this degradation process[2]. However, the composition of the oxide species formed, as well as their role in catalyst dissolution remains unclear. In this study, we employ a special arrangement of XPS (X-ray Photoelectron Spectroscopy), in which the Pt electrocatalyst is covered by graphene, making the in situ examination of the Pt oxidation/reduction under wet conditions possible. We use this assembly to investigate oxidation state changes of Pt within fuel cell relevant potential window. We show that above 1.1 V_RHE, a mixed Pt^{δ+}/Pt^{2+}/Pt^{4+} surface oxide is formed, with an average oxidation state that gradually increases as the potential is increased. By comparing a model based on the XPS data to the oxidation charge measured during potential spikes, we show that our description of Pt oxidation is also valid during the transient conditions of fuel cell SU/SD. This is due to the rapid Pt oxidation kinetics during the pulses. As a result of the irreversibility of Pt oxidation, some remnants of oxidized Pt remain at typical fuel cell operating potentials after a pulse.

References
Contributed Talk 7

Quantifying the strain-dependent surface defect equilibria of perovskites

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Understanding surface defect chemistry and its strain dependency is essential in the effort to develop the next-generation electrochemical devices. However, due to the nanoscale dimension of the surface defects, they cannot be accessed by conventional techniques used in bulk defect studies. Here, we present a generalizable framework for quantifying surface defect equilibria by integrating in-situ X-ray absorption spectroscopy, first principles calculations, and thermodynamic analyses. Using the (001)-terminated La$_{0.6}$Sr$_{0.4}$FeO$_3$ (LSF) as a model system, we systematically investigated its strain-dependent surface defect chemistry during oxygen incorporation/evolution reactions at elevated temperatures. We found that the electron holes in LSF are preferentially located on the oxygen sites and the surface oxygen anions are the dominant redox center. By examining the concentrations of the oxygen-centered electron holes on the LSF surface as a function of oxygen partial pressures (pO$_2$), we show that the tensile-strained LSF surface is more reducible than the compressive counterpart. Nevertheless, for both strain states, the surface was significantly more reducible than the stress-free bulk. Finally, we demonstrate that the surface defect chemistry can be largely captured by a bulk-like, ideal solution based point defect model. As a result, the transition from bulk defect equilibria to the strain-dependent surface defect equilibria is equivalent to a shift in pO2 by as much as 5 orders of magnitude at 400 °C.
Contributed Talk 8

Copper migration in intercalated topological insulator CuₓBi₂Se₃

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CuₓBi₂Se₃ is a topological insulator (TI) material in which Cu intercalation between the Bi₂Se₃ quintuple layers can yield superconductivity. Using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), we report copper migration from the bulk towards the surface in this material in controlled oxidizing environments as well as ambient conditions. The migration occurs on a timescale of hours to weeks after initial cleaving, and proceeds along with the oxidation of the sample surface. These results demonstrate dynamic surface chemistry, relevant for tailoring the topological surface states for utilization in ambient environments.
Contributed Talk 9

Surface Chemistry of NO$_2$ and CO on a Cu$_2$O(111) Surface

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Metal oxide catalysts, particularly CuO$_x$, are preferred in industrial chemical processes due to their low cost and availability compared to noble metal-based catalysts [1-5]. CuO$_x$ is also used in air filtration materials to absorb toxic industrial chemicals and chemical warfare agents [6-7]. In this application, the effect of atmospheric molecules, such as NO$_2$ and CO, on the performance of filtration and material lifetime is unknown. Therefore, it is important to probe the CuO$_x$ surface interaction with gases at relevant pressures to understand the adsorption and reaction mechanisms of gases in filter materials and catalytic processes.

In this project, we studied the surface chemistry of NO$_2$ and CO on a Cu$_2$O(111) single crystalline surface using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and under pressures up to ~1 mbar. Near-edge x-ray absorption spectroscopy fine structure (NEXAFS) was also used to investigate the interactions of NO$_2$ with a Cu$_2$O(111) surface. We also performed infrared reflection absorption spectroscopy (IRRAS) for the CO adsorption on Cu$_2$O(111), the first report of IRRAS data of a Cu$_2$O single crystal. The NEXAFS data reveals a pressure dependence of the oxidation of the Cu$_2$O surface to CuO by NO$_2$. APXPS results show NO$_2$ chemi- and physisorption on the Cu$_2$O surface and decomposition to NO and O, or to N and O, with the amount of the species also being pressure dependent. CO adsorbs on the Cu$_2$O(111) surface, forming carboxylate and carbonate species. Furthermore, polarization-dependent IRRAS demonstrated that CO bounds to the surface in a perpendicular geometry while CO$_2$ is parallel to the surface. This study shows how IRRAS can complement APXPS data to obtain the geometric orientation of adsorbed species. The combination of the spectroscopic techniques shows a comprehensive picture of NO$_2$ and CO adsorption with implications for catalysis and gas filtration materials.

References

In situ observations of ammonia synthesis

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Direct observation of ammonia syntheses was considered an impossibility even by Gerhard Ertl, who wrote of it “… spectroscopic measurements may never be performed under pressure conditions as applied for the [Haber-Bosch] reaction.” Since then, APXPS has advanced, and with POLARIS, an APXPS can measure reactions at one bar, and it is now possible to measure the system in situ. Herein we present the first APXPS data of ammonia synthesis over iron. We compare the Fe(110) and Fe(210) surfaces at pressures from 200 to 1000 mbar, with various gas ratios and temperatures. From this data, we have ascertained the turnover frequency of the two surfaces and shed new light on how surface steps affect the formation of ammonia. While many surface structures have been proposed included oxides, nitrides, and metallic states, for the first time, there is direct observation of the atomic structure of the surface in situ. We have resolved the contradictions between the ex situ studies and thermodynamic calculations by comparing the effects of various conditions, such as low temperature or low nitrogen content. We have shown that the surface is dynamic, with many states possible depending on the gas and temperature. Though many states can form, the metallic surface is the dominant state with low coverage of surface nitrogen under the highest turnover conditions.
Contributed Talk 11

Water inhibition effect and highly cationic Pd species detected by AP-XPS on Pd/Al₂O₃ catalysts for methane oxidation reaction

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Methane is an important energy carrier and has been widely used as a fuel for transportation and industrial applications due to its high-energy density and low emission of gaseous pollutants.¹,² However, the fraction of unburned methane gas present in the exhaust of natural gas vehicles (NGVs) still poses a threat to the environment, as it is a potent greenhouse gas and significantly contributes to global warming.³,⁴ Supported palladium catalysts are the most active in the complete oxidation of methane, the main treatment technology used to achieve the elimination of residual methane.⁵ Unfortunately, those catalysts suffer from strong deactivation at temperatures below 450°C in the presence of water, whose concentration is high in the exhaust of NGV.⁶,⁷ Explanation on how water actually inhibits the reaction is still a matter of debate and further efforts are required to fully understand the water inhibition effect in the low temperature range. Here we present a study on a 1% Pd/Al₂O₃ catalysts combining microscopy, activity measurements and ambient pressure X ray photoelectron spectroscopy carried out in both dry and wet conditions. Experimental results show the presence of highly-valent Pd species, which have not often been observed in the literature in both condition used. The inhibition effect of water is demonstrated combining reactivity tests with ambient pressure photoelectron spectroscopy measurement performed in situ. In the presence of water, higher temperature is required to detect the redox behavior of palladium, indicating that water competes with methane for cationic palladium sites, poisoning the surface with hydroxyl groups.

References:
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AP-XPS study of the adsorption of ethanol on rutile TiO$_2$ (110)

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The photoactivity of TiO$_2$ renders it surfaces of particular interest for the study of surface reactions. In particular, TiO$_2$ surfaces are active for hydrogen production, both via the water splitting process and via ethanol degradation under ultraviolet (UV) illumination. The selective photocatalytic dehydrogenation of TiO$_2$ is not fully understood yet, and an important question in this context is how ethanol adsorbs TiO$_2$ surface under ambient conditions.

Previously, the adsorption of ethanol on rutile TiO$_2$(110) has been studied ex situ using temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM).¹–⁶ These studies use conditions far removed from ambient, which can dramatically impact which species are present on the surface. Theoretical studies have expanded on the experimental results, concluding that dissociative adsorption, forming an ethoxide, is slightly more favourable energetically than molecular adsorption of an ethanol, with a difference in adsorption energies ranging from 0.11 eV to 0.28 eV.²,³,⁵ It is worth noting that these differences are very close to the uncertainty (±0.2 eV) of the DFT calculations.⁷

The surface sensitivity of synchrotron-based AP-XPS allows for an in-depth analysis of the surface species and their coverage as well as an estimation of the energy difference between the two species. We present the first in situ experimental studies on the absorption of ethanol on rutile TiO$_2$(110) at room temperature and near-ambient conditions. Through modeling of the O 1s core level and comparison to experimental results we show that both molecular and desociative adsorption of ethanol occur. The surface coverage calculated to be 0.56 ML, 0.32 ethoxide and 0.24 ethanol, which gives a 0.007 eV difference in energy for the two species, much smaller than previously thought. In addition, we show that at room temperature a multilayer distinguishable from the gas phase is formed with increasing pressure of ethanol.

