APXPS 2025

12th Ambient Pressure X-ray Photoelectron Spectroscopy Workshop

Hosted by Brookhaven National Laboratory

Long Island, New York

December 9-12, 2025

Brookhaven National Laboratory

U.S. DEPARTMENT of ENERGY

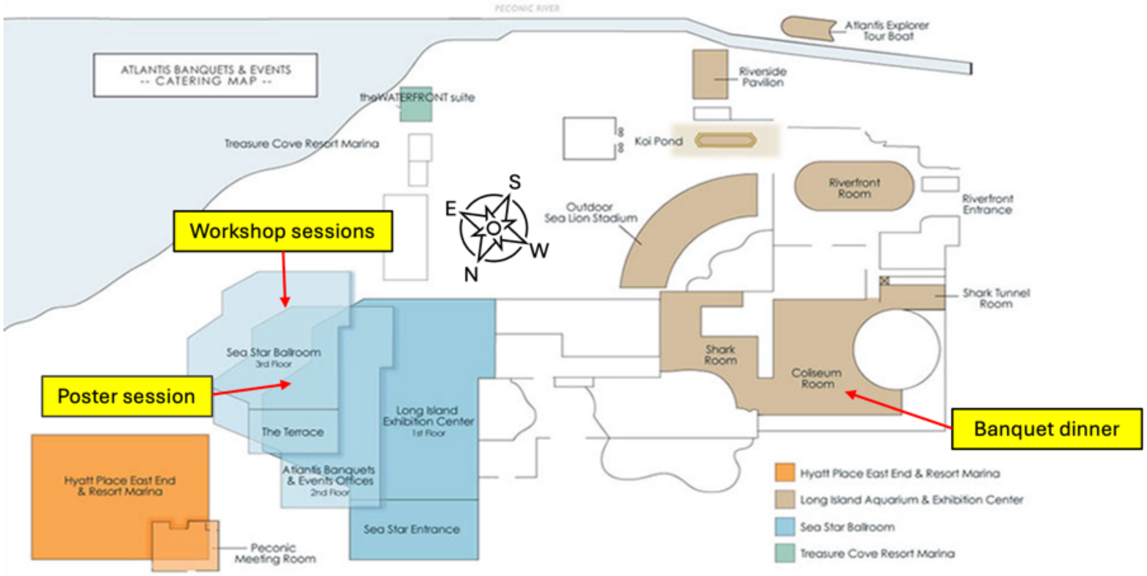
Venue Information

The APXPS-2025 Workshop venue is the **Atlantis Hotel and Conference Center** (also called **Atlantis Banquet and Events** on Google Maps). The room we will use is the **Sea Star Ballroom** on the third floor.

Address: 431 E Main St, Riverhead, New York 11901

The hotel is **Hyatt Place Long Island East End** directly adjacent to the venue (451 E Main St, Riverhead, New York 11901).

- Workshop sessions are held in the south side of the Sea Star Ballroom.
- Poster session (Wednesday, Dec. 10 at 6 - 8 pm) and meals take place in north side of the Sea Star Ballroom.
- Sponsor exhibition tables are located in the hallway outside the Sea Star Ballroom.
- The banquet dinner (Thursday, Dec. 11 at 6 - 8 pm, ticket required) will be held in the Coliseum Room of the Long Island Aquarium.



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- Ira Waluyo (chair)
- Ashley Head
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Plenary Speakers

- Miquel Salmeron (Lawrence Berkeley National Laboratory, USA)
- Frank de Groot (Utrecht University, Netherlands)

Invited Speakers

- Mark Biesinger (Western University, Canada)
- Baran Eren (Weizmann Institute of Science, Israel)
- Zbynek Novotny (Pacific Northwest National Laboratory, USA)
- Virginia Perez Dieste (ALBA Synchrotron, Spain)
- Jose Rodriguez (Brookhaven National Laboratory, USA)
- Charles Sykes (Tufts University, USA)
- Heloise Tissot (CNRS, France)
- Spiros Zafeiratos (University of Strasbourg, France)

Workshop Agenda (Eastern Standard Time, UTC-05:00)

Time	Tue, Dec. 9	Wed, Dec. 10	Thu, Dec. 11	Fri, Dec. 12
9:05 - 9:40 AM		Invited: C. Sykes	Invited: J. Rodriguez	Invited: B. Eren
9:40 - 10:00 AM		Contributed: V. Lal	Contributed: A. Islam	Contributed: D. Wu
10:00 - 10:20 AM		Contributed: A. Harrer	Contributed: G. Li	Contributed: Y. Murano
10:20 - 10:40 AM		Coffee Break	Coffee Break	Contributed: D. C. Oliveira
10:40 - 11:15 AM		Invited: Z. Novotny	Plenary: F. de Groot (online talk)	Coffee Break Facility Updates
11:15 - 11:35 AM		Contributed: M. De Col	Contributed: E. Ortega	
11:35 - 11:55 AM		Contributed: A. Saxena	Contributed: G. Anand	
11:55 AM - 12:15 PM		Contributed: J. Paudel	Group photo	Closing/Next workshop
12:15 - 1:30 PM	Registration/check in	Lunch	Lunch	Lunch
1:30 - 2:05 PM	Opening Remarks Invited: M. Biesinger	Invited: V. Pérez-Dieste	Plenary: M. Salmeron	Transfer by bus to BNL
2:05 - 2:25 PM		Contributed: R. Lindblad		Check in at BNL (please bring ID)
2:25 - 2:45 PM	Contributed: Q. Liu	Contributed: C. Fikry	Contributed: F. Grajkowski	Facility Tours
2:45 - 3:05 PM	Contributed: R. Jones	Contributed: R. Lindsay	Contributed: K. Kooser	
3:05 - 3:25 PM	Contributed: A. Kolmakov	Coffee break	Coffee break	
3:25 - 4:00 PM	Coffee break Technical discussion session	Invited: S. Zafeiratos	Invited: H. Tissot	
4:00 - 4:20 PM		Contributed: S. Mauri	Contributed: S. Schroeder	
4:20 - 4:40 PM		Contributed: H. Kondoh	Sponsor Talk: SPECS	Transfer by bus to hotel
4:40 - 5:00 PM		Contributed: P. Reinke	Sponsor Talk: Scienta Omicron	
5:00 - 6:00 PM		SAC Meeting (hybrid) Poster Setup Free time for attendees	Free time	
6:00 - 8:00 PM		Poster Session with Reception	Banquet (Coliseum Room)	

Day 1: Tuesday, December 9, 2025

12:15 PM – 1:30 PM	Registration/Check In
1:30 PM – 1:50 PM	**Opening Remarks – Jim Misewich (Associate Laboratory Director for Energy and Photon Sciences, Brookhaven National Laboratory)** Safety Message
Session Chair: Georg Held (Diamond Light Source, UK)	
1:50 PM – 2:25 PM	**Invited 1 – Mark Biesinger (Western University, Canada)** *“Advancing XPS Data Interpretation: Standards, Strategies, and Methodologies”*
2:25 PM – 2:45 PM	**Contributed 1 – Qianhui Liu (Uppsala University, Sweden)** *“Combining experimental design and software based image recognition for operando APXPS electrode/electrolyte interface potential probing”*
2:45 PM – 3:05 PM	**Contributed 2 – Rosemary Jones (Lund University, Sweden)** *“Advancing the operando study of ALD chemistry with time-resolved ambient pressure x-ray photoelectron spectroscopy”*
3:05 PM – 3:25 PM	**Contributed 3 – Andrei Kolmakov (NIST, USA)** *“Plasma XPS: The Origins of Binding Energy Shifts at the Plasma-Exposed Metal and Dielectric Samples and in the Gas Phase ”*
3:25 PM – 3:45 PM	Coffee Break
3:45 PM – 5:00 PM	**Technical Discussion Session** **Panelists:** • Mark Biesinger (Western University, Canada) • Georg Held (Diamond Light Source, UK) • Patrick Lömker (Scienta Omicron) • Virginia Pérez-Dieste (ALBA Synchrotron, Spain)) • Andreas Thissen (SPECS) • Piero Torelli (Elettra, Italy)

Day 2: Wednesday, December 10, 2025

Session Chair: Enrique Ortega (Universidad del País Vasco, Spain)	
9:05 AM – 9:40 AM	**Invited 2 – E. Charles H. Sykes (Tufts University, USA)** *“Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico”*
9:40 AM – 10:00 AM	**Contributed 4 – Vinita Lal (Tufts University, USA)** *“Facet-Resolved Insights into NiAg Single-Atom Alloys by Ambient-Pressure XPS: Linking Oxygen Speciation to Selective Oxidation”*
10:00 AM – 10:20 AM	**Contributed 5 – Anton Harrer (Stockholm University, Sweden)** *“Disentangling the Role of Octahedral Fe Carbides in Fischer-Tropsch”*
10:20 AM – 10:40 AM	Coffee Break
Session Chair: Héloise Tissot (Université de Lille, France)	
10:40 AM – 11:15 AM	**Invited 3 – Zbynek Novotny (Pacific Northwest National Lab., USA)** *“Understanding Electrochemical Stability of Interfaces: RuO_2(110) Corrosion and N-doped Graphene as a Stable Adsorption Template”*
11:15 AM – 11:35 AM	**Contributed 6 – Michela De Col (University of Trieste, Italy)** *“Surface-Dependent Re-Solvation of Cyanocobalamin: an In Situ Spectroscopic Study on Au(111) and Graphene/Ir(111)”*
11:35 AM – 11:55 AM	**Contributed 7 – Abhinav Saxena (Forschungszentrum Jülich, Germany)** *“NAP-XPS study on O-conducting membrane surfaces: Understanding the surface O-exchange mechanism ”*
11:55 AM – 12:15 PM	**Contributed 8 – Jay Paudel (Lawrence Berkeley National Lab., USA)** *“In Situ and Operando Characterization of Electronic and Chemical States of WO_3 During Electrochemical Proton Intercalation”*
12:15 PM – 1:30 PM	Lunch
Session Chair: Zbynek Novotny (Pacific Northwest National Lab., USA)	
1:30 PM – 2:05 PM	**Invited 4 – Virginia Pérez-Dieste (ALBA Synchrotron, Spain)** *“Near-Ambient Pressure Oxidation of Silver in the Presence of Steps”*

Day 2: Wednesday, December 10, 2025 (continued)

2:05 PM – 2:25 PM	**Contributed 9 – Rebecka Lindblad (Uppsala University, Sweden)** *“Chemical analysis of passive layers of multicomponent CrFeMnCoNi(C) during electrochemical oxidation”*
2:25 PM – 2:45 PM	**Contributed 10 – Chaimaa Fikry (Uppsala University, Sweden)** *“Understanding corrosion of TiCN in acidic and alkaline environments: a route to produce corrosion resistant coatings”*
2:45 PM – 3:05 PM	**Contributed 11 – Robert Lindsay (The University of Mancheser, UK)** *“Complexity at a Humid Interface: Throwing Fresh Light on Atmospheric Corrosion”*
3:05 PM – 3:25 PM	Coffee Break
Session Chair: Piero Torelli (Elettra, Italy)	
3:25 PM – 4:00 PM	**Invited 5 – Spiros Zafeiratos (Université de Strasbourg, France)** *“From bulk design to surface reactivity: Probing active site formation in Ni-based* CO_2 *methanation catalysts using soft and hard X-ray spectroscopies”*
4:00 PM – 4:20 PM	**Contributed 12 – Silvia Mauri (MAX IV/Lund University, Sweden)** *“Low-Temperature methane activation pathways on inverse ball milled* CeO_2/CuO *catalyst: a combined in situ DRIFT and ambient pressure operando NEXAFS study”*
4:20 PM – 4:40 PM	**Contributed 13 – Hiroshi Kondoh (Keio University, Japan)** *“In situ AP-sXAS observation of charge transfer in the cocatalyst-loaded* $SrTiO_3$ *photocatalyst for water splitting under UV-Vis irradiation”*
4:40 PM – 5:00 PM	**Contributed 14 – Petra Reinke (University of Virginia, USA)** *“Oxidation of Transition Metal Alloys Studied with AP-XPS and XPEEM”*
5:00 PM – 6:00 PM	Scientific Advisory Committee Meeting Poster Setup Free time for attendees
6:00 PM – 8:00 PM	**Poster Session with Reception**