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The State of Zn under Methanol Synthesis Conditions over Zn/ZnO/Cu(211) Catalyst

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Methanol is a highly attractive base chemical that can give an important contribution for closing the carbon cycle when formed from a mixture of CO, CO$_2$ and H$_2$. While the elements Cu and ZnO show very low turnover rates, the mixture of them results in highly active catalysts. Despite intense investigations there are still significant unresolved questions on the nature of Zn: whether it is in a metallic or (partly)oxidized state or if Zn forms an alloy with Cu during the reaction? Here I report on an experimental approach that allows investigation of the Zn state under operando conditions using a pressure greater than 180 mbar and variable temperature. We find that Zn dynamically responds to the chemical potential of the surrounding gas and becomes more metallic under CO hydrogenation conditions and more oxidized under CO$_2$ hydrogenation conditions. By comparing with brass and polycrystalline Zn sample we can distinguish the different states of Zn as Zn metal islands, ZnO and surface Cu-Zn alloy. Under all conditions we find that Zn is in a mixed oxide-intermetallic state. The mixture of CO, CO$_2$ and H$_2$ critically affects the local ZnO ⇌ Zn redox equilibrium and we conclude that the most active phase is stabilized in the simultaneous presence of balanced amounts of CO, CO$_2$ and H$_2$.

The results were achieved using the POLARIS instrument (Scienta Omicron, BarXPS) [1] [2], at beamline P22 of the Petra III synchrotron at DESY, Germany. This instrument was specifically designed to investigate catalysts under operando conditions at pressures of up to and beyond 1 bar in combination with elevated temperature capabilities. Using grazing-incidence hard X-rays from the synchrotron the experiment can be optimized to a specific aspect with respect to bulk or surface sensitivity. This is done by stepping though the critical angle of total external reflection.

References
Resolving the Nature of SMSI among Au-CoOx Model Catalyst

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Bicomponent heterogeneous catalysts, often composed of noble metals (NMs) supported on transition metal oxides (TMOs), attract much interest due to their prominent performance in catalytic processes. Results from Prof. Gabor Somorjai’s group [1] demonstrate a 500-fold higher reactivity of catalytic CO oxidation over Pt/CoOx catalysts than other oxide supported Pt nanoparticles (Fig.1, left). Typically, prior to catalytic reaction, pre-treatment under H2 atmosphere at 573 K is conducted, which produces metallic Pt and a partially reduced CoO substrate. More importantly, oxide moieties originating from the support further migrate over the metallic nanoparticles, and can totally cover the underlying NM. This newly-formed catalyst is known as the inverse catalyst, and hints at the atomic scale nature of active sites which can exhibit the so-called strong metal-support interactions (SMSI).

Herein, employing ambient pressure X-ray photoelectron spectroscopy (AP-XPS) on CoO/Au(111) model catalysts, we observed: (1) CoOx of monolayer thickness wetting onto Au(111) substrate after metallic bilayer Co island exposed to O2; (2) Reversible adsorption of CO on partially oxidized CoO (Fig.1, right); (3) Reduction of CoO after annealing in CO atmosphere. Due to the charge transfer between ultrathin CoO and electronegative Au substrate, the Co(II) atoms in direct contact with Au support have an unique electronic structures and we believe are responsible for the observed reactivity of the supported monolayer CoOx layer. We are currently pursuing investigations using ambient pressure scanning tunneling microscopy (AP-STM) and theoretical calculations to achieve more fundamental insights of SMSI effects at the atomic scale on CoO/Au(111) model systems.

Fig.1 (left) Performance test of oxide supported Pt nanoparticles towards CO oxidation; (right) C1s XP spectra of partially oxidized CoOx /Au(111) after being exposed at room-temperature to CO (bottom) and subsequent pumping to UHV (upper).

References
Pressure hopping: Investigating CO and CO\textsubscript{2} hydrogenation on Rh in the borderlands between \textit{operando} and \textit{post-mortem}

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Catalytic reactions have to be probed by XPS in one of two ways. One can either perform the spectroscopy under reaction conditions (\textit{operando}) or in vacuum after exposure to the reaction conditions (\textit{post-mortem}). But do we really have to choose?

Thanks to the small volume of the virtual pressure cell of the POLARIS instrument\textsuperscript{[1]} - situated at beamline P22, DESY, Hamburg – we can rapidly change the pressure from 1700 mbar (a regime where no photoelectrons gets through the gas phase) down to 200-300 mbar (which are measurable reaction conditions for the set-up). The hypothesis is that a remnant of the high pressure surface after the drop could be acquired by XPS if the acquisition is fast enough. We have used this approach in order to study lingering C 1s adsorbates of high-pressure reaction conditions immediately after a pressure jump. The investigated chemical systems are the CO\textsubscript{2} and CO hydrogenation reactions on Rh(211) and we have compared the results to previous studies of the pure \textit{operando} studies undertaken at 150 mbar static pressure.

In the CO\textsubscript{2} hydrogenation reaction, the system reverses back to the original surface after each jump and reveals small but significant impact on the hydrocarbon peak, the pressure induced changes to the surface are seemingly gone within 5 minutes after the jump. This is the case up until 2000 mbar which is the highest pressure we could investigate.

The results on CO hydrogenation on the other hand indicate a dramatic pressure impact on the CO hydrogenation reaction. The attached figure displays the dynamic response of the hydrocarbon peak to pressure changes at time-frames even minutes after the jump. The coverage of hydrocarbons undergoes complex changes after each jump – even after an apparent saturation coverage is reached.

![Graph showing XP intensity of C 1s adsorbates as a function of time, during pressure jumps between 1700 and 300 mbar of a H\textsubscript{2} and CO mixture. T=350 °C.]

References

Oxidation of amorphous metal alloy surfaces studied using ambient pressure X-ray photoelectron spectroscopy

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Amorphous metal thin films (AMTFs) are of increasing interest due to their unique mechanical properties and chemical stability. AMTFs have an advantage over polycrystalline metal films due to the lack of grain boundaries which gives added durability and smoother surfaces. For this reason, AMTFs have been investigated for a wide range of applications such as protective layers in microelectromechanical systems, coatings for biomedical tools, and as metal-insulator-metal tunnel diode electrodes. However, AMTFs are known to be structurally and chemically unstable at higher temperatures.

The present study is focused on the characterization of the thermal and chemical stability of a ternary AMTF with the composition Ta\textsubscript{54}W\textsubscript{27}Si\textsubscript{19}. We have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to track the surface composition and oxidation states of the growing oxide layer \textit{in situ} as the AMTFs are heated to varying temperatures and O\textsubscript{2} partial pressures. Typical experiments were performed at 1 mbar O\textsubscript{2} partial pressure with temperatures ranging from 25 to 300° C. AP-XPS data have been obtained at relatively short time intervals to track reaction kinetics, and the resulting spectra were modeled using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. This analysis allows determination of oxide growth rates and oxide compositions. Experiments were also performed on elemental Ta, W, and Si, and the results are compared to the AMTF. An example of how the oxide composition changes during time is shown in the figure. AP-XPS results indicate that Ta in TaWSi films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta\textsubscript{2}O\textsubscript{5}) layer on the surface. Large differences were observed for the rate of oxidation for the pure elements and those in the AMTF. An overview of the results, including apparent energies for oxidation will be presented.

AP-XPS results indicating the oxide composition for TaWSi alloy and pure elements for oxidations at T = 300 °C and P\textsubscript{O\textsubscript{2}} = 1 mbar versus time, where 0 = no oxidation and 1 = full oxidation.
In-situ evolution of structure and chemical state during nanoparticle exsolution from perovskite hosts by reduction in H₂

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Nanoparticle catalysts supported on transition metal oxides play a critical role in chemical production, and energy conversion and storage processes. Catalytic activity is affected by nanoparticles’ composition, size, structure, stability, and their interaction with the support. Decreasing nanoparticle size increases their specific surface area and the density of low-coordination sites, often increasing activity. However, nanoparticle coarsening, agglomeration, and coking can decrease the activity through structural transformations and decreases in available active sites.

Recently, nanoparticle exsolution from perovskite hosts during reducing treatments has produced socketed nanoparticles with excellent stability and coking resistance, and tunable size and distribution.[¹] While these exsolved nanoparticles present deactivation resistance, exsolution of lattice constituents can generate instability in the parent material, and some nanoparticle material can remain embedded in the perovskite host rather than migrating to the surface, thus becoming inactive.

To understand and address these issues, we used a recently developed combination of Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS), and Ambient Pressure Grazing Incidence X-ray Scattering (AP-GIXS)[²] to monitor the chemical and structural evolution of Ni nanoparticles exsolved from SrTi₀.₉Nb₀.₀₅Ni₀.₀₅O₃₋δ(STNNi) films through the exsolution process in an H₂ gas environment. Ni is reduced as it migrates to the surface to form nanoparticles, while Sr and Ti retain their oxidation states. At the same time, the initial surface structure evolves as the nanoparticles nucleate and grow. Because both techniques possess tunable depth sensitivity, this approach is well suited to further studies of surface and subsurface chemical and structural evolution of these and other catalyst systems.

References
Using Ambient Pressure XPS to study ALD in real-time

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Atomic Layer Deposition (ALD) is a technique for growing highly uniform and conformal layers of material with very accurate precision. The advantages of the technique originate from the self-limiting manner in which the individual atomic layers grow. There is an increasing need for detailed understanding of the chemical nature of the layer growth. Over the years, several experimental techniques have been devoted to measuring the created surfaces before and after the growth, but not many techniques are capable of resolving detailed chemical changes on the surface during the deposition process. Ambient pressure X-ray photoelectron spectroscopy (APXPS) has recently been utilized as a powerful tool for studying ALD-related surfaces in reaction-relevant pressure and temperature conditions. We have developed an ambient pressure (AP) cell, which is dedicated for ALD research. The cell allows to study the surface of a substrate where ALD reactions take place, thereby opening up the possibility for acquiring information of the surface chemistry in real-time as the ALD precursor molecules react with the surface. These experiments have gained noticeable traction in the past few years [1,2].

The system is installed on the SPECIES beamline [3] at the MAX IV Laboratory in Lund, Sweden. SPECIES is a soft X-ray beamline with one branch dedicated for APXPS. The beamline offers a wide photon energy range of 30-1500 eV, which enables studying the core-levels of most elements using XPS but also facilitates access to valence band measurements using lower energies towards the VUV range.

The ALD cell has been designed with realistic precursor gas flow dynamics in mind and the cell can be operated with a maximum pressure of 20 mbar. The inlet pipes are placed very close to the sample surface, thereby ideally creating a laminar-like flow across the surface of the substrate. The reaction products can be also measured using mass spectrometry: both the outlet line of the cell and the pre-lense of the analyser house mass spectrometers for monitoring ALD reaction products that can be later correlated to the XPS measurement, allowing to correlate the appearance of certain gas phase precursor ligands with reactions on the surface.

Here, we give a brief overview of the system including its design and operating parameters. Some results from example experiments are given, which demonstrate the capabilities of the ALD cell.

Anodized aluminium as a model catalyst support material in the complete oxidation of methane

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Natural gas can provide a greener alternative to traditional fuels, but the persistence of unburnt potent greenhouse gas methane in exhaust feeds is a significant issue. Exhaust catalysts for methane conversion often comprise of palladium on alumina, or other oxide supports. Near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) provides insight into surface chemistry under reaction conditions. Insulating materials, including many metal oxide supports, undergo “charging” under the x-ray beam, making data collection and analysis more complicated. [1]

Thin layers of alumina have been developed using an electrochemical method, wherein the top few nanometers of an aluminium foil are oxidized. This provides a thin layer of the desired alumina support, which does not show any significant charging behaviour under NAP-XPS measurements (Fig 1). Deposition of palladium and subsequent NAP-XPS experiments in methane oxidation conditions showed that the support material was stable up to 450 °C. The palladium particles on the support surface behaved broadly like those on conventional powder supports, with dynamic redox behaviour related to the reaction condition (Fig 2).

Palladium was more readily oxidized at lower temperatures in dry conditions, but generally reduced again at higher temperatures (300 °C and above), as shown in Fig 2. In contrast, Pd continued to oxidize under wet conditions up to the maximum test temperature (450 °C). Wet conditions also allowed Pd to be more oxidized, with a maximum of 76% Pd(II) compared to 50% in dry conditions. Higher doses of Pd produced larger particles, which were more resistant to oxidation in both dry and wet conditions.

This work has shown anodization to be a reliable way of producing thin, stable, x-ray spectroscopy-friendly alumina substrates, which are suitable as model catalyst supports for oxidation reactions.

References
Single crystalline Co(0001) Fischer-Tropsch observations at 550mbar (and above) using a virtual cell approach and hard X-rays

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Catalytical reactions are both societally important and difficult topics for fundamental research. The importance can be easily demonstrated by recalling the numerous products (fertilizer, fuels, plastics …). especially in combination with the need to move towards a CO2 neutral procedures long standing paradigms need to be challenged. Fischer-Tropsch reactions in particular can be run to produce very different product distributions, adding another layer of complexity.

Despite knowing that this catalytic reaction exists, available literature detailing the debated reaction mechanisms is lacking[1, 2]. Indeed, only indirect measurements (e.g. by QMS), observations far away from reaction conditions (XPS < ~10mbar) or after the reaction can be found. As seen by many publications XPS can address the reaction mechanisms in question. However, combining ultra-high vacuum (UHV), as it is required to transfer photoelectrons without scattering and high pressures (above 1 bar), as it is required for the catalytic reaction, has posed significant technical challenges and caused the pressure gap above the ~10mbar range.

The POLARIS setup (Stockholm University) is in operation at P22, PETRA III [3] and can readily be employed above this pressure gap by utilizing a virtual cell concept. Here we set out with the goal of observing the FT reaction at pressures as close as possible to the pressures applied in industrial catalysis and compare isobars at 150, 550 and 1000 mbar. Onto the single crystalline cobalt we direct mixtures of CO:H2, CO2:H2 and CO:CO2:H2. We obtain Co2p, C1s and O1s core level spectra and quantify the adsorbed species under these conditions. Our results reflect recently published results from operando STM[4] and show significant differences to findings from post-reaction XPS[5].

References
In situ study of alloy degradation in high temperature CO₂

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Understanding the degradation of structural materials in high temperature gases is an important problem in the power generation, aerospace, chemical, and other industries. Material failures caused, for example, by excessive oxidation (gas-phase corrosion) of an alloy are often dangerous and costly. The high temperature corrosion community has studied these problems extensively since the early 20th century, resulting in a rich understanding of the thermodynamic and kinetic factors influencing degradation as a function of alloy composition, gas composition, temperature, etc. However, one limitation that has partially hindered understanding has been the ex situ nature of the analysis. That is, researchers apply microscopic and/or spectroscopic techniques to characterize the oxidized surface, after the reaction has occurred. While this certainly offers a wealth of information, some mechanistic details simply cannot be revealed in this way. AP-XPS in combination with sample heating offers the opportunity to bridge this gap—particularly for understanding chemical processes at the oxide/gas interface. Herein we describe results of the degradation of alloys in high temperature CO₂ to inform materials selection for next-generation supercritical CO₂ power plants. Model Fe-Cr and Fe-Ni-Cr alloys were analyzed by AP-XPS in flowing CO₂ at pressures of 0.1-1 mbar and temperatures from 20 to 530 °C. Combined with post-exposure TEM and APT, the study revealed important details about the oxidation and carburization mechanisms beginning at the very first stages of exposure [1]. The results are discussed with an emphasis on the information revealed by AP-XPS that was inaccessible by other techniques. An outlook is provided on the potential of AP-XPS to study important problems in the high temperature corrosion community.

References
Tailoring of Catalyst Surfaces for Energy Conversion – In-situ Studies of Electrochemical driven Nanoparticle Exsolution

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In heterogeneous catalysis surfaces decorated with uniformly dispersed, catalytically highly active (nano)particles are a key requirement for excellent performance. We present here an innovative, time efficient route to obtain and tailor the formation of nanoparticles on the catalyst surface directly during reaction by combining catalysis and electrochemistry. Perovskite-type catalysts can incorporate catalytically highly active guest elements as dopants. When applying reductive conditions (gas atmosphere or applied electric potential) these dopants emerge from the oxide lattice to form catalytically active nanoparticles on the surface (by exsolution), causing a strong enhancement of catalytic reactivity [1].

For the newly synthesized perovskite materials Nd₀.₆Ca₀.₄Fe₀.₉Co₀.₁O₃₋δ, we show by in-situ near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) combined with electrochemical impedance spectroscopy (EIS) how we can control the formation of catalytically active nanoparticles on the surface. With Scanning Electron Microscopy (SEM) the size of the formed particles could be determined. The crucial factor to trigger exsolution is the oxygen partial pressure (pO₂), which can be adjusted and controlled either by the reaction environment or by the applied electrochemical potential. For reverse water gas shift reaction (rWGS) the formed nanoparticles are strongly enhancing the catalytic activity [2].

Figure 1: Nanoparticle exsolution can be either achieved by reducing reaction conditions or by applying polarization as driving force.

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References

APXPS investigation of atomic layer deposition of HfO$_2$ on SiO$_2$: evidence for a bimolecular reaction mechanism in the initial metal half-cycle

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Atomic layer deposition (ALD) [1] is among the most important methods for thin film growth [2], in semiconductor device technology and increasingly also for, e.g., solar energy conversion, catalysis and energy storage materials. Ideal ALD processes exhibit excellent dimension control in the direction perpendicular to the surface onto which the thin film is deposited. The high degree of control derives from a well-defined surface chemistry based on the saturative adsorption and reaction of the ALD precursors. Real ALD processes deviate, however, from the idealised reaction mechanisms [3,4]. This results in deviation from ideal film growth and loss of deposition control. Detailed insight into ALD reaction mechanisms is necessary for a knowledge-based improvement of ALD processes and improved ALD materials. In situ and operando characterization during thin film deposition can contribute greatly to the development of such a proper understanding of ALD [5-7]. Here, we used a combination of ambient pressure x-ray photoelectron spectroscopy (APXPS) and density functional theory (DFT) to study the ALD of HfO$_2$ on a SiO$_2$ surface from tetrakis(dimethylamido) hafnium (TDMAHf) and water.