Day 3: Thursday, December 11, 2025

Session Chair: Spiros Zafeiratos (Université de Strasbourg, France)	
9:05 AM – 9:40 AM	**Invited 6 – José Rodriguez (Brookhaven National Lab., USA)** *“AP-XPS Studies for the Transformation of* CO_2 *and* CH_4 *on Inverse Oxide/Metal Catalysts”*
9:40 AM – 10:00 AM	**Contributed 15 – Arephin Islam (Brookhaven National Lab., USA)** *“AP-XPS study of supported MgO Nanostructures for Low-Temperature conversion of Methane”*
10:00 AM – 10:20 AM	**Contributed 16 – Gengnan Li (Argonne National Laboratory, USA)** *“In situ microscopy and spectroscopy study on dynamics of nanostructure in catalysis for energy”*
10:20 AM – 10:40 AM	Coffee Break
Session Chair: Mark Biesinger (Western University, Canada)	
10:40 AM – 11:30 AM	**Plenary 1 – Frank de Groot (Utrecht University, The Netherlands)** *“The core XPS spectral shape”* (online talk)
11:30 AM – 11:50 AM	**Contributed 17 – Enrique Ortega (Universidad del País Vasco, Spain)** *“Structure and chemistry of NO over a curved Rh surface at ambient pressure”*
11:50 AM – 12:10 PM	**Contributed 18 – Gaurav Anand (Technical University of Munich, Germany)** *“Investigating Metal-Support Interactions on Reducible Oxides for Gas Phase Photocatalysis using Near Ambient Pressure XPS”*
12:10 PM – 12:25 PM	Group Photo
12:25 PM – 1:35 PM	Lunch
Session Chair: Baran Eren (Weizmann Institute of Science, Israel)	
1:35 PM – 2:25 PM	**Plenary 2 – Miquel Salmeron (Lawrence Berkeley National Laboratory and UC Berkeley, USA)** *“Synchrotron spectroscopies for studies of materials in solid, liquid, gas phase, and their interfaces”*

Day 3: Thursday, December 11, 2025 (continued)

2:25 PM – 2:45 PM	**Contributed 19 – Filip Grajkowski (Massachusetts Institute of Technology, USA)** *“Electrochemically-induced cation redistribution and surface phase oscillations promote high selectivity in the partial oxidation of methane”*
2:45 PM – 3:05 PM	**Contributed 20 – Kuno Kooser (University of Tartu, Estonia)** *“Single- and Dual-Chamber Spectroscopic Study of LSTN Anode Material Under Operating Conditions of a Solid Oxide Cell”*
3:05 PM – 3:25 PM	Coffee Break
Session Chair: Virginia Pérez-Dieste (ALBA Synchrotron, Spain)	
3:25 PM – 4:00 PM	**Invited 7 – Héloise Tissot (Université de Lille, France)** *“Model Catalysts Under Operando Conditions: Oxidation Dynamics and Beam-Induced Artifacts”*
4:00 PM – 4:20 PM	**Contributed 21 – Sven Schroeder (University of Leeds, UK)** *“Probing Volatile Organic Solids and Solutions In Situ with Near-Ambient Pressure XPS”*
4:20 PM – 4:40 PM	**Sponsor Talk 1 – SPECS TII**
4:40 PM – 5:00 PM	**Sponsor Talk 2 – Scienta Omicron**
5:00 PM – 6:00 PM	Free Time
6:00 PM – 8:00 PM	**Banquet Dinner** (Coliseum Room, Long Island Aquarium)

Day 4: Friday, December 12, 2025

Session Chair: Sven Schroeder (University of Leeds, UK)	
9:05 AM – 9:40 AM	**Invited 8 – Baran Eren (Weizmann Institute of Science, Israel)** *“Dual Insights from a Single X-ray Beam: Simultenously AP-XPS and GIXS Measurements on Nanopattered Ceria in Hydrogen”*
9:40 AM – 10:00 AM	**Contributed 22 – Dongshuang Wu (Nanyang Technological University, Singapore)** *“Seeing beyond the surface: uncovering electrochemical interfaces by near ambient-pressure operando HAXPES”*
10:00 AM – 10:20 AM	**Contributed 23 – Yu Murano (The University of Tokyo, Japan)** *“The Real Ambient Pressure Photoelectron Spectroscopy Measured with Soft X-ray”*
10:20 AM – 10:40 AM	**Contributed 24 – Daniela Coelho de Oliveira (Brazilian Synchrotron Light Laboratory, Brazil)** *“Preliminary Design and Overview of a new Ambient Pressure XPS beamline at the Brazilian Synchrotron Light Laboratory, Sirius”*
10:40 AM – 11:00 AM	Coffee Break
11:00 AM – 12:00 PM	**Facility Updates** • Georg Held (Diamond Light Source, UK) • Hiroshi Kondoh (Keio University, Japan) • Virginia Pérez-Dieste (ALBA Synchrotron, Spain) • Sven Schroeder (University of Leeds, UK) • Robert Temperton (MAX IV, Sweden) • Piero Torelli (Elettra, Italy)
12:00 PM – 12:15 PM	**Closing** **Announcement of Next Workshop**
12:15 PM – 1:30 PM	Lunch
1:30 PM – 2:10 PM	Bus transfer to BNL
2:10 PM – 2:30 PM	Arrival and check in at BNL (please bring photo ID)
2:30 PM – 4:30 PM	**Facility Tours**
4:30 PM – 5:00 PM	Bus transfer back to hotel in Riverhead

Poster List

#	Presenting Author	Affiliation
1	**Yeslie Carrillo Cabrera**	**University of Texas at El Paso, USA**
	X-ray Photoelectron Spectroscopy of Tetrametallic Phosphate (Co-Ni-Fe-Mn) Electrocatalyst Activation for the Oxygen Evolution Reaction (OER)	
2	**Hao Chen**	**Stanford University/SLAC, USA**
	Operando APXPS maps active phases and promoter effects in cobalt catalysts	
3	**Varun Raj Damerla**	**Uppsala University, Sweden**
	XPS investigation of KOH-induced corrosion in FeCrMnCoNi alloy	
4	**Thu Ngan Dinhová**	**Charles University, Czech Republic**
	Oxidation and Structural Evolution of Ruthenium Nanoparticles supported on $CeO_2(111)$ *and* $Co_3O_4(111)$	
5	**J. Trey Diulus**	**NIST, USA**
	Operando Plasma-XPS of high performance tin oxide photoresist for extreme ultra-violet photolithography	
6	**Sabrina Gericke**	**Brookhaven National Laboratory, USA**
	Size-dependent charge transfer between nanoscale Rh species and rutile TiO_2	
7	**Elizabeth Happel**	**Tufts University, USA**
	Ag(111) Remains Signficantly Reduced In Situ Under Simulared Ethylene Epoxidation Conditions	
8	**Ashley Head**	**Brookhaven National Laboratory, USA**
	Recent Upgrades in APXPS Sample Environments at the Center for Functional Nanomaterials	
9	**Georg Held**	**Diamond Light Source, UK**
	Operando XPS and NEXAFS Reveal Oxidation Dynamics and Active Oxygen Species in Iridium and Ruthenium–Iridium Oxide OER Catalysts	
10	**Zong-Jhe Hsieh**	**Tamkang University, Taiwan**
	Thermal Annealing Process, Water Storage, and Water Permeation Application of Graphene Oxide Membranes	
11	**Adrian Hunt**	**Brookhaven National Laboratory, USA**
	The In Situ and Operando Soft X-ray Spectroscopy (IOS, 23-ID-2) Beamline at NSLS-II: Science Highlights and Future Plans	
12	**Beomgyun Jeong**	**Korea Basic Science Institute, South Korea**
	In situ AP-HAXPES of Pt oxidation state in a hygroscopic electrochemical cell	

Poster List (continued)

13	**Jackson King**	**University of Notre Dame, USA**
	Surface Analysis of Photonic-Cavity Photocatalysts via NAP-XPS: Assessing the Role of Structural Order	
14	**Esko Kokkonen**	**MAX IV Laboratory, Sweden**
	An APXPS setup for studying atomic layer deposition	
15	**Anand Kumar**	**Paul Scherrer Institute, Switzerland**
	Resonant Auger-Meitner Electron Spectroscopy of nitrate ions: from crystalline powder to deliquesced solution	
16	**Neelesh Kumar**	**Lehigh University, USA**
	Probing Surface Chemistry of Co infiltrated Ni/YSZ Cathode Catalysts with in situ NAP-XPS	
17	**Patrick Lömker**	**Stockholm University, Sweden**
	Tracing Haber-Bosch Under AP-XPS Conditions: The Effect of Potassium Promotion on Iron	
18	**Silvia Mauri**	**Lund University & MAX IV Laboratory, Sweden**
	Spin Polarization Effects in Catalysts studied with x ray Spectroscopies at Ambient Conditions (SPECTRA MSCA project)	
19	**Igor Messias**	**Argonne National Laboratory, USA**
	Understanding Activity, Stability, and Durability in Oxygen Electrochemistry through In Situ Detection of Reactive Oxygen Species	
20	**Yu Murano**	**The University of Tokyo, Japan**
	In-situ observation of CO_2 activation in the presence of H_2 on Ni(111) and Ru(0001) surfaces by Ambient-Pressure X-ray Photoelectron Spectroscopy	
21	**Alessandro Namar**	**University of Trieste, Italy**
	Bio-inspired Surface Catalysis: Hemin Reactivity	
22	**Kaline Nascimento Da Silva**	**Argonne National Laboratory, USA**
	In-situ mapping of variables that govern Iridium electrochemical stability	
23	**Hariprasad Parayil Kalappurackal**	**Lund University, Sweden**
	In situ and operando investigation of molecular layer deposition using APXPS	
24	**Ravi Ranjan**	**ALBA Synchrotron, Spain**
	Co_3O_4 for sustainable CO_2 reduction and possible fine-tuning towards selective CO production	

Poster List (continued)

25	**Kali Rigby**	**Argonne National Laboratory, USA**
	Investigation of Electrochemical Dissolution Using Online Inductively Coupled Plasma Mass Spectrometry	
26	**Sven L. M. Schroeder**	**University of Leeds, UK**
	High-Precision Core Level Binding Energy Shifts of Potassium in Catalysts by Near-Ambient Pressure (NAP) XPS in the Home Laboratory	
27	**Okkyun Seo**	**Japan Synchrotron Radiation Research Institute, Japan**
	Preliminary study of a multimodal chamberless HAXPES and XRD system	
28	**Marius Steinmetz**	**Freie Universität Berlin, Germany**
	Oxophilicity of Ternary Ga-Ag-Pt and Ga-Cu-Pt Liquid Metal Solutions	
29	**Michael Vorochta**	**Charles University, Czech Republic**
	Surface chemistry of Ru on ceria: a model catalyst approach	

Poster Session Details

- Poster session with reception will take place on Wednesday, Dec. 10 at 6 – 8 pm, in the north side of the Sea Star Ballroom. Please set up your poster before this time.
- Posters must fit within a 36” (horizontal) x 48” (vertical) area (approximately A0 size).
- Posters can remain on display until lunch break on Friday, Dec. 12.
- Students and postdocs are eligible for a poster competition. Winners will receive a framed certificate and a gift bag.

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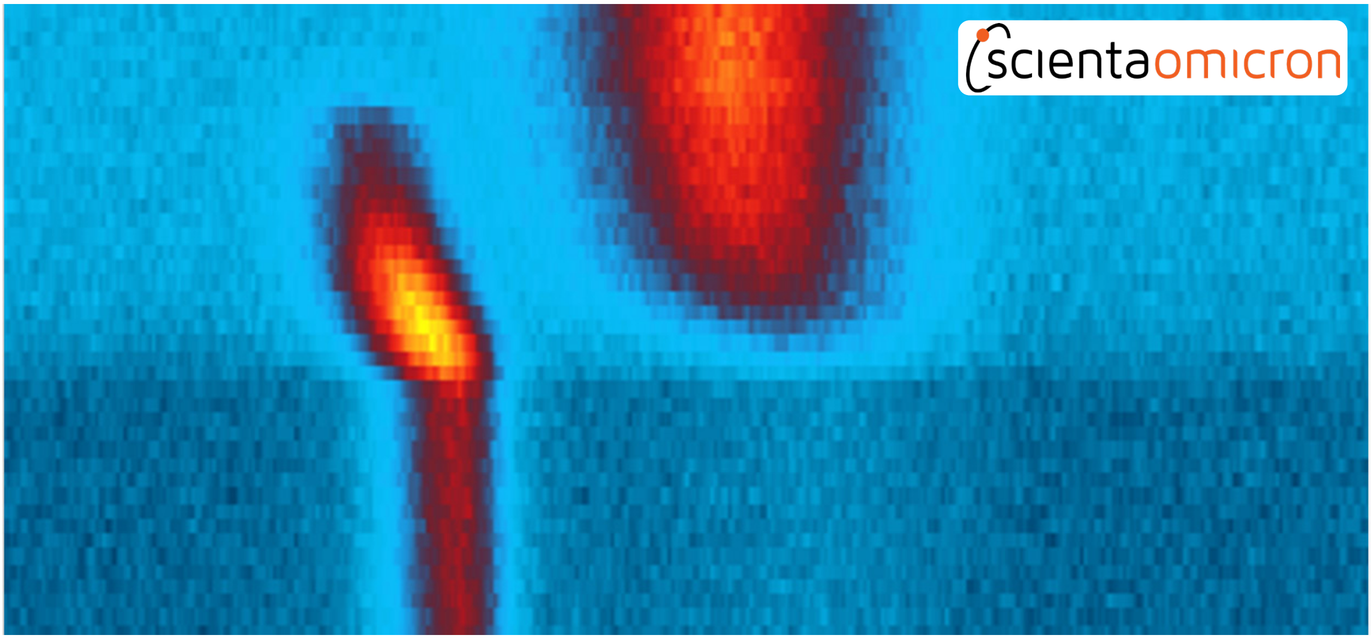

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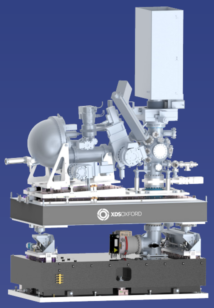
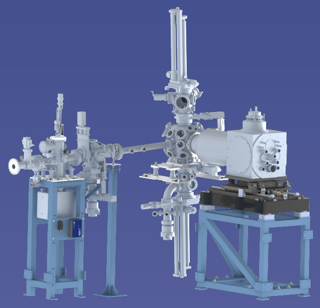


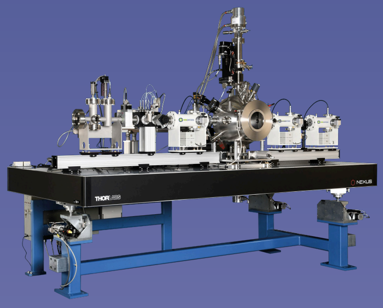
In Situ and Operando Soft X-ray Spectroscopy

XDS Oxford can supply multimodal endstations for a range of Spectroscopy applications including AP-XPS, XAS, XES/RIXS and IRRAS techniques. In this design, a common support structure and motion mechanism is provided for a UHV analysis chamber and its vacuum components. Provision has been made to allow the scientists to integrate further equipment including sample preparation and load lock chambers, a sample manipulator, transfer and heating systems, together with an AP-XPS electron analyzer, RIXS spectrometer system, and IR optics/detector.