The APXPS and DFT results provide evidence for a bimolecular surface reaction mechanism in the initial half-cycle of ALD. This bimolecular mechanism proceeds via a $\beta$-hydride elimination reaction between two neighbouring, surface-adsorbed TDMAHf complexes. Without this intermolecular interaction any conceivable surface chemical reaction mechanism is so endothermic that it does not proceed under standard reaction conditions. Surface hydroxyls are found not to play any role in the initial surface chemistry of the TDMAHf ALD on SiO$_2$; indeed, our results provide a straightforward explanation of why the process is possible on hydroxyl-free surfaces, even though standard ligand exchange reaction models of transition metal amido complex ALD require the presence of hydroxyls. The APXPS and DFT results provide detailed insight also into the chemistry of subsequent half-cycles.

References
(RT-14) Pre-Recorded Contributed Talk 14

Subsurface oxygen in oxide derived Cu catalyst for CO₂ reduction

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CO₂ reduction reactions attract lots of interest thanks to their potential of turning CO₂ from greenhouse pollutant into feedstock for base chemicals and fuels. Copper is the only transition metal that is capable of converting CO₂ into, e.g., higher alcohols.[1] Oxide-derived copper (OD-Cu), prepared from an oxidation and reduction cycle of copper, has shown to boost the activity and selectivity towards multi-carbon products.[2] However, the detailed mechanism is still not understood. Subsurface oxygen near the surface may play an important role. It has been hypothesized that if subsurface oxygen is present, it mitigates the σ-repulsion of Cu for CO intermediates. However, the presence of such oxygen species is under debate.[3]

Following the preparation of OD-Cu inside the POLARIS instrument[4], the oxygen species in the OD-Cu was studied using hard X-ray photoelectron spectroscopy (HAXPES) with grazing incidence and normal emission geometry. Photons on the energy range between 3266 eV and 9030 eV were delivered by beamline P22[5] at Petra III, DESY, Germany. This enables non-destructive depth-profiling of oxygen species in the OD-Cu specimen.

The HAXPES depth-profiling reveals the existence of two subsurface oxygen species with different distributions within the OD-Cu. These are identified as interstitial oxygen in the copper lattice (O_{int}) and oxygen in copper vacancy and lattice defect sites (O_{Cu, vac}). Here, details on the interpretation of oxygen distribution within the Cu will be presented and a conclusion be drawn on the existence of subsurface oxygen; that has previously been reported not being stable in the surface-most region.[3b]. The presence of oxygen in copper vacancies and lattice defects close to the surface gives support to the hypothesis that the enhanced reactivity towards CO₂ reduction on OD-Cu is caused by subsurface oxygen, which mitigates the σ-repulsion of Cu for CO intermediates, providing important information about the mechanistic understanding of the process.

References
Quantification and reporting of XPS data taken under Near Ambient Pressure conditions – chances and challenges in acquisition speed, beam damage, sensitivity, reliability, reproducibility and repeatability

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Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.
Lab-Based NAP-XPS at the Lehigh University Materials Characterization Facility

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Lehigh University’s custom-built SPECS NAP-XPS system has opened the door for quick and simple XPS measurements at pressures up to 10 mbar and temperatures between –40°C and 600°C. Utilizing a small environmental cell, we are able to quickly switch between gas flow conditions. In its first two years of operation, this instrument has found uses in the fields of catalysis, thin film characterization, glass science, and many others.

As lab-based NAP-XPS is still in its infancy, these early projects have required the concurrent development of best practices for sample mounting, charge neutralization, temperature control, and data interpretation. In particular, the quantification of XPS data becomes much more complex under NAP conditions due to the dependence of photoelectron attenuation on gas composition, temperature, and analyzer settings. Empirical instrument sensitivity factors have been calculated for several such permutations, but a more complete analysis is currently underway.

This talk will discuss the practical considerations of a multi-user lab-based NAP-XPS instrument and highlight a few of the ongoing projects that have benefited from it.
In situ analysis of a Pt thin film H₂ gas sensor surface by AP-XPS

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Recently, a Pt thin-film sensor has been developed, which can detect H₂ gas in air or exhaled air with high sensitivity [1]. When H₂ molecules are adsorbed on the Pt surface, the chemical state (oxidation/reduction state) and structure of the surface are assumed to change, but the behavior of the sensor surface under operating conditions has not been fully understood, yet. In this study, we performed in situ analysis of the Pt sensor surface in the presence of H₂ gas using a combination of AP-XPS and electronic resistivity measurements.

AP-XPS measurements were performed at BL-13B of the Photon Factory (PF), Japan [2]. The X-ray energy was set to 150 eV and 630 eV for Pt 4f and O 1s core-levels, respectively. The H₂ gas was exposed to the surface up to 0.1 Torr. To measure the change in resistivity (∆R/R) with exposing H₂ gas, a voltage of 0.1 V was applied to the sensor surface using a source meter.

From the resistivity measurement, it was found that the resistivity decreased to -2.6% in H₂ gas ambient. It guarantees the Pt surface works as a H₂ gas sensor. Fig. 1 shows Pt 4f7/2 XPS from the Pt thin-film sensor with and without H₂ gas. The two components are assigned as Pt bulk and surface Pt bonding with H (Pt_{bulk}/Pt-H), and Pt oxide (Pt-O), respectively. Exposing H₂ gas to the surface, the peak intensity of Pt oxide decreased. It indicates that the Pt surface changes from an oxidized state to a metallic state during sensor operation. The O 1s XPS also showed a decrease of the Pt oxide. In-situ analysis combined with surface analysis and resistivity measurement revealed that the chemical state change of the Pt surface due to H₂ gas is correlated with the sensor property.

Fig. 1 Pt 4f7/2 XPS taken from a Pt thin-film sensor with and without H₂ gas.

References
Electrode-Electrolyte Interface Sensitivity in soft X-ray absorption spectroscopy via electron/ion yield
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Obtaining chemical information on solid-liquid interfaces is crucial to understand important processes, such as corrosion and electrochemistry. Unfortunately, very few techniques can give this information under in situ conditions.

Several years ago, soft X-ray absorption spectroscopy (XAS) was used to probe the Au-electrolyte interface [1]. In these measurements, the X-ray absorption was measured via the sample drain current. Resembling the total-electron yield XAS of solid samples in vacuum, surface sensitivity was assumed. The sample of interest was deposited onto a SiNx membrane thin (ca. 100 nm) enough to be X-ray transparent (Fig 1).

However, more recently a similar measurement mode was introduced, labelled as “total-ion yield”. It was claimed to be sensitive to the bulk of the liquid [2].

In this work[3], the TiO2-electrolyte interface is probed via both total-electron-yield and total-ion-yield configurations. The TiO2 was deposited using atomic layer deposition, giving precise control over its thickness (6 nm). Both the total-electron and total-ion yield give essentially the same information, and both are interface sensitive (order of a few nanometers), contrasting previous claims that total-ion-yield measurements are bulk sensitive [2]. This is clearly visible after comparing the O K edge spectra of TiO2 in H2O (Fig 2a) with that of TiO2 in vacuum (Fig 2b). In the former, the spectral features of oxidic O are dominated over those from H2O. These findings are the first hard proof of surface sensitivity and convincingly show the potential of this technique to gain in situ understanding of fuel cells, batteries, and electrocatalysts.

References
(RT-19) Pre-Recorded Contributed Talk 19

Understanding the gas sensing mechanisms by NAP-XPS

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In this study, we would like to present an application of laboratory-based near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) for in-situ/operando investigation of gas sensing mechanisms of a spectrum of different sensing materials. Simple gas sensors were realized by depositing a sensing material on a special sensor platform with electrical contacts and investigated in-situ under exposure to the reactive atmosphere at elevated temperatures employing NAP-XPS. The equipment allowed us to follow the resistivity of the sensing layer simultaneously with NAP-XPS measurements during the gases exposure. With the new methodology, we examined the ethanol sensing mechanism of some popular metal oxide chemiresistors, such as nanostructured SnO₂ and ZnO layers. Also, the ethanol and nitrogen dioxide sensing mechanisms of more specific Cu₂O nanowire-based and Zn-Phthalocyanine-based gas sensors were studied. Photoelectron spectroscopy analysis of the chemical processes on the surface of the layers during exposure to analytes allowed us to obtain new valuable information about the sensory properties of the studied materials.