Near Edge X-ray Absorption Fine Structure

For Near Edge X-ray Absorption Fine Structure applications (NEXAFS), XDS Oxford is delivering an upgrade to an existing through station. Whilst additional beamtubes, supports and bellows are being supplied, the existing vacuum equipment (pumps and gauges) will be reused. A 10,000-element detector will be mounted on a new support stand which must have precision locating points to accurately reproduce its position on the floor after removal and replacement. Fine manual positioning of the detector with respect to the experiment chamber is provided together with additional precise motorised remote positioning of the detector in relation to the sample position.





Extended X-ray Absorption Fine Structure

For EXAFS experiments, an experimental endstation mounted on a motorised optical table enabling motorised pitch, roll and yaw has been provided. All the experimental components have also been supplied by XDS Oxford, with a number of standard Detector and Diagnostic products being employed in the design.

This system enables high, low and room temperature transmission, fluorescence EXAFS and in situ X-ray diffraction experiments for solids, liquids, and gases to be undertaken. The experiments can be performed in a continuous temperature range between 50k to 750K, and at pressures up to 20 Bar.

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XDS Oxford also designs and manufactures a wide range of standard and customised Detector and Diagnostic products to complement endstation experiments.

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Plenary Talk 1

The core XPS spectral shape

Frank de Groot

Debye Institute for Nanomaterials Science, Utrecht University
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The interpretation of core XPS spectral shapes will be reviewed using the two-state cluster model as starting point to explain (at least conceptually) all XPS spectral shapes [1.2]. The general characteristics of the two-state cluster model [3] will be explained and using a series of examples the different interactions and phenomena will be highlighted. The main parameter in the two-state cluster model is the core hole potential Q. Actually it is not the core hole potential itself, but the difference in electronic state shifts due to the core hole potential; For example in a transition metal oxide the 3d states will shift more due to the core hole than the 4s and 4p states. I will discuss the interactions within the two-state cluster model including the core spin-orbit coupling, the core-valence electron-electron interactions (aka multiplets), the crystal field. In addition I will discuss additional interactions that must be included for a more accurate spectral shape simulation, including (a) a third configuration, (d) additional 4th and 5th configurations, non-local screening, configuration-interaction between core levels and the band structure, with a discussion of the asymmetric line shapes of platinum and sp-metals.

Resonant photoemission and resonant Auger will be briefly discussed, especially its options to disentangle features in the core XPS spectral shapes and its potential advantages in operando XPS experiments [4].

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Plenary Talk 2

Synchrotron spectroscopies for studies of materials in solid, liquid, gas phase, and their interfaces

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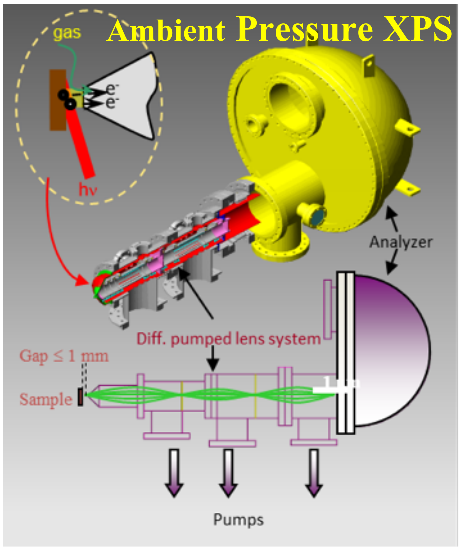
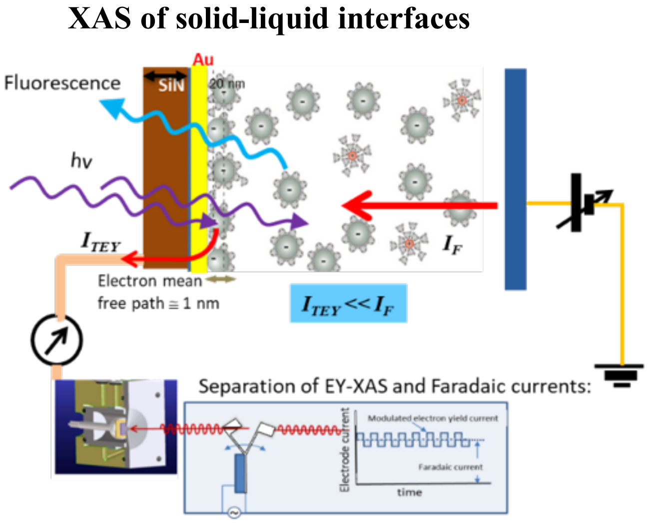
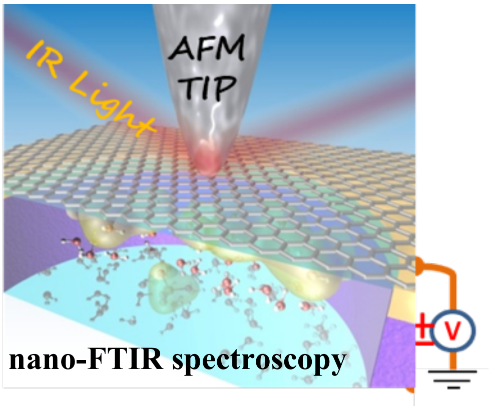
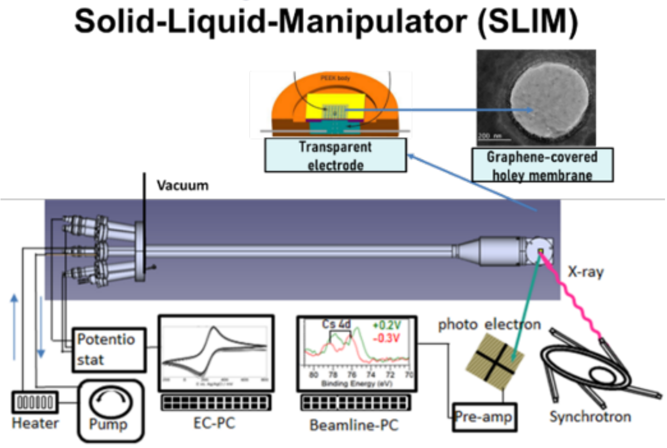
The development of spectroscopic techniques for fundamental studies of materials in various phases: solid, liquid, and gas, has made enormous progress since the pioneering work of Prof. Kai Siegbahn in the early 1980's. New Instrumental developments since the early 2000's in X-ray spectroscopy techniques like Ambient Pressure XPS (APXPS), NEXAFS, and others, have made it possible to use them under ambient gases from Torr to Atmospheric pressure and has been extended to solid-liquid interfaces. These instruments, commercially available today, have revolutionized Catalysis, wetting, corrosion, atmospheric sciences, and more. With Synchrotrons providing intense, highly coherent beams of photons, from hard X-rays to Infra-Red energies, are greatly expanding the scientific areas with new developments that will have a great impact in electrochemistry and biology. I will review some of them with examples from my Laboratory. I will also present developments that open the way for ultrafast acquisition of XAS spectra.









Invited Talk 1

Advancing XPS Data Interpretation: Standards, Strategies, and Methodologies

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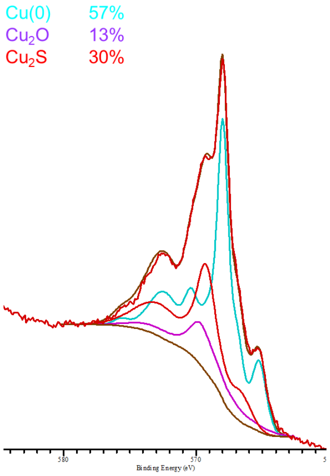
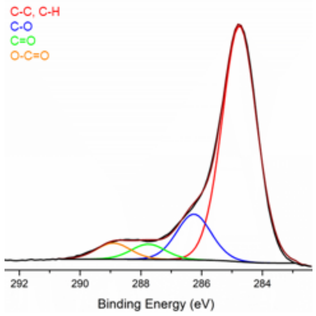
Effectively identifying and quantifying chemical states and unique species by X-ray photoelectron spectroscopy (XPS) can range from the relative ease of analysis for well separated singlet peaks, to the vastly more complex curve-fitting methodologies needed for spectra containing doublet features, overlapping binding energies, asymmetries, multiplet splitting, shake-up and other satellite features. This is particularly true for the first row first row transition metals where our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.



The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and quantify the various species present in mixed species systems [1,2]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots for compounds of Ni, Cu, Ga, In, Cd, and Zn. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [3], as well as for Ni, Zn, In and Cd, have also been shown to be of great value for chemical speciation.



Examples that further incorporate the often overlooked information from surveys scans, analysis of the sometimes very complex oxyen 1s peak, along with film thickness analyses, showcase the ability to form a very complete picture of the surface of studied materials by XPS.

Also discussed with be charge corrections procedures using adventitious cabon (AdC) [4], work on defining the nature of AdC [5], and procedures for the removal of AdC related oxygen from the O 1s signal.

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Invited Talk 2

Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico

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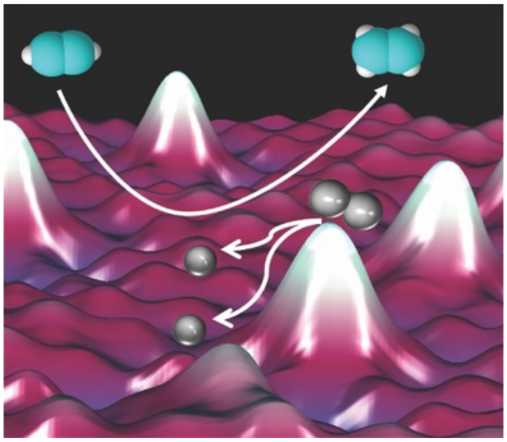
In this talk I will discuss a new class of heterogeneous catalysts called *Single-Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.[1-7] These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between atomic-scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. In collaboration with Maria Flytzani-Stephanopoulos these concepts derived from our surface science and theoretical calculations have been used to design *Single-Atom Alloy* nanoparticle catalysts that are shown to perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective hydrogenation and dehydrogenation reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis (Oxford University) and Michaelides (Cambridge University) that predicts reactivity trends for a wide range of *Single-Atom Alloy* combinations for important reaction steps like H-H, C-H, N-H, O-H, and CO_2 activation. Overall, I hope to highlight that this combined surface science, theoretical, and catalyst synthesis and testing approach provides a new and somewhat general method for the a priori design of new heterogeneous catalysts.



Scanning tunneling microscope (STM) image showing atomically-dispersed palladium atoms in a copper surface. The palladium atoms activate hydrogen enabling the industrially important acetylene-ethylene conversion with 100% selectivity.

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Invited Talk 3

Understanding Electrochemical Stability of Interfaces: RuO_2(110) Corrosion and N-doped Graphene as a Stable Adsorption Template

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Many important chemical and biological processes occur at solid–liquid interfaces. Using three case studies, this talk will demonstrate how APXPS, complemented with other techniques, can be applied to probe these complex interfacial environments.

First, oxide surfaces often show dynamic behavior at their active sites. This is exemplified by the competitive adsorption of formic acid and water on TiO_2(110). Formic acid dissociatively adsorbs to form a strongly bound bidentate formate–hydroxyl pair, thought to contribute to the surface's hydrophobicity, yet the formate species can be readily displaced by water already in the medium-vacuum range [1].

A second example highlights oxide stability under electrochemical conditions. RuO_2, an isomorph of rutile TiO_2, is a highly active oxygen evolution reaction catalyst but is unstable during operation. Using APXPS, we examined RuO_2(110) in 0.1M H_2SO_4 and observed, for the first time, the in-situ formation of dissolved Ru ions once the oxygen evolution potential was reached.