References
Spectroscopic Insights to Pt-, Pd- and Rh-Ga Alloys as Models for SCALMS Catalysts during Oxidation

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Palladium, Rhodium and Platinum become very active, selective and stable catalysts for the dehydrogenation of short alkanes such as butane and propane when incorporated in a matrix of liquid gallium on oxidic support particles. This catalytic concept was pioneered at FAU and is termed SCALMS, for supported catalytically active liquid metal solutions.\cite{1} The remarkable properties of these catalysts are attested to the atomic dispersion of the active transition metal in liquid gallium nano-droplets and the dynamics at the liquid metal/gas interface. Our research focusses on the composition of the liquid metal/gas interface with the aid of model systems such as macroscopic alloys and PVD prepared supported particles. Temperature dependend XPS studies allowed us to link changes in the reactivity of the catalyst to the dissolution/precipitation of intermetallic transition metal-Gallium phases, leading to transition metal enrichment/depletion of the liquid Ga phase.\cite{3} The reaction of the Ga-transition metal system to oxygen is of special interest since Ga and its alloys are highly prone towards forming oxides.\cite{3,4} For real world application, oxidation, due to handling in air or possible traces of oxygen in the feedstock, is almost unavoidable. We present \textit{in situ} oxidation studies for macroscopic Pt-Ga, Pd-Ga and Rh-Ga alloy droplets with different phase compositions. Interestingly, these systems show different oxidation behaviors despite their chemical similarity. For further insights, we investigated Rh-Ga nanoparticle systems utilizing synchrotron based XPS and high-resolution temperature dependent transmission electron microscopy. Based on these experiments, ab initio molecular dynamics simulations and density functional theory calculations were performed.

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\end{itemize}
Operando Probing of the Energetics of Protective Coating for Solar Fuels Production

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Stabilization coatings are essential to tuning the energetics, kinetics, and selectivity of photocatalytic liquid junctions. Narrow bandgap semiconductors can be protected by conductive coatings, consisting of tunable intermediate bands (IBs). This combination presents stability and efficiency for (photo)electrochemical and photocatalytic reactions. Investigation on the energetics at the coating/liquid junction, namely potentiostatic and redox potential dependent band edge shifting behavior, is crucial for understanding how this new class of material works under operating conditions. Understandings on how to manipulate these bands enable design strategies for photoabsorber-coating combinations to make novel photocatalysts for various desirable solar fuel reactions, including hydrogen evolution, CO₂ reduction, and N₂ reduction. In this talk, we present our strategies of using lab-scale near ambient pressure x-ray photoelectron spectroscopy (APXPS) to perform in situ/operando measurements on the energetics of the coating/liquid junction, therefore elucidate the working principles of efficient and selective coating materials. We first show our liquid cell designs tailored for coatings grown by atomic layer deposition (ALD). We then present preliminary results of testings on the liquid cell and show its ability to measure the solid-liquid interface. Furthermore, we present a COMSOL Multiphysics model which simulates the energetics of coatings and their IBs and corroborate the APXPS results. Finally, we propose future experiments to finally achieve in situ/operando measurements of ALD grown coatings and their energetics at solid-liquid interface.

References
Water adsorption behavior on anatase TiO$_2$ (111) utilizing Near Ambient Pressure XPS

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Because of its wide applications in heterogeneous catalysis, photocatalysis, and photoelectrocatalyst, TiO$_2$ is an extensively investigated material [1]. Especially, the water adsorption behavior on TiO$_2$ has been studied because the surface cannot avoid the moisture environment in these applications. Many researchers have focused on anatase (101) and (001) surface because they show stability and activity [2]. In contrast, it is unfavored by nature to prepare {111} facet structure on anatase TiO$_2$ nanoparticles due to much higher surface energy compared to other low-index facets [3], which is why adsorption behavior of reactants on {111} facets have not been studied well so far [4]. However, in 2013, it was reported that it is possible to – prepare a stable anatase {111} facet structure with a special method [5]. Near ambient-pressure X-ray photoelectron spectrosocopy (NAP-XPS) is a powerful technique to investigate not only the adsorbent features but also the surface chemical states [6].

In this study, the water adsorption behavior on the stoichiometric and sputtered surfaces of natural anatase TiO$_2$ single crystal as cutted (111) direction was studied by utilizing NAP-XPS. At relative humidity (RH) ~ 10% (P = 2.5 mbar of water at 300 K), the stoichiometric (nearly defect-free) surface and the sputtered (artificial defect) surface had different surface states. Oxygen-containing carbons (C-O, C=O, O-C-O, and etc) accompanying water exposure for NAP-XPS standard experiment are not adsorbed on the sputtered surface, whereas adsorbed on the stoichiometric surface. This can be explained by the adsorption mechanism of oxygen-containing carbon, i.e. bidentate bonding. These results suggest that artificial defects may play an important role in designing strong TiO$_2$ from carbon contamination.

References
Surface Reconstruction in In$_2$O$_3$/$m$-ZrO$_2$ Catalyzed CO$_2$ Hydrogenation

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Carbon dioxide hydrogenation reaction (CO$_2$HR) to form transportable liquid fuels such as methanol represents a promising way to mitigate the emission of a major greenhouse gas and to generate valuable energy carriers [1-3]. Recently, In$_2$O$_3$-based catalysts have been recognized as highly active and selective with practical prospect for methanol synthesis via direct CO$_2$ hydrogenation. Ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be an excellent tool to investigate the surface chemical and electronic properties of heterogeneous catalysis and is here combined with information from practical catalysis, TPR, TEM, XRD, TPD etc. The chemical and structural dynamics at the interface of In$_2$O$_3$/$m$-ZrO$_2$ and their consequences on CO$_2$ hydrogenation reaction (CO$_2$HR) before, during and after reaction conditions were investigated. We found that, under catalytically relevant conditions (523 - 673 K), bare In$_2$O$_3$ can be largely reduced and form an (In metal + InO$_x$)/In$_2$O$_3$ (0 < x < 1.5) core-shell structure. When loaded onto a semiconducting/insulating support, the In$_2$O$_3$ domains were progressively reduced and formed InO$_x$ at the topmost region under elevated temperatures (523 K - 673 K), but with less tendency to form metallic In, a primary surface species that leads to catalyst deactivation. The high dispersity of In$_2$O$_3$ nanostructures onto $m$-ZrO$_2$ prevents their over-reduction under catalytically relevant conditions, when bare In$_2$O$_3$ is unavoidably reduced into metallic phase (In$^0$). Therefore, $m$-ZrO$_2$ serves as a chemical and structural modifier of In$_2$O$_3$ that directly governs the outcome of the CO$_2$HR. Our findings on the large-scale surface reconstructions, support effect, and the reaction mechanism of In$_2$O$_3$/$m$-ZrO$_2$ for CO$_2$HR may apply to other related metal oxide-catalyzed CO$_2$ reduction reactions.

References


(PP-01) Poster Presentation 1

The In Situ Spectroscopy beamline at the Swiss light source

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This poster will describe the In Situ Spectroscopy beamline at the Swiss light source. Since 2012, the beginning of ambient pressure photoelectron spectroscopy development at the Swiss light source synchrotron (Paul Scherrer Institute, Switzerland), there have been several advancements of the project. The endstation, which adopts a modular design consisting of a Scienta R4000 HiPP-2 electron analyzer equipped with interchangeable analysis chambers, is now permanently connected to the X07DB site and, as a beamline, is open to external users. The photon source is a bending magnet, and the available photon energy range goes from 350 to 1500 eV. The following reaction chambers are offered to users:

- solid-gas interface chamber [1,2]. Such a module has a small analysis cell (ca. 150 cc) adopting a flow tube configuration. Once introduced in the cell, samples (foils, drop-cast powders, pellets) can be scanned in situ (check for beam-induced effects). Two manipulator inserts, allowing either high temperature (room temperature – 870 K) or low temperature (170 K – room temperature) experiments are available. Gases can be dosed either in static configuration or in flow mode. Thanks to the small volume of the cell and the flow configuration, transient experiments are possible. Photoemission peaks can be acquired while a gas/gas mixture is modified (time resolution down to the second). Such a setup is suited for catalysis and environmental chemistry measurements.

- solid-liquid interface chamber [3]. Such a module consists of a preparation and an analysis chamber connected by means of a transfer chamber. The former offers the possibility of in situ sample preparation (sputtering/annealing, molecular beam epitaxy, low energy electron diffraction-Auger). The latter offers the possibility to investigate both the solid-gas interface (chamber backfilling) and the solid-liquid interface (dip&pull method). Due to the available energy range, only ex situ experiments concerning the solid-liquid interface are possible.

References
APXPS investigation of photocatalytic nitrogen reduction reaction in Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$: the critical role played by oxygen vacancy

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The photocatalytic nitrogen reduction plays a critically important role in realizing the artificial synthesis of ammonia in sustainable energy economy. Compared with the traditional industrial ammonia production via the Haber process, the photocatalytic method offers an attractive alternative of low energy consumption and low emission of carbon dioxide. However, the hurdle of low conversion efficiency needs to be crossed. A series of bismuth oxyhalide compounds (Bi$_x$O$_y$X$_z$, X = Cl, Br, I) have been reported to exhibit high yield in photocatalytic reduction of nitrogen. The high yield is attributed to readily available oxygen vacancies in the materials that in turn enhance the nitrogen adsorption and activate the nitrogen molecules, leading to an increasing ammonia production rate. In this study, the ambient pressure X-ray photoelectron spectroscopy (APXPS), capable of identifying surface species present at close to real reaction condition, has been used to assess the influence of oxygen vacancies present on the Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$ on NRR, to track the evolution of surface reaction intermediates, and to delineate the reaction mechanism of NRR. APXPS O 1s data offer clear evidence of oxygen vacancies creation via visible light illumination. A concomitant enhancement of molecular nitrogen adsorption on Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$ surface is also concluded from APXPS N 1s data. In addition, after the speciation of reaction intermediates on the surface of Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$, one can conclude that the reaction mechanism of NRR on Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$ is likely to follow the associative alternating pathway.

![Fig. 1 Schematic diagram of NRR on Bi$_5$O$_7$Br$_{0.5}$I$_{0.5}$](image)
An in situ APXPS characterization of Al$_2$O$_3$ supported NiMo catalyst

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Renewable feedstocks are an important element in a green economy, as they have the potential to replace fossil fuels in the future. But the conversion of biomass to renewable fuels remains a challenge. The natural polymer lignin is believed to have considerable potential as a renewable feedstock. Lignin can be converted to high quality renewable fuels via catalytic hydrotreatment over NiMo catalysts [1]. The development of future NiMo catalysts benefit from an understanding of the underlying reaction mechanisms of lignin conversion. However, details of these mechanisms are currently unknown and remain difficult to explore.

To gain a better understanding of the behavior of NiMo catalysts, we investigate the H$_2$-interaction of Al$_2$O$_3$ supported NiMo catalysts under in situ conditions using ambient pressure photoelectron spectroscopy (APXPS). We present APXPS measurement from the Hippie beamline at MAX IV comparing Al$_2$O$_3$ supported NiMo catalysts with model systems of these catalysts such as Ni- and Mo-foil. The measurements indicate that Al$_2$O$_3$ support has a strong influence on the reduction of Ni and Mo and that Ni and Mo facilitate each other’s reduction.

Figure 1: Ni 2p and Mo 3d APXPS spectra of Al$_2$O$_3$ supported and unsupported NiMo catalysts in 1 mbar H$_2$ at 200 °C, 400 °C and 600 °C.

References
(PP-05) Poster Presentation 5

Unveiling the active oxygen species in ethylene epoxidation over silver by ambient pressure X-ray photoelectron spectroscopy

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The ethylene epoxidation (EPO) is one of the most important industrial catalytic reactions and silver-based catalysts have outstanding activities and selectivities in this reaction. It has been widely proven that surface oxygen species participate in the catalytic cycle and their property is a key factor in the selectivity of EPO. Silver-based model catalysts (foils, powder, single crystals) have been extensively used to investigate the fundamental steps of EPO. Such a knowledge can be extended to actual catalysts, helping to understand reaction mechanisms and to improve the materials. In the current work, silver foil was fully characterized as the starting step of a project aiming at the investigation of industrial catalysts, and extending to the chemical looping process. Ambient pressure X-ray photoelectron spectroscopy was used to investigate the effects of temperature and gas environment under both steady state and transient condition experiments. Surface active species evolve as a function of the reaction conditions. The key role of electrophilic oxygen species is revealed over silver foil during the EPO process.

References
Mo oxide catalysts provide a viable approach for enhancing reactivity and selectivity of biofuel production from biomass.\cite{1} It has been found that the addition of Ni further improves the performance of catalysts in the hydrodeoxygenation (HDO) reaction of anisole, a model compound for lignin biomass;\cite{2} however, an in-depth understanding of the role of Ni or Mo is unclear in the industrially used nickel molybdenum oxide catalysts. Three oxide catalysts, including Ni only, Mo only, and combined nickel molybdenum catalysts were characterized using in situ infrared (IR) spectroscopy to give a direct comparison of surface species and chemical behavior upon dosing anisole from room temperature to 350 °C. In addition, the oxidation status of the catalysts was studied under HDO reaction conditions via ambient pressure X-ray photoelectron spectroscopy (APXPS). Ni only catalyst featured a different pathway of anisole adsorption at room temperature, while Mo only and NiMo catalysts showed similar behaviors. The sharp feature of a new methyl group at 1398 cm\(^{-1}\) along with changes and shifts of C-C stretching peaks in 1480-1600 cm\(^{-1}\) in the IR data was observed at high temperatures on Mo only and nickel molybdenum catalysts, indicating the formation of new aromatics with a directly attached methyl group. The IR data show significant interactions between anisole and Mo, while the formation of Mo\(^{4+}\) and Mo\(^{5+}\) are seen in the APXPS data, indicating the reduction of Mo\(^{6+}\) plays a key role in the catalysis. The combined results of in situ IR and APXPS characterizations of oxide catalysts during the HDO of anisole show that Mo reduction plays a primary role in the enhancement of the catalysis.

References
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Investigation of ball-milled Pd/CeO$_2$ catalysts under operando methane combustion conditions

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We have recently developed a novel Pd-CeO$_2$ catalyst synthesized by ball milling, which outperforms conventional Pd/CeO$_2$ catalysts by lowering the light-off temperature by more than 50 K and boosting the reaction rate [1,2]. This unprecedented activity was ascribed to a unique Pd-CeO$_2$ architecture created during the mechanochemical synthesis. In this work, we have investigated the chemical state of Pd and Ce after one combustion cycle up to 1173 K and monitored their evolution by near-ambient pressure X-ray photoelectron spectroscopy (AP-XPS) during methane complete combustion (CH$_4$/O$_2$=1/4, balanced in Ar).

After the TPC treatment at 1173 K, Pd 3d spectra (see Figure 1) revealed that Pd was fully oxidized and contained a mixture of Pd$^{2+}$ (48.2%) and Pd$^{4+}$ (51.7%) species. During reaction at 750 K, up to 39.7% Pd$^0$ species were formed and the concentration of Pd$^{2+}$ decreased to 32.4%, indicating a dynamic evolution of Pd species under reaction conditions. The oxidation at 750 K recovered the amount of Pd$^{2+}$, but it caused a reduction in the amount of Pd$^{4+}$ species (45.5%). Finally, under the presence of CH$_4$+Ar at the same temperature, the Pd$^0$ concentration reached 22.7%, accompanied by both Pd$^{2+}$ (44.4%) and Pd$^{4+}$ (33.0%), indicating that oxidized palladium species are stabilized on the ceria surface even under reducing conditions. Interestingly, in a recent theoretical study, it has been reported that the facile transition between metastable Pd$^{4+}$ and Pd$^{2+}$ ions inserted into the ceria lattice was key for an enhanced methane oxidation reactivity [3].

The presence of highly dynamic Pd$^0$/Pd$^{2+}$/Pd$^{4+}$ species was detected during the whole series of experiments on the ball-milled Pd-CeO$_2$ catalyst.

References
Exploring chemical/electronic change of environment of platinum atom on Pt$_3$M (M=Ti,V) alloy surface under oxidation process

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The surface chemical/electronic dynamics of Pt-based alloys, Pt$_3$M (M=V, Ti), are investigated with ambient pressure x-ray photoelectron spectroscopy (AP-XPS). After annealing under UHV condition, Pt$_3$V exhibits enrichment of Pt while Pt$_3$Ti shows mixed Pt and Ti atoms on the surface. As temperature increases, surface segregation and oxidation of the metal atoms take place under elevated pressure condition for CO oxidation, P(O$_2$) = 0.3 mbar and P(CO) = 0.03 mbar. Under ambient pressure condition, Pt skin surface in Pt$_3$V is no longer stable due to segregation of V atoms to the surface, displaying various forms of vanadium oxides on surface. In the case of Pt$_3$Ti, numerous forms of Ti oxides start to appear during oxidation process. In addition, as surface temperature increases, XP spectra of Pt 4f core level show increase in sign of metallic phase of Pt state for both alloy surfaces, suggesting the redistribution of charges of Pt to 3d transition metal and oxides.
Catalytic reactivity study on an atomically modified glassy carbon surface

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This research aims to develop the Fe-N-C single atom catalyst supported on Glassy carbon, which is promising cathode material of Proton exchange membrane fuel cell (PEMFC)\(^1,2\). We applied rather simple fabrication process and investigated the properties of the sample. Figure 1 shows the schematic diagram of the experimental procedures. First three inset figures show the fabrication processes that aim production of Fe-N-C single atom catalyst and the rest figures show the environments applied to the sample for studying oxygen reduction reaction (ORR) capability of the sample. Normally the ORR process around the cathode in PEMFC happens under acidic environment, which means that hydrogen ions reside already. Notifiable point in this research is that the sample produced water from mere mixture of hydrogen and oxygen gases while there is no stimulus, i.e. beam exposure, heat, and any electrical bias. In order to produce water in this circumstance, \(\text{H}_2\) molecules must be dissociated under the premise that Fe-N-C single atom catalysts have been made. As shown in figure 2, we observed the presence of peaks which have lower binding energy than 284 eV, and those are barely observed at regular C species. Some research teams reported that C vacancy in graphite structure can affect nearest neighbor carbons to have lower binding energy than general C peaks\(^3,4\). These carbons thought to be unstable or reactive are being considered as natural dissociation of the molecules.