Finally, to achieve stable and conductive substrates for future studies, we are developing N-doped graphene-based materials. These can be prepared by graphite exfoliation or by chemical vapor deposition on metals, with N introduced by low-energy ion irradiation [2]. Our results show that the support (metal vs. metal-free) strongly influences the type and thermal stability of N functionalities, as well as their interaction strength, which was probed by exposure to atomic hydrogen [3]. For oxide nucleation and growth—illustrated by thermal sublimation of MoO_3 powders—N-doping plays a limited role, while the substrate effectively controls the crystallographic orientation of the oxide cluster growth. Future work will examine how these systems interact when exposed to water as a few-layer thick films first dosed at cryogenic temperatures using a molecular beam, followed by liquid water exposure to probe these systems under realistic ambient conditions.

Together, these studies highlight how interfacial chemistry, substrate effects, and material design guide the development of stable and functional catalytic surfaces.

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Invited Talk 4

Near-Ambient Pressure Oxidation of Silver in the Presence of Steps

Frederik Schiller[1], Khadiza Ali[1], Anna A. Makarova[2], Sabine V. Auras[1], Fernando García-Martínez[1], Alaa Mohammed Idris Bakhit[1], Rodrigo Castrillo Bodero[1], Ignacio J. Villar-García[3], J. Enrique Ortega[1] and Virginia Pérez-Dieste[3]

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The oxidation of Ag crystal surfaces has recently triggered strong debate around the presence of sulphur-containing, carbonates, or adsorbed dioxygen species that have all been proposed as active in ethylene epoxidation. [1-3] A significant challenge to achieve a clear understanding is the variety of procedures and experimental conditions employed in the existing studies, including the specific sample cleaning and pre-treatment, or the reactant gases purity.

Using a curved silver crystal, we investigate the oxidation of the Ag(111) surface and its vicinal crystal planes simultaneously to further examine by Ambient Pressure X-ray Photoelectron spectroscopy the surface species under oxygen atmosphere, in the temperature range of interest for ethylene epoxidation. The curved geometry allows a straightforward comparative analysis of the oxidation kinetics at different crystal facets, enabling a precise correlation of the evolution of the nucleophilic and electrophilic oxygen species and the buildup of sulphur, as a function of the crystal orientation.[4]

We observe that emission from both surface and bulk oxide contributes to the characteristic nucleophilic oxygen core-level peak, which arises during oxygen dosing and rapidly saturates below temperatures of 180 °C. The electrophilic oxygen peak appears later, growing at a slower but constant rate, at the expenses of the atomic surface oxide. On all crystal facets, the electrophilic oxygen and sulphur species evolve in parallel with each other, although they grow faster and are more prominent at vicinal surfaces featuring B-type steps with {111} microfacets.

Our study confirms the link among the formation of the electrophilic species and the presence of adsorbed SO_4, and points to a higher catalytic activity of B-type stepped silver surfaces for alkene epoxidation.

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Invited Talk 5

From bulk design to surface reactivity: Probing active site formation in Ni-based CO_2 methanation catalysts using soft and hard X-ray spectroscopies

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CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is of significant environmental interest as a sustainable pathway for energy production and storage [1]. Ni-based catalysts are widely used in this reaction due to their low cost and high CH_4 selectivity. These systems typically consist of nanoscale Ni particles dispersed on high-surface-area oxide supports such as Al_2O_3, SiO_2, or CeO_2. The support plays a crucial role in controlling Ni particle dispersion, morphology, and stability through metal–support interactions. However, stabilizing Ni nanoparticles under reaction conditions remains challenging, as they tend to agglomerate, leading to performance degradation. In this context, exsolution, a high-temperature process that drives metal nanoparticles initially dissolved in the parent oxide to emerge at the surface, has gained attention as a way to create strongly anchored particles with improved resistance to sintering [2].

In this presentation, we focus on Ni-doped CeO_2 and $LaNiO_3$ perovskite as precursors that, upon thermal activation, form the active surface phase [3-5]. To gain insight into the structural and chemical evolution of these materials, we employ a combination of advanced *in situ* and *operando* spectroscopic methods, across a wide pressure range (from mbar to bar) and probing depths (from nm to µm), conducted at five European synchrotron facilities. These include ambient-pressure soft and hard X-ray photoelectron spectroscopies and absorption spectroscopies (*static* and *time-resolved* APXPS, HAXPES and XAS). This multi-technique approach allows us to directly monitor critical surface transformations during activation and under working conditions. Notably, we identify a highly active ionic Ni species, previously unrecognized in CO_2 methanation, which exhibits significantly higher mass-specific activity than conventional metallic Ni. We also investigate the influence of thermal treatments under controlled oxidative and reductive atmospheres on the formation and stability of the active catalytic phase. Overall, this talk highlights the critical role of an integrated operando approach, combining multiple probing depths and pressure regimes, in uncovering structure–function relationships, with the goal of guiding the design of next-generation Ni-based catalysts for efficient and durable CO_2 methanation.

Invited Talk 6

AP-XPS Studies for the Transformation of CO_2 and CH_4 on Inverse Oxide/Metal Catalysts

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Inverse oxide/metal catalysts have proven to be excellent systems for studying the role of the oxide and the oxide-metal interface in catalytic reactions [1-4]. To prepare these materials, different methods (physical or chemical vapor deposition, impregnation, coprecipitation, etc) have been proposed to disperse nanoparticles of oxides on metals [1]. As a consequence of strong oxide-metal interactions, oxide phases which are not seen, or are metastable, in a bulk oxide become stable in an oxide/metal system, opening the possibility for new chemical properties [1]. Using these systems it has been possible to explore in detail correlations between the structural, electronic and catalytic properties of oxide-metal interfaces and obtain a fundamental understanding of factors which determine catalytic performance in reactions useful for the synthesis of methanol by hydrogenation of CO_2 or the partial oxidation of CH_4 [1,3,4]. Characterization strategies that combine AP-XPS (chemical state and surface chemistry) with scanning tunneling microscopy (structure and morphology) and catalytic testing (activity and selectivity towards methane formation) will be discussed [1-4].

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Invited Talk 7

Model Catalysts Under Operando Conditions: Oxidation Dynamics and Beam-Induced Artifacts

Héloise Tissot,[1]* Michele De Rocco,[1] Beniamino Sciacca,[2] Jean-Jacques Gallet,3 Fabrice Bournel,3 Francois Rochet,[3] Sylvain Cristol,[1] Pardis Simon[1], Chunlei Wang,[4] Jonas Weissenrieder,[4] J.F. Paul.[1]

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Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) has emerged as a powerful tool for studying heterogeneous catalysts under operando conditions, bridging the pressure gap between ultra-high vacuum surface science and realistic reaction environments. However, the interpretation of NAP-XPS data requires careful consideration of both the chemical processes of interest and potential X-ray beam induced effects that can complicate the true surface chemistry.

This presentation explores surface oxidation dynamics in Cu_2O model catalysts, progressing from well-defined single crystal $Cu_2O(100)$ surfaces to size-controlled nanocubes (12-300 nm) exposing the same crystallographic facet. Single crystals provide fundamental insight into the oxidation mechanism, where O_2 exposure initially increases surface hydroxyl group coverage (due to trace moisture in the reaction gas), followed by Cu_2O-to-CuO conversion at 1 mbar. Nanocubes synthesized via aqueous methods reveal size-dependent effects: below 50 nm, we observe significant changes in oxidation temperatures.

A critical aspect of this work addresses beam-induced artifacts in NAP-XPS measurements. Synchrotron experiments (750 eV) showed Cu_2O nanocubes oxidation at room temperature with CuO desorption at 450 K, whereas laboratory XPS (1486 eV) required 600 K for oxidation without desorption even at 770 K. X-ray irradiation can drive unintended chemical transformations that may be misinterpreted as intrinsic catalytic behavior. We present systematic studies of beam damage effects not only in Cu_2O but also in other model systems including Co nanoparticles supported on silica and sodium halide aqueous solutions. These comparative studies reveal common patterns and system-specific vulnerabilities to beam damage, providing practical guidelines for distinguishing genuine chemical dynamics from experimental artifacts.

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Invited Talk 8

Dual Insights from a Single X-ray Beam: Simultenously AP-XPS and GIXS Measurements on Nanopattered Ceria in Hydrogen

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Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) is the workhorse for in situ surface chemistry, yet it seldom captures the simultaneous structural response that governs function. I will present a single-beam approach that records AP-XPS and grazing-incidence X-ray scattering (GIXS) concurrently from the same illuminated area, eliminating run-to-run variability and enabling direct correlation of chemical state, electron density, and nanoscale morphology under reaction conditions. Applied to model ceria under H_2 and H_2+CO_2, the dual readout resolves three coupled trends: (i) subsurface hydrogen uptake (hydride/oxyhydroxide signatures in Ce 4d and O 1s), (ii) increases in electron density tracked via the ceria–Si relative critical angle, and (iii) reaction-induced roughening with essentially unchanged external height. These correlations show how hydrogen incorporation and re-oxidation by CO_2 reshape both the surface & near-surface chemistry and the scattering response, revealing relationships that AP-XPS (or any other spectroscopy) alone can miss.

I will outline the analysis workflow clarifying which observables are safely transferable across measurement sets. Practical aspects of sample design, gas handling, and fitting strategy will be summarized.

Together these advances aim to generalize this single-probe, dual-insight methodology from ceria to broader families of reducible oxides and supported catalysts, making AP-XPS a truly chemical-and-structural in situ & operando tool for materials chemistry. I will close with future prospects for this novel platform.

Contributed Talk 1

Combining experimental design and software based image recognition for operando APXPS electrode/electrolyte interface potential probing

Qianhui Liu[1], Laura King[1], Helena Wagner[2], Tove Ericson[1], Robert Temperton[3], Maria Hahlin[1,2]

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Probing the electrode/electrolyte interface with operando APXPS in the dip-and-pull setup remains large challenges on 1) looking for an electrolyte with suitable vapor pressure, 2) searching for an interface region with a liquid layer thinner than the XPS probing depth, in the meantime, 3) probing at an electrochemically active interface. Apart from the fundamental challenges, the experimental uncertainties on the liquid layer variation over time, space, and irradiation effect amplifies the difficulties on operando interface probing.

In this work, an efficient interface probing methodology is realized through experimental design combined with advanced data processing. Scanning APXPS is employed with programmed route periodically probing across the dry-wet boundary near the top edge of the liquid layer to capture the interface spectroscopic feature (Figure 1a). To distinguish and select the interface-featured spectra from the mixed signals of dry-solid and thick liquid region, software based spectroscopic recognition are developed including two methods 1) intensity attenuation recognition which distinguish the interface-featured spectra from the intensity attenuation pattern of the electrode peaks when scanning across different regions 2) potential recognition which selects the interface-featured spectra by its BE shift pattern over the height in the meniscus.

Further by translating the relative intensity of the electrode and electrolyte peaks into liquid thickness through equation, a spectro-microscopic image of the liquid distribution (Figure 1b, c) with topographical resolution is obtained. Combining with the spectral energies and chemical distribution information, it sees strong correlation between the energetics/potential and the liquid layer thickness of the probing position, which is suggested to do with the EDL potential drop in the probed region (Figure 1d). In addition, the variation of the chemical composition of the electrode (lithiation, etc) in the vertical direction in the meniscus also highly affects the electron energetics, showing as BE shifts in the spectra.

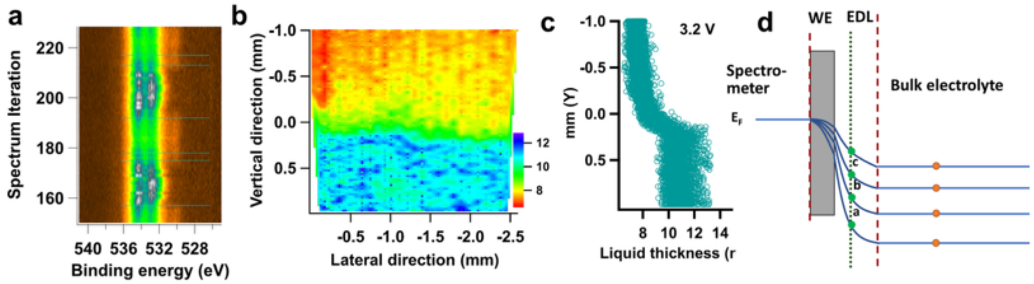

Figure 1 a) Heatmap of O 1s spectra from a Lithium cobalt oxide (LCO) WE system probed with scanning APXPS routinely across the dry/wet boundary of the liquid edge. b) Spectro-microscopic imaging of the liquid distribution with topographical information and c) its side view, and d) schematic illustration of interface potential at different applied voltages.

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Contributed Talk 2

Advancing the *operando* study of ALD chemistry with time-resolved ambient pressure x-ray photoelectron spectroscopy

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The cyclic nature of thin film growth using atomic layer deposition (ALD) provides an especially interesting testbed for extracting useful time-resolved information on the exact role of the surface states during the deposition process. Ambient pressure x-ray photoelectron spectroscopy (APXPS) allows acquiring such surface sensitive data on many ALD processes. Combining APXPS data acquisition with advanced time-resolved data analysis techniques enables obtaining accurate time-resolved data on the deposition mechanisms from the raw oscillatory surface data. By averaging data from several ALD cycles together it becomes possible to resolve information from the data even with low signal-to-noise ratio. Another advanced data analysis technique is treating it by using Fourier transform (FT) analysis which allows to focus only on the oscillating (changing) portion of the surface data.

Data averaging or FT approaches are commonplace in many techniques, but in XPS analysis, they have only seen limited use. Here, we apply these techniques to study the growth of TiO2 using titanium(IV) isopropoxide (TTIP) and H2O process, which is a well-understood and -studied method. The TiO2 films were grown on Si substrates with native oxide. With APXPS we can make continuous XPS measurements on interesting surface core levels and plot such data as a function of time. After the initial deposition is done, the created film is thick enough to completely obscure the bulk signal when measuring XPS with high surface sensitivity. Therefore, in this so-called steady-growth regime, the XPS signals are completely reversible from one ALD cycle to another, allowing to sum together the data from many cycles in order to increase the signal-to-noise ratio, or to use FT methods.

This study focused on the Ti 2p, O 1s, and C 1s core level which are all measured at a photon energy which yields high surface sensitivity. In addition, the Si 2p core level was used to confirm the disappearance of the bare substrate signal. We have recorded XPS continuously while pulsing the TTIP and H2O precursor into the experimental setup with a specific pulsing pattern. The data from several ALD cycles was later averaged together, in order to probe weaker signals that are not typically visible in just one ALD cycle due to low statistics. In addition, by taking a special look into the gas phase products just above the substrate surface using XPS, it is possible to identify minority, short-lived, products that are not possible to detect with other methods. For example, we can identify residual water vapour signal after the TTIP half-cycle which coincides with a changed surface chemistry and is therefore at a slightly different binding energy. Furthermore, clear signals from the intact TTIP molecule from the -O-CH, methyl, and -OCH= components in the O 1s and C 1s regions can be seen.

The FT analysis allows us to further dive into the data to obtain more detailed information. For example, the FT analysis on the C 1s region only shows the components which oscillate with time, e.g. the methyl and -OCH= components which get adsorbed on the surface and removed with each TTIP water half-cycle, respectively. FT analysis neatly removes any surface contamination peaks from the C 1s region, because they are constant and do not oscillate with time. Similarly, the O 1s spectra show the TiO2 peaks that oscillate out of phase with each other i.e. with each TTIP and H2O pulse, respectively.

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Contributed Talk 3

Plasma XPS: The Origins of Binding Energy Shifts at the Plasma-Exposed Metal and Dielectric Samples and in the Gas Phase

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In-plasma X-ray photoelectron spectroscopy (plasma-XPS) emerges as a powerful platform for real-time, in operando chemical analysis under conditions relevant to semiconductor processing and other plasma-enabled technologies [1]. In previous work [2], we highlighted the influence of plasma chamber wall reactions on sample surface chemistry and showed that plasma-XPS can capture plasma chemistry both on the sample and in the gas phase.

In this study, we investigate the origins of binding energy (BE) shifts and the formation of "satellite" peaks observed during plasma-XPS measurements across conductive, dielectric, and gas-phase systems. Using a standard laboratory-based APXPS apparatus with an attached AC-driven capacitively coupled plasma source, we show that metastable surface species that are hardly accessible using conventional UHV XPS can now be detected during plasma exposure. In dielectric samples, we observe unomaleous pressure- and plasma-type-dependent BE shifts up to >60 eV. Additionally, we noted plasma-induced binding energy shifts and peak splitting when measuring XPS from the plasma gas phase. The mechanisms that explain these shifts have been proposed.

Overall, plasma XPS metrology is a new, powerful analytical capability and yet a largely unexplored application space for the APXPS community. It's particularly valuable in fields like semiconductor fabrication and defects mitigation [3], biomedical treatments, aerospace applications, and new materials synthesis.

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Contributed Talk 4

Facet-Resolved Insights into NiAg Single-Atom Alloys by Ambient-Pressure XPS: Linking Oxygen Speciation to Selective Oxidation

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Silver is the benchmark catalyst for selective ethylene epoxidation, yet its performance relies heavily on chlorine and other promoters to increase selectivity. Recent studies showed that incorporating isolated Ni atoms into Ag(111) lowers the barrier for O_2 activation and enables chlorine-free ethylene oxide formation. To better understand NiAg nanoparticles, which exhibit high epoxide selectivity without additional promoters, we employ ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) to probe how Ni alters oxygen speciation and reactivity across different Ag facets and oxidation reactions.

Under simulated ethylene-epoxidation conditions on NiAg(100), Ni stabilizes higher oxygen coverages and coexisting carbonate species relative to Ag(100) under reducing ethylene feeds, demonstrating that the promotional effects of Ni are not confined to the (111) facet. To test whether these effects extend to other oxidation chemistries, we examined methanol partial oxidation on NiAg(111). AP-XPS reveals a broader distribution of reactive intermediates than on Ag(111), including methoxy, carbonate, and subsurface oxygen species. Enhanced methoxy formation on NiAg suggests a Mars–van Krevelen-type mechanism in which subsurface oxygen directly participates in selective formaldehyde production and is replenished by molecular oxygen from the gas phase.

Together, these results demonstrate that Ni fundamentally alters oxygen activation and consumption on Ag in both ethylene epoxidation and methanol oxidation. By directly comparing NiAg(100) and NiAg(111), we show that Ni stabilizes unique oxygen states absent on pure Ag, enabling higher oxygen coverages and the formation of key intermediates such as methoxy. This study on two Ag facets establishes NiAg as a versatile model system for selective oxidation catalysis and highlights the value of AP-XPS in quantifying reactive oxygen species under near-ambient conditions.

Contributed Talk 5

Disentangling the Role of Octahedral Fe Carbides in Fischer-Tropsch

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The Fischer-Tropsch synthesis (FTS) is the conversion of syngas (CO and H_2) to hydrocarbons, e.g., for synthetic fuels.[1] When using Fe as a base catalyst material, the process relies on the formation of carbides as active phase during the reaction.[2] However, several different carbide phases, structurally classified into trigonal prismatic and octahedral carbides, have been reported to be active during the conversion.[3] Their coexistence complicates assessing the activity of each species and their exact role in FTS. *In situ* X-ray photoelectron spectroscopy is uniquely poised to study adsorbate distribution and surface carburization with full sensitivity to both ordered and non-ordered structures, as opposed to Mössbauer spectroscopy and X-ray diffraction, which are often used due to their compatibility with industrial pressures.[4]

Based on previous work of our group, we hypothesized an octahedral carbide species to be more active than anticipated in literature. By following carbide formation on Fe(110) in reaction mixture of 3:1 H_2:CO at 600 K and 500 mbar (conditions that thermodynamically favor growth of trigonal prismatic carbides)[5], we were able to discern octahedral carbides as a short-lived species, preceding the evolution of other carbides (Figure 1a). Moreover, when removing CO from the gas stream, our data suggests that the octahedral carbides are also active in the hydrogenation step of the reaction (Figure 1a), whereas the trigonal prismatic carbides are hydrogenated away independently of the hydrocarbons (Figure 1b, c). Contrary to reports of trigonal prismatic carbides being of highest importance as active phase for Fe-based FTS[5], we could reveal octahedral carbides to play a central role, both in the carbide formation and in the hydrogenation steps.

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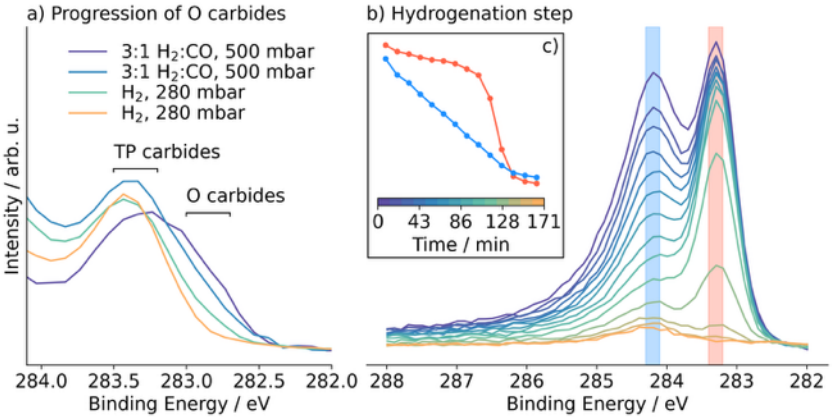

Figure 1. X-ray photoelectron spectra of the C 1s core level in FTS reaction conditions. a) compares spectra (carbide region only) recorded at start and end of carbide formation and hydrogenation steps of FTS, respectively (TP: trigonal prismatic, O: octahedral); b) shows how the trigonal prismatic carbides (red) and the adsorbate hydrocarbons (blue) disappear in a hydrogen atmosphere; c) shows the temporal progression of both species marked in b).

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Contributed Talk 6

Surface-Dependent Re-Solvation of Cyanocobalamin: an *In Situ* Spectroscopic Study on Au(111) and Graphene/Ir(111)

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A biomimetic approach based on 2D metalorganic frameworks (MOFs) proved to be extremely attractive towards the design and synthesis of new functional materials for applicative purposes in various fields [1]. While lateral interactions and ligation in 2D tetrapyrrolic layers have been recently investigated [1-2], the second coordination sphere has not been addressed yet. Its role cannot be disregarded since the hosting cage contributes to both selectivity and stability [3]. Cyanocobalamin (vitamin B12) was selected as a model system to tackle the role of *trans* and second coordination at non-interacting surfaces, specifically graphene/Ir(111) and Au(111). To prevent thermal degradation, deposition was carried out in UHV exploiting ESIBD [4]. A re-solvation experiment was conducted *in situ* at approximately 1 mbar of water pressure at room temperature. When exposed to water, the B12 molecule behaves differently when in contact with the hydrophobic graphene or with the more strongly interacting gold substrate. In the latter case, AP-XPS [5] reveals that water molecules replace the residual ethanol solvent, promoting the rearrangement of cyanocobalamin, which swells up. In contrast, on graphene/Ir(111), the inherently hydrophobic character of graphene prevents re-hydration of the layer. PM-IRRAS [5] measurements further support the conclusions drawn from photoemission experiments with several vibrational modes of the B12 molecule becoming clearly visible on Au(111) at NAP upon re-hydration, corresponding to the CH_2 twisting, C-N and C-C stretching of the corrin ring, H_2O and amide bending modes.

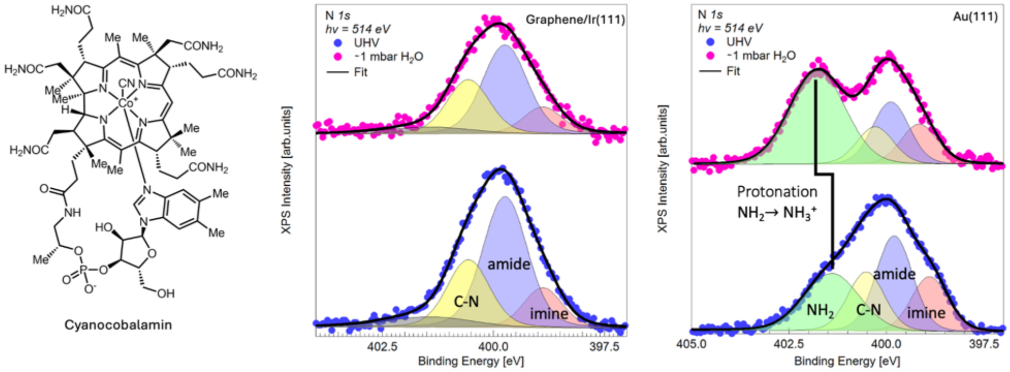

Figure 1: on the left, skeletal formula of cyanocobalamin; in the middle, N1*s* core level of cyanocobalamin on graphene/Ir(111) in UHV (blue) and at 1 mbar H_2O (pink); on the right, N1*s* core level of cyanocobalamin on Au(111) in UHV (blue) and at 1 mbar H_2O (pink).

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Contributed Talk 7

NAP-XPS study on O-conducting membrane surfaces: Understanding the surface O-exchange mechanism

Abhinav Saxena[1,2], Genrikh Shterk[2], David N. Mueller[1], Heinrich Hartmann[1], Christoph Baeumer[2], Astrid Besmehn[1], Stefan Baumann[1], Wilhelm Albert Meulenberg[1,2], Leon Lefferts[2]

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Oxygen conducting membranes(OCMs) are widely studied due to their dual functionality i.e., O-separation from a gaseous mixture and the ability to convert gaseous reactants (CO_2, H_2O etc.) via corresponding O-exchange to produce valuable feed stocks[1]. One of the key steps in designing high performance OCMs lies in understanding the O-exchange mechanism at the solid-gas interface. Ambient pressure-X ray photoelectron spectroscopy (AP-XPS) has already been successfully applied to study such interfaces by virtue of its potential to determine the surface chemical state under operando conditions[2]. In this work, Co-doped $SrTiO_3$ (STC) - a promising model OCM[3] is investigated for surface O-exchange under varying gas atmospheres (i.e. O_2, CO_2 & H_2O) at temperatures up to 500°C. O1s spectra reveal the dynamic formation and decomposition of intermediate/adsorbates, corroborated by Sr3d and Co2p signatures associated with their respective compounds with these intermediates/adsorbates. Under CO_2 atmosphere, C1s and O1s confirm the transient formation of carbonate intermediate, which decomposes at elevated temperatures in parallel with a distinct change in the gas-phase. This transformation is consistent with CO_2-thermal programmed oxidation (CO_2-TPO) results and is therefore proposed to be one of the proprietary steps in a reverse Mars Van Krevelen type O-exchange during CO_2 to CO conversion. In contrast, exposure to O_2 atmosphere yields stable surface oxo species that remain intact and increases even at the highest investigated temperatures, as evidenced by persistent O1s signals. Notably, interaction with steam reveals low thermal stability of hydroxyls, as evidenced by O1s and associated hydroxides (with Sr and Co). Parallel studies on Co-free system are underway to elucidate the dopant's role in mediating surface O-exchange.