References

Structure-activity evolution of platinum species supported on ceria during Water-Gas Shift Reaction

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Oxide-supported noble metal catalysts have been extensively studied for decades for the water-gas shift (WGS) reaction, a catalytic transformation central to several processes that utilize or produce hydrogen. Among those catalysts, Pt/CeO$_2$ is one of the most promising candidates for the WGS process. Discussions remain about the nature of the active species, whether they are atomically dispersed or nanoparticles, and their reactivity. The WGS environment lacks oxidants and it has long been reported that hydrogen or carbon monoxide can promote the re-agglomeration of atomically dispersed platinum. Recently, we have characterized Pt/CeO$_2$ atomically dispersed and nanoparticle catalysts by means of in situ XPS under WGS operating conditions. Ex situ activity test have been carried out under the same dilution conditions (mbar level). The atoms or nanoparticles of platinum gradually reduce in the WGS reaction environment, and cannot be re-oxidized after returning to the initial condition. This is consistent with the results of the activity test: used catalysts are more active than fresh ones. In addition, the surface hydroxyl and carbonate/carboxyl groups show opposite evolution, indicating their interconversion behavior during the reaction, thus revealing the reaction pathway of WGS.

References

Nature of surface space charge layer on *undoped* SrTiO$_3$ (001)

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Having ABO$_3$-type perovskite structure, SrTiO$_3$ has been a popular choice for many important heterostructure systems, *e.g.*, ferroelectric thin films and superlattices. As these exotic electronic phenomena are closely related to delicate electron/ion exchanges at interfacial layer, most of previous research have been focused on the characterization of surface/interfacial properties of SrTiO$_3$, especially on surface defect chemistry. In most cases of SrTiO$_3$ research, Nb-doping is applied on SrTiO$_3$ surface in order to characterize electrical properties with negligible effect of contact potential between SrTiO$_3$ and overlayer. On the other hand, the presence of doping can easily interfere with correct interpretation of the surface defect states which become critical to apprehend the electrical properties of heterostructures. To have better understanding on surface/interfacial properties of SrTiO$_3$, the surface of *undoped* SrTiO$_3$ (001) surface is investigated utilizing an ambient-pressure XPS (AP-XPS) and low energy electron diffraction (LEED). We identified the complete chemical/structural/electronic states of O and Sr vacancies on *undoped* SrTiO$_3$ surface from ultra-high vacuum (UHV, $<10^{-9}$ mbar) to O$_2$ gas pressure of 0.1 mbar condition. Under oxygen pressure condition, chemically stable SrO$_{1+x}$ surface oxide with c(6×2) superstructure is formed, generating electron depletion and band bending, *i.e.*, the formation of a space charge layer underneath the surface. On the other hand, under UHV, the surface oxide comes from the O vacancy, which has different electronic properties from that of Sr vacancy-related oxide. [1] According to our results, the modification of surface electronic structures is mainly responsible for the alteration of the interfacial properties which is related to the transport properties of SrTiO$_3$-based devices.

References

(PP-12) Poster Presentation 12

Ambient Pressure X-ray Photoelectron Spectroscopy Study of Room-Temperature Oxygen Adsorption on Cu(100) and Cu(111)

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We investigated the room-temperature chemisorption of oxygen on Cu(100) and Cu(111) using ambient-pressure X-ray photoelectron spectroscopy (APXPS). A shoulder-to-shoulder comparison between the oxygen gas titration on the two surfaces reveals that Cu(100) is the more active for oxygen dissociative chemisorption when the surfaces are clean. The (2√2x√2)R45° missing-row reconstruction appears in Cu(100)’s LEED image after about 10⁴ Langmuir of oxygen exposure, whereas on Cu(111), no long-range ordering was observed throughout the whole experiment. A native oxide layer consisting of cuprous and cupric oxide shows up on Cu(111) at an oxygen exposure that is significantly lower than for Cu(100). This observation suggests that the (2√2x√2)R45° missing-row reconstruction may serve as a passivating layer for Cu(100) which slows down oxidation. It has been widely reported in the literature that the surface orientation and morphology influences copper oxidation, an observation that is supported in the current study also for the case of Cu(111).
Induced reduction by H$_2$ exposure at room temperature of ceria ultrathin films grown by atomic layer deposition

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In the last decades, atomic layer deposition (ALD) has gained prominence in the materials and surface science communities owing to its high potential for integration as a scalable process in microelectronics, allowing well-controlled layer-by-layer deposition and conformal growth on 3D structures. Yet, the ALD technique is also well known to lead to amorphous and defective, non-stoichiometric films, resulting in modified materials properties that can also be affected by film/substrate interaction in the case of ultrathin deposits. Nevertheless, the conjunction of these factors may be highly beneficial for certain applications. For instance, in ceria ultrathin films these defects could help to enhance their reactivity at ambient conditions by facilitating the Ce$^{4+}$/Ce$^{3+}$ conversion. In situ XPS measurements of ceria ultrathin films deposited on Al$_2$O$_3$/Si and SiO$_2$ substrates show an initial Ce$^{3+}$/Ce$^{4+}$ mixture dependent on the substrate interaction that almost entirely re-oxidizes after the sample is exposed to ambient conditions. As demonstrated by AP-HAXPES measurements performed at SpAnTeX endstation, BESSY II, these initial defects allow ALD-grown ceria films to become weakly reduced at room temperature (RT) under 20 mbar of H$_2$/N$_2$ (5%/95%), which is reversed after exposing the sample to ambient conditions for 10 minutes. These preliminary results are very promising for decreasing the operating temperature of multiple sensing and catalytic devices based on ceria as the active layer, and highlight the necessity of a deeper in situ characterization of the film/substrate interaction during the ALD growth to understand the nature of these initial defects.

Figure 1. AP-HAXPES Surface (a) and bulk (b) sensitive measurements of the Ce 2p$_{3/2}$ (a, see ref. 1) and Ce 3d (b) core levels performed on as introduced, reduced (RT, H$_2$/N$_2$, P(H$_2$) = 1 mbar) and re-oxidized ALD-CeO$_x$/SiO$_2$ samples. The mean valence estimated from the XPS Ce 3d fit is indicated at the right side.

References

Voltage dependent kinetics and surface chemistry of solid oxide cell electrodes

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Solid oxide electrochemical cells are are efficient devices for conversion of fuels into electrical energy and vice versa. In these, the rate-limiting electrochemical reactions – such as oxygen reduction, hydrogen oxidation or CO₂ splitting – take place at the solid-gas interface. Consequently, ambient pressure XPS is a great tool to deeply understand the reaction mechanisms and the surface chemistry of the electro-catalysts in operando.¹,² Mixed ion and electron conducting oxides are promising electrode materials, since on these, the entire surface is electrochemically active. We lay special focus on perovskite-type materials like La₀.₆Sr₀.₄FeO₃₋δ (LSF) due to their stability in oxidizing and reducing conditions, as well as the highly tunable stoichiometry by doping. Here, we present the insight that we gained on optimized solid oxide model cells and sample stages³ that allow determination of the surface chemistry at controllable temperature, overpotential and cell current density with simultaneous impedance spectroscopic characterization (see Figure 1). We observe overpotential-dependent binding energy shifts that depend on the sample’s Fermi level, carbonate coverages or deposition of graphite, as well as the exsolution of catalytically active metallic Fe, Ni or Co particles in reducing conditions. Since these effects all happen on solid oxide cell electrodes, we can simultaneously observe the effect of these surface-chemical alterations on the catalytic activity of the electrode materials.

Figure 1. Photograph of the high temperature solid state electrochemistry sample stage at TU Wien and setch of an optimized model cell.

References
Monitoring the Behavior of Pt Loaded TiO$_2$(110) under Oxidizing and Reducing Conditions

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The encapsulation of noble metal particles on reducible supports, termed strong metal-support interaction (SMSI), upon annealing under reductive conditions is known since the 1970s.$^{[1]}$ The phenomenon has been extensively studied both on applied powder catalysts and on single crystal model catalysts. However, there is still an ongoing debate on important aspects such as the influence of oxygen or hydrogen treatment on the encapsulating overlayer as well as the role of the size of the particles being encapsulated.$^{[2,3,4]}$ The intrinsic complexity and heterogeneity of applied catalyst systems often prevents investigations at the atomic scale, while results obtained from model catalysts under ultra-high vacuum conditions may not be transferrable to realistic conditions due to a pressure gap of more than seven orders of magnitude.

In this study, we utilize synchrotron-based NAP-XPS to investigate the SMSI for Pt loaded TiO$_2$(110) single crystals and the influence of up to 100 mtorr H$_2$ or O$_2$, respectively, to close this ‘pressure gap’. The combination of high energy resolution, tunable surface sensitivity, and well-defined, contamination-free reaction conditions enables us to delineate two different, pressure-dependent phenomena occurring at 800 K in an O$_2$ atmosphere, namely, an oxidation of Pt particles and a loss of Pt signal intensity. While the oxidation can be partially reversed in vacuum, the intensity of the platinum signal cannot be recovered even by the exposure to a hydrogen atmosphere. In addition, by comparing size-selected Pt$_{10}$ clusters with in situ grown larger Pt nanoparticles, we find that there is no significant size effect.

References

Tailored Mass Spectrometry Solutions for the Gas Analysis of APXPS Systems at Different Pressure Ranges

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Mass spectrometry is a versatile, powerful and fast technique that allows analyzing gas components and component concentrations and therefore enables an insight into the reaction that takes place at the sample surface during APXPS measurements. The possibility to perform online measurements during catalytic reactions (e.g. water gas shift, methanol steam reforming) permits kinetic studies and the ability to draw conclusions about the reaction mechanism.