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Contributed Talk 8

In Situ and Operando Characterization of Electronic and Chemical States of WO_3 During Electrochemical Proton Intercalation

Jay R. Paudel[1,2], Aaron J. Kaufman[1,2], Nikos Papamatthaiakis[3], James R. McKone[4], Giannis Mpourmpakis[3,4], Ethan J. Crumlin[1,2]

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Proton intercalation in oxide materials is central to numerous technologies, including chemical sensing, hydrogen storage, battery electrodes, and electrochromic devices. Tungsten trioxide (WO_3) is a particularly attractive host due to its structural stability and reversible proton uptake, forming tungsten bronzes that play an active role in the hydrogen evolution reaction (HER). Although proton-coupled electron transfer (PCET) is expected to significantly alter the electronic structure of WO_3, direct observations of its chemical and electronic state evolution during intercalation and HER remain limited. In this work, we employ *in situ* and *operando* ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) to track the electronic and chemical transformations of WO_3 during proton intercalation and HER under applied reducing potentials. Our results show that PCET governs the intercalation dynamics, with progressive reduction of tungsten driven by electron transfer, followed by proton incorporation into lattice oxygen sites to form hydroxyl species. Depth-resolved XPS further reveals that these intercalated species extend into the subsurface, demonstrating that proton intercalation in WO_3 is a bulk phenomenon. Under sufficiently negative potentials to drive HER, we find that proton intercalation precedes gas evolution, and the reduced tungsten bronze phase serves as the active host, involving surface-adsorbed and/or intercalated species. Complementary first-principles DFT calculations corroborate that the emergence of reduced W electronic states originates from the PCET mechanism. Collectively, this work elucidates the fundamental mechanistic pathway of proton intercalation in transition metal oxides under realistic operating conditions.

Keywords: Proton intercalation, solid-liquid interface, oxide materials, ambient pressure photoelectron spectroscopy (APXPS), materials characterization

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Contributed Talk 9

Chemical analysis of passive layers of multicomponent CrFeMnCoNi(C) during electrochemical oxidation

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Corrosion is a destructive attack of a metal due to reactions with its environment, which converts a refined metal to a more chemically stable form such as oxides or hydroxides. Corrosion causes problems for construction materials as well as in electrochemical devices that operate in a corrosive environment. Adding a thin protective coating can enhance the corrosion resistance while keeping the materials mechanical properties. In this work, the focus is sputter-deposited thin coatings of the multicomponent material CrMnFeCoNi(C), where all metals are in near-equiatomic ratios. The material is similar to stainless steel regarding the high concentrations of Cr, Fe and Ni. In stainless steel, Cr forms a thick and stable oxide that enhances the corrosion resistance. While this is likely to happen also in CrMnFeCoNi(C), the effect of the other metals is the focus of this work.

We combine electrochemistry with photoelectron spectroscopy both ex-situ using soft x-ray PES and in-situ using AP-XPS. In this way can features in the linear sweep voltammogram be related to changes in oxidation state, oxide formation and metal dissolution. Different photon energies are used to distinguish the outermost surface oxide from the metal/oxide interface. Samples with different carbon content are compared, as well as corrosion in different acetic media.

The results show that the native oxide is rich in Mn, while Cr is the dominating element after 40 min in open circuit conditions in acetic media. After polarizing to positive potentials of 1.4 V vs Ag/AgCl, the surface chemical composition depends on the acidic electrolyte, where Cr dominates the oxide formed in H_2SO_4, while Mn dominates the surface oxide formed in HCl with higher oxidation state at the outermost surface. With this knowledge, it is possible to tune the material composition as to optimize for a certain corrosive environment.

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Contributed Talk 10

Understanding corrosion of TiCN in acidic and alkaline environments: a route to produce corrosion resistant coatings

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Titanium carbides and nitrides are known for their low contact resistance and high hardness, making them suitable for coating applications. Combining these two materials into carbonitride (TiCN) would lead to high corrosion resistance and high conductivity. This material can play a significant role as a coating material for bipolar plates (BP) in fuel cells. These components are located between Membranes Electrons Assembly (MEA), where the oxido-reduction reactions take place. This harsh environment risk corroding the BP, leading to a decrease of the fuel cell performance, hence the need of a corrosion resistant protective coating. For this purpose, further information on the corrosion of TiCN are needed. In this study, we accelerate the corrosion reaction by performing electrochemical measurements in acidic and alkaline conditions, to simulate the harsh environment in a fuel cell.

By performing electrochemical and XPS measurements within the same ambient-pressure chamber, we have followed the evolution of the passive film over a defined potential range. Using the dip-and-pull method, each current step can be directly correlated with the corresponding oxidation state. Results from in-vacuo measurements at the HIPPIE beamline (MAX IV) show differencies in the evolution of the oxide layer when the sample is exposed to acidic (0.05M HCl) and alkaline solution (0.05M NaOHl). A reduction of the native oxide is observed in the N1s core level spectrum after simple exposure to both acidic and alkaline solution (OCP - figure 1b, 2b). However, in alkaline conditions, a nitrogen oxidation starts already at -0.19V vs Ag/AgCl, indicating the formation of a new passive film (figure 2a,b). Whereas in acidic solution, this increase is observed only at potentials above +1.00 V vs Ag/AgCl (figure 1a,b). Further interpretation of other core-levels spectra will be presented.

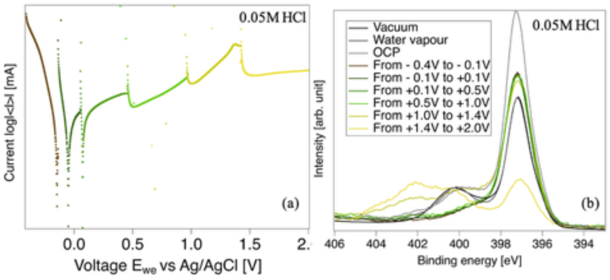

Figure 1 (a) Potentiodynamic curve of TiCN in 0.05M HCl. (b) N1s core level spectrum before and after electrochemical treatment.

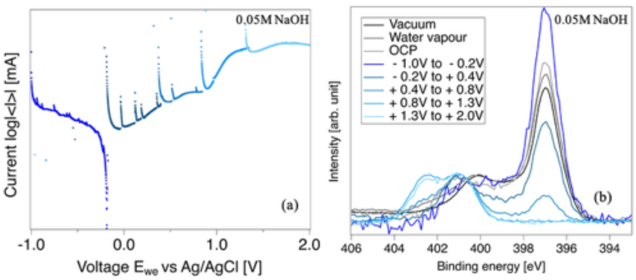

Figure 2 (a) Potentiodynamic curve of TiCN in 0.05M NaOH. (b) N1s core level spectrum before and after electrochemical treatment.

Contributed Talk 11

Complexity at a Humid Interface: Throwing Fresh Light on Atmospheric Corrosion

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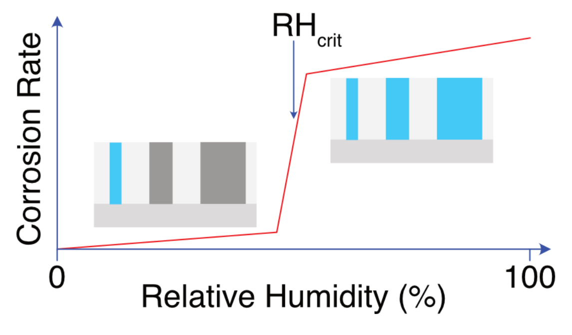

Cartoon showing capillary condensation in channels through the adventitious carbon layer covering the zinc substrate as a function of relative humidity. RH$_{crit}$ indicates the critical relative humidity for the onset of atmospheric corrosion.

Atmospheric corrosion of metals arising from exposure to water vapour is a pervasive problem across a wide range of practical scenarios, including nuclear material storage and historical artifact conservation. Frequently, it is hypothesised that this phenomenon becomes an issue once the number of monolayers of water growing atop a substrate is sufficient to facilitate corrosion chemistry, but supporting evidence remains scarce. In this study, near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and vibrational sum frequency spectroscopy (VSFS) have been employed to provide fresh insight into the onset of atmospheric corrosion through examining the interaction of water vapour with zinc, a common engineering substrate for corrosion protection applications. XPS data demonstrate that prior to water exposure the zinc substrate is terminated by a layer of zinc oxide/hydroxide topped by adventitious carbon; formation of the latter layer is essentially inevitable upon exposure to the atmosphere. O 1s NAP-XPS core level spectra acquired as a function of relative humidty indicate that the quantity of surface sorbed water varies with this parameter, but that a simple layer-by-layer growth model is not an appropriate description. Instead, it is concluded that water sorption occurs through capillary condensation in channels through the adventitious carbon layer. VSFS spectra are consistent with this water uptake model, and variation in signal intensity with relative humidity suggests a distribution of channel sizes. Consequently, it is argued that the onset of corrosion coincides with the filling of channels in the adventitious carbon layer that are large enough to facilitate corrosion chemistry. Besides providing a step change in our understanding of atmospheric corrosion, this study suggests that the role of adventitious carbon should not be overlooked as potential key factor in other interfacial phenomena.

Contributed Talk 12

Low-Temperature methane activation pathways on inverse ball milled CeO_2/CuO catalyst: a combined *in situ* DRIFT and ambient pressure *operando* NEXAFS study

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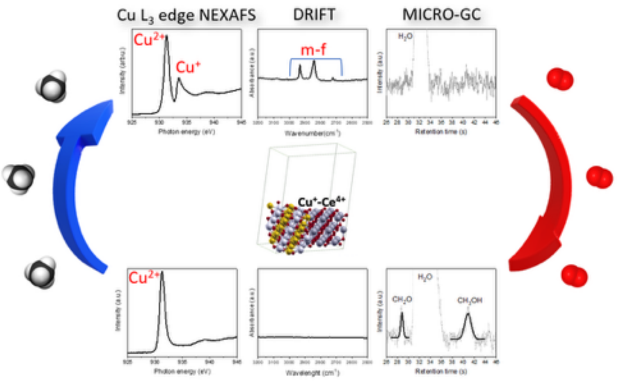
Methane (CH_4) is increasingly recognized as a valuable resource, and its selective conversion into partial oxidation products like methanol (CH_3OH) is a key goal in the energy transition. Among emerging catalysts, the "inverse" CeO_2/Cu(111) system has shown promising CH_4 to CH_3OH conversion with high selectivity, attributed to an active Cu_2O monolayer at the CeO_2–Cu interface[1]. However, while this remains a model system, its translation to real-world, industrial-grade catalysts is still a distant prospect. In this work [2], we tried to mimic the properties of the CeO_2/Cu(111) model system, exploiting a simple, scalable, and green synthetic route—ball milling—to produce an inverse CeO_2/CuO composite capable of activating methane at 250 °C. Combining *in situ* DRIFT spectroscopy, *operando* ambient pressure Soft X-ray NEXAFS, and DFT calculations, we were able to link the catalytic activity to interfacial Ce^{4+}/Cu^{+} redox pairs. These are formed via charge transfer from Ce^{3+} defective surface sites to Cu^{2+} atoms, driven by mechanical energy during synthesis. DRIFT analysis reveals methane chemisorption as oxidation intermediates (mainly methoxy and formate species), while 1bar NEXAFS shows partial reduction of Cu^{2+} to Cu^{+}. Upon exposure to an oxidizing agent, gas-phase products—CO_2, H_2O, CH_2O, and CH_3OH—are released, as detected by micro-GC connected to the *operando* NEXAFS cell at the APE-HE beamline of Elettra Synchrotron [3]. NEXAFS spectra continuous fast acquisition shown that this oxidative step restores the catalyst's original electronic structure, enabling multiple catalytic cycles without deactivation. Spectroscopic data under real reaction conditions, supported by DFT modeling, identify the active sites as oxygen atoms near the CeO_2/CuO interface, responsible for CH_4 activation. These findings validate the ball milling approach for generating functional interfaces and highlight CeO_2/CuO composites as promising candidates for methane valorization.



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Contributed Talk 13

In situ AP-sXAS observation of charge transfer in the cocatalyst-loaded $SrTiO_3$ photocatalyst for water splitting under UV-Vis irradiation

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We developed an *in situ* observation system for photoinduced surface phenomena under ambient pressure conditions based on the soft-X-ray absorption spectroscopy (AP-sXAS). We applied this technique to *in situ* observation for photoinduced hole transfer in a highly efficient photocatalyst, Al-doped $SrTiO_3$ (STO:Al), with co-catalysts, Rh/Cr_2O_3 for hydrogen evolution reaction (HER) site and CoOOH for oxygen evolution reaction (OER) site [1]. *In situ* Co L-edge AP-sXAS measurements under saturated water vapor conditions revealed that UV-Vis irradiation readily induces oxidation of Co in the CoOOH OER site, which provides evidence for photoinduced hole transfer from the STO:Al to the OER site [2]. Interestingly, without loading the Rh/Cr_2O_3 HER site, or without introducing water vapor, no photoinduced hole transfer to the CoOOH OER site takes place. Coexisting of the Rh/Cr_2O_3 HER site and water vapor on the STO:Al surface is crucial to the hole transfer to the OER site under photoirradiation.

We also measured the chemical-state evolution in Co under working conditions to track the electron and hole transfer to the CoOOH cocatalyst in Rh/Cr_2O_3–CoOOH/STO:Rh,Sb photocatalyst system, where Rh and Sb are doped into the STO resulting in visible light (> 400 nm) absorption as well as UV light (< 400 nm) absorption. We found that the type of charge carrier transferred to the CoOOH cocatalyst is switched by the excitation-light wavelength; holes for UV light and electrons for visible light as seen in the figure [3]. Remarkably, the photocatalytic activity disappears under visible light irradiation, although the visible-light photons are readily absorbed by the photocatalyst. We propose a possible scheme of charge transfer and consumption processes which is likely related to the water splitting activity.

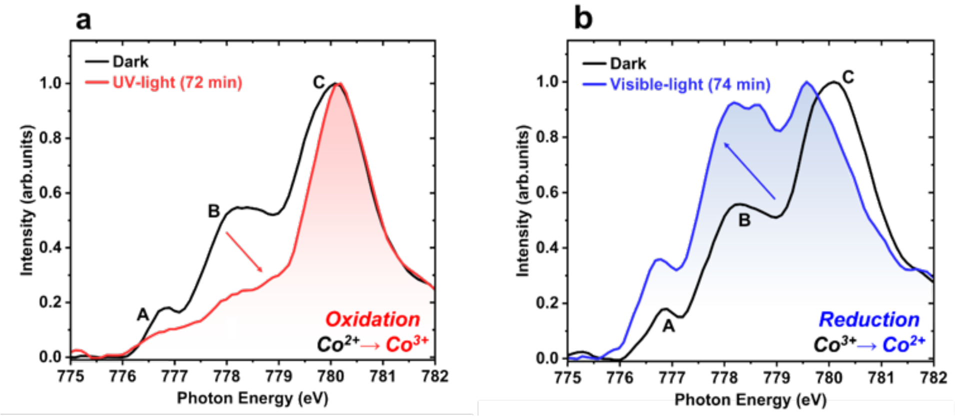

Figure: Co-L_3 edge AP-sXA spectral changes of the CoOOH cocatalyst surface on STO:Rh,Sb under the UV-light irradiation (a), under the visible-light irradiation (b).

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Contributed Talk 14

Oxidation of Transition Metal Alloys Studied with AP-XPS and XPEEM

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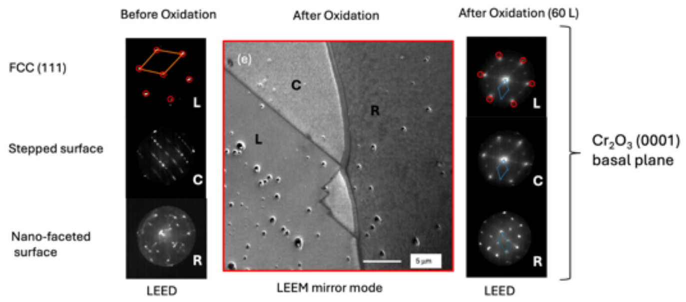
Understanding the oxidation and corrosion of alloys is critical to limiting materials degradation and inform alloy design. The properties of the oxide are modulated by alloy composition, microstructure and environmental parameters and best passivity is achieved with dense oxides such as chromia. Our work targets the initial reaction steps in the conversion of the alloy surface to oxide. We study alloys with increasing levels of complexity from dilute alloys (Ni-Cr, Ni-Cr-Mo/W) to microstructures with intermetallic precipitates ($Al_{0.3}Cr_{0.5}Fe_2Mn_{0.25}Mo_{0.15}Ni_{1.5}Ti_{0.3}$). The reaction conditions are in a regime where thermodynamic preferences and kinetic limits are intertwined and competing reaction pathways impart compositional, electronic, and structural heterogeneity.

AP-XPS and XPEEM experiments were used to observe the reaction sequence with time and spatial resolution to understand what promotes or inhibits the formation of passive dense oxides. The third element effect where small amounts of Mo/W promote chromia formation was studied with AP-XPS and DFT using alloys with varying composition and showed the competition between different oxides. It was discovered that preferential O adsorption at W-Cr sites lowers the chromia nucleation barrier and an additional microstructural contribution from grain boundary diffusion is likely. XPEEM studies in operando mode exploited the combined spatial and time resolution and unlocked a direct view of the chromia nucleation as a function of crystallographic orientation. The transition to a layer growth is evident in the Ni-Cr-Mo alloy (Figure 1). XPEEM was also used to capture the oxidation, and oxide heterogeneity on the two phase alloy and separated the oxidation reaction on the nanoscale. The two phase structure of the alloy is imprinted on the oxide and the sharp interface is retained. The XPEEM studies used several imaging and spectroscopic modes (XAS, mirror mode and diffraction) and necessitated implementation of new methods for image alignment, segmentation, and analysis of hyperspectral images.



The surface of Ni-22Cr-6Mo immediately prior to oxidation imaged with LEEM mirror mode **(a)** with corresponding LEED diffraction patterns of the **(b)** left, **(c)** center and **(d)** right grains labeled. **e** LEEM mirror mode image of the same surface region after oxidation with corresponding LEED diffraction patterns in **(f–h)**. The red circles in the LEED diffraction pattern **(b)** and **(f)** indicate the FCC (111) reflexes for the alloy, the blue rhombus in **(f–h)** indicates the Cr_2O_3 (0001) basal plane unit cell. The green crosses in **(a)** are instrument markers. Electron energy for LEED measurements was 45 eV **(b)**, and 40 eV in all other LEED patterns.

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Contributed Talk 15

AP-XPS study of supported MgO Nanostructures for Low-Temperature conversion of Methane

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Natural gas, primarily composed of methane, is a versatile energy vector with strong potential for efficient utilization. A key challenge is converting methane into valuable hydrocarbons like ethane and ethylene at low temperatures without catalyst deactivation. MgO nanostructures, known for their unique surface properties, and Cu-based catalysts, which enable selective methane oxidation at reduced temperatures, show promise for this transformation.

This study investigates MgO nanostructure growth and reactivity on Au(111) and Cu_2O/Cu(111) substrates using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and scanning tunneling microscopy (STM). Mg deposition on the "29" structured Cu_2O/Cu(111) film facilitates oxygen transfer, forming MgO and CuO_x phases. The resulting structures include embedded MgO clusters (1–3 Mg atoms) and dispersed nanoparticles.

STM and AP-XPS reveal that MgO nanostructures (0.2–0.5 nm wide, 0.4–0.6 Å high) embedded in Cu_2O/Cu(111) activate methane at room temperature, dissociating it into CH_x ($x = 2$ or 3) and H adatoms with minimal carbon formation. At 500 K, these structures promote C–C coupling into ethane and ethylene with negligible carbon deposition and no catalyst deactivation—far outperforming bulk MgO, which requires >700 K.

Density functional theory (DFT) calculations confirm methane activation is energetically favorable on MgO/Cu_2O/Cu(111), driven by electron transfer from Cu and under-coordinated Mg and O atoms. Formation of O–CH_3 and O–H bonds lowers the barrier for C–H cleavage. Smaller Mg_2O_2 clusters show stronger binding and lower activation barriers, while larger Mg_3O_3 clusters enhance C–C coupling due to weaker $*CH_3$ binding.

To assess Cu's role, MgO was also deposited on inert Au(111), with similar XPS analysis. These findings underscore the importance of MgO nanostructure size in optimizing selective methane conversion.

Contributed Talk 16

In situ microscopy and spectroscopy study on dynamics of nanostructure in catalysis for energy

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With increasing energy demand, supplying clean and affordable energy is a critical challenge. Among various clean energy sources, hydrogen (H_2) is one of the most promising energy carriers [1]. Currently, over 95% of hydrogen is produced from steam reforming of fossil fuels. To eliminate the carbon monoxide (CO) present in product streams, the water-gas shift reaction (WGSR) is required to produce hydrogen with a high purity for ammonia synthesis and fuel cell applications [2]. Therefore, understanding the atomistic structure of the active site during catalytic reactions is of paramount importance in both fundamental studies and practical applications, but such studies are challenging due to the complexity of heterogeneous systems.

Using Pt/CeO_2 as an example, we reveal the dynamic nature of active sites during the water-gas-shift reaction (WGSR) by combining multiple in situ characterization tools to study well-defined CeO_2 nanoshapes with different exposed facets [3]. We show that metallic Pt is present on the CeO_2(111) surfaces, while oxidized Pt species are dominant on CeO_2(110) and (100) surfaces after O_2–H_2 pretreatment. AP-XPS results indicate that the different concentrations of interfacial $Pt^{\delta+} - O - Ce^{4+}$ moieties at Pt/CeO_2 interfaces are responsible for the rank of catalytic performance of Pt/CeO_2 catalysts: Pt/CeO_2-rod > Pt/CeO_2-cube > Pt/CeO_2-oct. For all the catalysts, metallic Pt is formed during the WGSR, leading to the transformation of the active sites to $Pt^0 - O_v - Ce^{3+}$ and interface reconstruction. These findings shed light on the nature of the active site for the WGSR on Pt/CeO_2 and highlight the importance of combining complementary in situ techniques for establishing structure-performance relationships.

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Contributed Talk 17

Structure and chemistry of NO over a curved Rh surface at ambient pressure

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Using a curved Rh(111) crystal in combination with ambient-pressure X-ray photoemission, we investigate the influence of Rhodium (Rh) surface steps on the nitric oxide (NO) dissociation at 0.05 mbar—a critical step in the NO reduction reaction. At 100ºC the O 1s core-level reveals that dissociation occurs exclusively for NO molecules adsorbed at terrace-hollow sites that diffuse to the lower step edges, while NO species adsorbed on terrace-top and step sites remain inactive. The detailed O1s analysis of the entire surface at the very onset of the dissociation process (Fig. 1) allows its quantitative evaluation in terms of the NO diffusion length from terraces to steps, and desorption and dissociation probabilities at steps. At 200ºC, surface oxidation begins, first on Rh(111) and its B-type vicinal surfaces. Surface X-ray diffraction was used to characterize the evolution of the such surface oxides, revealing similar structures on Rh(111), A-type Rh(223), and B-type Rh(553). However, the oxide builds up on the Rh(553) plane itself, while on Rh(223) faceting is observed. These results underscore the structural sensitivity of NO dissociation and highlight the key role of the facet orientation in determining the catalytic behavior of Rh under NO reduction conditions [1].

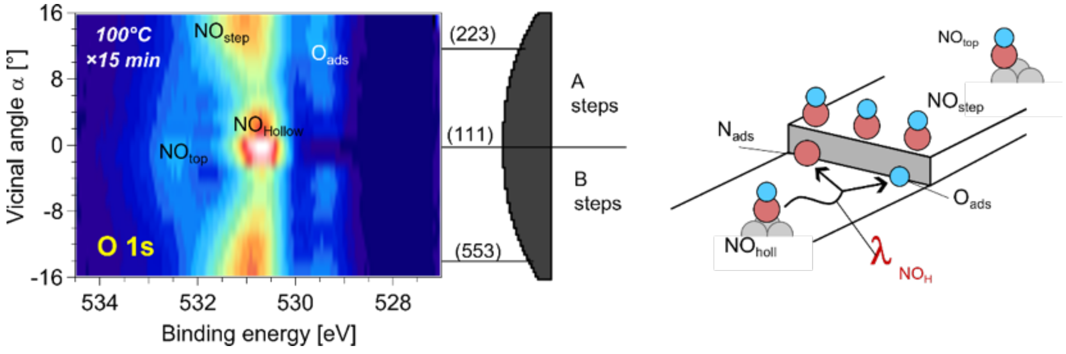

Fig. 1. O 1s intensity map (left) across the curved Rh(111) crystal (center) at the NO dissociation onset. The direct correlation of NO_{holl} and O_{ads} intensities proves that NO_{holl} is the main species involved in the dissociation at the lower step edge, which is limited by the ability to reach the step (diffusion-length λ_{NO})

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Contributed Talk 18

Investigating Metal-Support Interactions on Reducible Oxides for Gas Phase Photocatalysis using Near Ambient Pressure XPS

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Metal nanoparticles supported on reducible oxides are an important class of catalysts that play a central role in both thermal and photocatalytic transformations.[1] While model systems have been studied extensively to deconvolute various mechanistic effects in thermal catalysis, the additional complexity introduced under light illumination remains less well understood. Here, specific challenges include low quantum efficiencies, rapid exciton recombination, and the inability of single materials to drive complete redox reactions.[2]

In both thermal and photocatalysis, a promising approach is to deposit metal nanoparticles on well-defined reducible oxide supports, providing a good model platform for heterogeneous catalysis and additionally benefitting from improved exciton separation through Schottky effects at the metal-semiconductor interface. In the case of Au nanoparticles (NPs) under visible light illumination, the NPs can further act as optical antennas, generating localized surface plasmon resonance (LSPR) that creates concentrated electromagnetic fields and extends the absorption range of the semiconductor support.[3]

We employ a lab-based near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) setup with a three-line excitation source and an illumination source, complemented by other surface-sensitive techniques, to disentangle the interplay of metal–support interactions, particle oxidation state, stability and light excitation by tracking chemical state changes of both the metal particles and oxide support under reaction conditions. In the example of sub-nm Pt clusters and NPs on rutile TiO_2(110), we find distinct differences in oxidation behavior and thermal stability between particles of different size, which are further modulated by the support stoichiometry and oxygen pressure.[4] Finally, we evaluate critically under which conditions a single crystalline model can represent more realistic powder catalysts.