An intelligent gas inlet system offers the possibility to connect only one gas analysis system to various sampling points at high pressure and ambient pressure reaction cells even when high pressure differences are present. Inlet setups for various ranges are available which can be used for example with high pressure reaction cells (1 - 20 bar), ambient pressure setups (1 - 250 mbar) and in high vacuum.

We are going to present different system concepts based on InProcess Instruments gas analysis systems to address the most common analytical requirements of modern APXPS systems. The adaptability of the gas inlet systems to different pressure ranges and gas types is realized by a sophisticated system design and smart valve sequences. Thus allowing the determination of the gas composition during different stages of sample preparation and in-situ surface analysis.
Investigation of surface oxidation on Pt$_3$V alloys using ambient pressure XPS

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Under oxidation conditions, the physical/chemical alteration of polycrystalline Pt$_3$V alloy surface is investigated with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and X-ray absorption spectroscopy. It is well known that most of Pt-3$d$ transition metal (Pt-M) alloys show surface segregation of Pt after high temperature UHV annealing process. Then, under elevated oxygen pressure, the underneath transition metal is pulled to the surface and transition metal oxides are formed on surface. [1,2] While most of Pt-M alloys surfaces are well characterized and investigated, it is rather difficult to find any oxidation study on Pt$_3$V alloys.

To investigate the surface segregation and oxidation states of Pt$_3$V, XPS depth profiling technique is utilized under various oxygen and elevated-temperature conditions using AP-XPS. Under oxidation condition, V 2p spectra display various oxidation states at surface, which are verified by X-ray absorption spectra for V L-edge. Furthermore, Pt 4f spectra exhibit fine splitting at lower binding energy side, signifying the sign of charge redistribution between Pt and V. [3] Also, the oxidation states of vanadium near surface region show “non-stoichiometric” vanadium oxides. [4] Overall, our results show that Pt$_3$V undergoes Pt diffusion to bulk layer while vanadium forms non-stoichiometric surface oxide under elevated pressure oxygen environment.

References

Figure 7. V 2p, Pt 4d and O 1s photoemission spectra for polycrystalline Pt3V under various oxidation conditions
Oxidation kinetics of Ru(0001) studied by NAP-XPS

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Ruthenium is known as functional material, for example as catalyst\textsuperscript{1} or for protective coatings.\textsuperscript{2} These applications often require ruthenium in its metallic state, whereas at elevated oxygen pressures and temperatures oxidation occurs. The oxidation of ruthenium has been extensively investigated, and interesting properties such as a high threshold pressure and autocatalytic oxidation have been observed. At low pressure (10\textsuperscript{-4} mbar O\textsubscript{2}) and low temperature (20-200°C) oxidation of ruthenium shows Cabrera-Mott (CM) oxidation kinetics.\textsuperscript{3} Diulus et al. determined the equilibrium oxidation states for 20-400°C in 10\textsuperscript{-2}mbar O\textsubscript{2} with near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), but the reaction proceeds too fast under those conditions to obtain information on kinetics.\textsuperscript{4} By combining NAP-XPS at lower pressure with a broad temperature range, we follow the oxidation kinetics in situ and gain insights into the nature of Ru oxidation and its energetics.

In the present study, NAP-XPS is used to follow the oxidation state of a Ru(0001) single crystal during exposure to 10\textsuperscript{-4} mbar O\textsubscript{2} at 200-400°C. At each temperature, series of in situ XPS spectra are taken to quantify the metal to oxide ratio in the surface region as a function of time. Using the electron attenuation length in Ru and RuO\textsubscript{2}, an average layer thickness is calculated from the intensity ratio of the different species.\textsuperscript{5} The oxide growth is modeled with CM kinetics, comparing different rate laws used in literature to describe the layer thickness as a function of time. From the oxidation rates at different temperatures, we determine the activation energy for the rate-limiting step of Ru oxidation. Above 300°C, a transition to faster kinetics is observed, indicating that the oxide growth can no longer be described by the CM mechanism.

Figure 1. Ruthenium oxidation at 300°C in 10\textsuperscript{-4} mbar O\textsubscript{2}, A) Ru 3d XPS spectrum of pristine (red) and oxidized (black), B) in situ Ru 3d XPS spectra, C) ruthenium oxide thickness evolution as a function of time calculated from in situ NAP-XPS measurements.

References
Ambient pressure/ UHV X-ray Photoelectron Spectroscopy End Stations at TPS BL43A

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Conventional X-ray photoelectron spectroscopy (XPS) is one of the powerful surface analysis tools and can be applied to study the chemical state and elemental composition of surface layers in solid samples. In contrast to the high vacuum requirement of conventional XPS, ambient pressure XPS (APXPS) can carry out the real-time investigation of gas-solid, liquid-solid, and liquid-gas heterogeneous reactions at the pressure up to mbar range. The experimental stations related to conventional XPS and APXPS have been planned to be installed at Taiwan Photon Source (TPS) BL 43A of the National Synchrotron Radiation Research Center (NSRRC), and this construction plan has been included in the phase III projects of TPS from 2021 to 2026 as well. In this presentation, we will introduce the preliminary beamline specifications, optics layout and the design of end stations shown in Figure 1. The X-ray source of this beamline is from an elliptically polarizing undulator (EPU 56 mm) provides the photon flux higher than $10^{12}$ photons per second with the beam size smaller than $50 \times 20 \, \mu m^2$ in the photon energy range from 200 to 3000 eV. Three experimental end stations are planning to be installed at this beamline by tandem like structure. The Ultra-high vacuum (UHV) XPS end station is dedicated to performing the conventional surface science research topics including the surface physics, surface chemical reaction, and materials science. An APXPS end station has been constructed and opened to users at Taiwan light source (TLS) beamline 24 A in 2017. This APXPS end station will be upgraded and relocated to be APXPS end station I at TPS 43A to carry out the vapor-solid reactions at the high-pressure region. A new APXPS end station II will be designed to carry out the liquid-solid reaction, especially in electrochemistry applications. The more detailed design concept of this beamline and end stations will be addressed in this presentation.

![Figure 1. Preliminary beamline specifications, optics and end stations layout for TPS BL43A.](image-url)
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Investigation of Redox Reaction of Platinum during Electrochemical Catalysis Reaction by Ambient Pressure XPS

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In order to improve and optimize the efficiency of catalytic reaction, scientists dedicate to develop innovative techniques for understanding the real-time changes of catalytic reaction. So as to probe the interaction between catalyst and reactant on the catalyst’s surface, the novel near ambient pressure x-ray photoelectron spectroscopy (APXPS) is highly recommended. Recently, some liquid reaction cells adapted with electrochemical apparatus have been developed and allow us to study the liquid-solid interface, such as the changes of an electrochemical catalyst, in electrochemistry applications. Understanding changes in electronic structure of a working electrode will provide us more information to depict the mechanism of the reaction. In this research, we fabricated a homemade in-situ liquid cell to study the redox reaction of the iconic Pt catalyst under different electrochemical condition (Figure.1) at the APXPS end-station of TLS BL24A, at NSRRC. Pt film that sandwiched between membrane and monolayer graphene were mounted on a water reservoir to provide an operational condition. The operando spectra of Pt film under different bias revealed the evolution of surface oxidation and reduction. With the combination of online mass spectrometry, we could monitor the oxygen production under different potential. The fitting spectra results showed that the Pt catalyst would tend to be oxidized to Pt\(^{2+}\) prior to the production of oxygen gas while Pt\(^{4+}\) would appear as the signal increased obviously. The changes of the surface species on electrocatalyst could inspire us to know the preference surface condition under OER reaction. The more detailed results will be discussed in this presentation.

Figure.1 The setup of in-situ experiment of Pt redox reaction investigation.
Surface chemical states of carbon-steel utilizing near ambient pressure XPS

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Carbon steel is the most important group of engineering alloys. In many industries, it is inevitably exposed to harsh environments that oxidize and corrode, resulting in loss of stability. Naturally, these phenomena are strongly affected by the nature of the steel surfaces. However, it is seen that the majority of recent oxidization and corrosion investigations are limited to optical microscopic observing, electrochemical testing, and the structural change of the bulk, with ex-situ analysis of the treated steels [1,2]. With the advanced synchrotron-based techniques (e.g. X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, X-ray diffraction spectroscopy, etc) [3], real-time and in-situ experiments can be carried out to reveal new insight of engineering the carbon steel structure [4]. Especially, near ambient-pressure XPS (NAP-XPS) is suitable for investigating the surface chemical states close to realistic reaction conditions.

In this work, we investigated the carbon-steel by utilizing NAP-XPS with Cr Ka source and synchrotron facility. The carbon-steel was thermally treated by IR laser within sub-minute from RT to 900 °C, and the surface chemical states were monitored by fast XPS with 0.1 seconds per spectrum, simultaneously. Interestingly, iron carbide (Fe₃C, austenite) was formed on the surface as the sample temperature arrived at 300 °C. This temperature is rather lower than that of the bulk transformation between 685 °C and 822 °C [4]. In addition, it was confirmed that more austenite was formed on the surface by observing the C1s state of the surface and subsurface by varying the probing depth. Further, the austenitized surface was exposed to water vapor of 0.1 mbar at 550 °C. These results will help synthesize corrosion-resistant carbon steel surfaces.

References