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Contributed Talk 19

Electrochemically-induced cation redistribution and surface phase oscillations promote high selectivity in the partial oxidation of methane

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~25% of industrial catalytic processes involve heterogeneous oxidation of hydrocarbons. Ethylene production, for instance, is highly carbon-intensive (>300 Mt CO_2/yr) and ethylene is among the most widely produced chemicals (>200 Mt/yr worldwide).[1] To decarbonize ethylene, we are exploring the electrochemical oxidative coupling of methane (EOCM) to directly convert CH_4 to C_2H_4 with lower CO_2 emissions. However, CH_4 oxidation over oxide catalysts is challenging as CO/CO_2 are significant side products and are favored by reaction thermodynamics. Hence, novel and intrinsically selective CH_4 activation mechanisms are critical to overcoming these barriers.

Herein, we explore the surface chemistry of (La,Sr)$TiO_{3+\delta}$ (LST), a promising CH_4 activation catalyst,[2] and its response to external stressors such as electrochemical potential and gas environment. The defect chemistry of LST is dominated by its ability to accommodate either oxygen excess ($\delta>0$) or oxygen deficiency ($\delta<0$) depending on the La doping content.[3] We will discuss how to leverage this oxygen defect chemistry to favor selectivity in CH_4 activation by oscillating between oxidized and reduced surface states. First, we will discuss how the surface dynamically undergoes La segregation under catalytic conditions due to the applied electrochemical potential driving cation motion. This segregation modifies the surface chemistry and sets up a surface state amenable to oxygen-driven surface oscillations which dynamically form and destroy extended shear oxygen defects. Results from ambient pressure XPS and XAS studies, collected at NSLS-II and ALS, under operando catalytic conditions reveal how the cation dynamics and oxygen stoichiometry couple to yield high selectivity. By tuning the surface chemistry to oscillate between the highly active and selective surface state and the unselective but inactive surface state, we can modulate CH_4 activation to favor the partial oxidation products. Overall, our work combines ambient pressure surface measurements, defects and electrochemistry to tailor the active oxygen species which activate CH_4, enabling tuneable partial oxidation selectivity.

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Contributed Talk 20

Single- and Dual-Chamber Spectroscopic Study of LSTN Anode Material Under Operating Conditions of a Solid Oxide Cell

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$La_xSr_{0.9-x}Ti_yNi_{1-y}O_{3-\delta}$ (LSTN) has been proposed as a promising group of mixed ionic-electronic conductive (MIEC) perovskites for solid oxide fuel cell and electrolysis cell applications, aiming to improve the reliability and reduce the complexity of these systems. It has been demonstrated that, at elevated temperatures and in a reducing atmosphere, the B-site dopant (Ni) exsolves to the perovskite surface, forming nanometer-scale catalyst particles [1]. The exsolution process can be accelerated by applying electrochemical polarization.

However, even though the reaction zone in MIEC oxides is located at the two-phase boundary of the MIEC oxide–gas interface—significantly larger than the three-phase boundary in Ni-cermet electrodes - the activity of MIEC ceramic electrodes is still lower than that of Ni-cermet electrodes and requires improvement. To enhance both the activity and stability of MIEC electrodes, it is crucial to understand how the chemical and structural properties of the electrode surface influence its electro-chemical behavior. This necessitates collecting chemical information from the electrode surface under operating conditions. Due to the high temperatures involved (600–900 °C), this is an experimentally challenging task.

In this study, we present the results of simultaneous AP-XPS and electrochemical characterization of a $La_{0.31}Sr_{0.58}Ti_{0.97}Ni_{0.03}O_{3-\delta}$ electrode in both single and dual-chamber SOFC setups [2, 3], under varying H_2/H_2O ratios and electrode potentials at temperatures above 650 °C. The ratio of A-site elements (La, Sr) on the sample surface is strongly influenced by the exsolution process. The reduction of the B-site element Ti is accelerated due to exsolution in a hydrogen environment and under applied electrode polarization. The exsolvation of Ni to the surface is also detected, despite its low concentration. The presence of H_2O vapor on the anode side has an additional effect on the electrochemical activity of the LSTN|gas interface and on the chemical composition of the sample surface.

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Contributed Talk 21

Probing Volatile Organic Solids and Solutions *In Situ* with Near-Ambient Pressure XPS

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Organic phases in the form of solutions and solid-liquid interfaces are ubiquitous in nature and of enormous economic relevance. Examples range from cell membranes, peptides and proteins in biological systems, to the crystallisation of organic chemicals from solution, the production of formulations by compression and suspension, or the dissolution of pharmaceutical tablets. The need for probing the 1s core levels of C, N and O has for a long time presented significant challenges for the relevant organic materials surface and interface science. Many organic materials were incompatible with UHV analysis (so were the solvents), while well-defined organic substrates cannot be prepared by sputter/heat cycles. The development of NAP XPS and NAP NEXAFS enables for the first time surface science studies of such systems. For example, solvent adsorption/desorption studies provide insight into the molecular basis for dynamic vapour sorption (DVS) measurements, a technique that has been used widely in industrial and academic formulation laboratories for several decades. In situ humidity-dependent measurements allow studies of the interfacial transport phenomena that cause powder caking and agglomeration. The condensation of liquid films onto the surfaces of organic materials provides realistic model systems for studying speciation at the solid/liquid interface. Liquid flow systems enable studies of both bulk dissolution and interfacial crystallisation as a function of time, temperature and solvent/solution composition. In situ studies allow us to determine the molecular basis for interfacial nucleation and crystallisation studies in traditional laboratory reactors. Use of gas cluster ion beam sources overcomes the surface cleanliness limitations that have traditionally plagued organic crystal surface science.

Contributed Talk 22

Seeing beyond the surface: uncovering electrochemical interfaces by near ambient-pressure operando HAXPES

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We employ ambient-pressure hard X-ray photoelectron spectroscopy (AP-HAXPES)[1] in a *dip-and-pull* three-electrode configuration to probe working electrochemical interfaces relevant to the oxygen reduction reaction (ORR). The cell enables potentiostatic control of Pt nanoparticle electrodes in 0.5 M $HClO_4$ while maintaining a thin liquid layer suitable for photoemission. Systematic measurements as a function of electrode potential/atomsphere reveal channel-dependent responses. The Pt 3d and Cl 1s binding energies remain essentially invariant across the conditions examined, whereas the O 1s signal shows reproducible potential/atomsphere-dependent shifts and intensity changes. The Pt 3d and Cl 1s are also correlated to reveal the influence of electrolyte on the catalysts surface under different atmosphere. In addition, the Pt valence band can be resolved at multiple potentials, enabling comparison of electronic structure under operando-like conditions. Together, these results demonstrate that dip-and-pull AP-HAXPES provides chemically specific, depth-sensitive access to buried solid–liquid interfaces without disrupting realistic electrolyte environments. The approach offers a general pathway to track how interfacial composition and electronic states evolve under working ORR conditions, while leaving room for complementary methods to establish detailed assignments for oxygen-containing species.

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Contributed Talk 23

The Real Ambient Pressure Photoelectron Spectroscopy Measured with Soft X-ray

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Soft X-ray photoelectron spectroscopy under the real ambient pressure (1 atm) has been demanded to elucidate the surface states of functional materials such as catalysts and electronic devices under the practical conditions. However, it has been considered difficult to detect photoelectrons emitted from the sample under 1 atm of reactant gases due to the attenuation of the light source and the signal intensities [1]. Nevertheless, we have successfully achieved ambient pressure X-ray photoelectron spectroscopy (APXPS) under 1 atm by combining the synchrotron-based high-brilliance soft X-ray and the newly developed experimental equipment with specially arranged differential pumping system [2].

The APXPS experiments were performed at the soft X-ray beamline BL08U of the newly constructed synchrotron facility, NanoTerasu Synchrotron Light Source in Sendai, Japan [3]. The photon energy was 800 eV for all the spectra. Path lengths of the soft X-ray and photoelectrons were set to 5 mm and < 60 um, respectively. The sample was a Au film which was prepared by gold evaporation on a metal substrate. Helium (He) or hydrogen (H_2) gases up to 1 atm, and nitrogen (N_2) gas up to 0.4 atm were exposed onto the sample surface.

Figure 1 shows APXPS spectra of Au 4*f* core-level under 1 atm of He and H_2, and 0.4 atm of N_2 gases. The acquisition time was 3, 8, and 45 minutes, respectively. The signal intensities under the gases decreased in the order of He, H_2, and N_2, which is strongly related to the soft X-ray transmittance and the electron scattering cross section under each gas. Furthermore, based on the linear relationship between the distance from the sample surface to the analyzer nozzle and the logarithmic intensity, the local pressure of the surface was confirmed to be same as the global pressure of the chamber (1 atm).

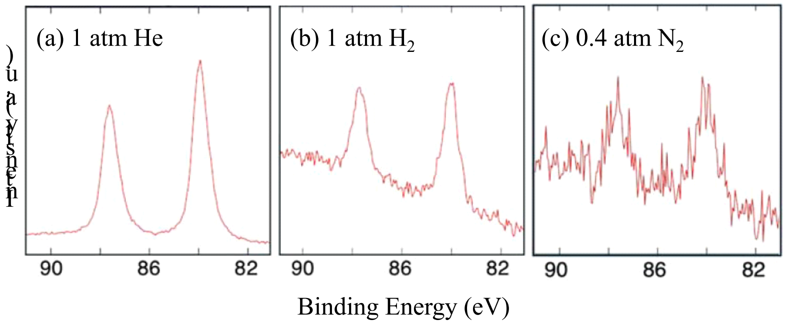

Figure 1. Au 4*f* APXPS spectra under 1 atm of (a) He and (b) H_2, and 0.4 atm of (c) N_2 gases [2].

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Contributed Talk 24

Preliminary Design and Overview of a new Ambient Pressure XPS beamline at the Brazilian Synchrotron Light Laboratory, Sirius.

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The need of probing material structure, composition, and function information through (Near)-Ambient Pressure X-Ray Photoelectron Spectroscopy (APXPS) has been a growing demand to many scientists seeking to understand different materials under *in situ* and *operando* conditions [1,2]. More than catalysts studies, the implementation of a new beamline providing a new technique at Sirius will reinforce the importance of the Brazilian 4th generation synchrotron source in the study and development of new materials in several areas such as electrochemistry, thin films, sensors, polymers and vacuum-sensitive biological materials [3]. In this sense, PITANGA beamline (**P**hotoabsorption and em**I**ssion spec**T**roscopies **A**t **N**ear **A**mbient Pressure) will be able to provide this capability through the combination of two endstations, one dedicated to liquid-jet XPS and the other dedicated to solid-gas reactions and surfaces (XPS and XAS), with microfocus beam sizes (~ 5x5 µm and ~30x30µm respectively) and high photon flux (estimated at $1x10^{11}$ ph/s/0.1A @600eV) obtained by a 1.2m APU58 undulator source. PITANGA optical design is based on a elliptical mirror (M1), a Variable Line Spacing Plane Grating Monochromator (VLS-PGM) with multiple gratings varying line spacing to achieve high resolution and flux, and the exit slit. After the exit slit a third (M3) and fourth (M4) elliptical mirrors will be used to optimize and refocus the beam to each endstation. The soft X-Ray energy range (400eV-2500eV) of the beamline will provide access to the absorption K-edges of light elements, as well as L-edges of the first row transition metals and M-edges of rare earth elements.

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Poster 1

X-ray Photoelectron Spectroscopy of Tetrametallic Phosphate (Co-Ni-Fe-Mn) Electrocatalyst Activation for the Oxygen Evolution Reaction (OER)

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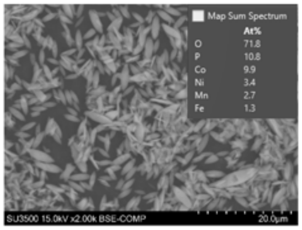
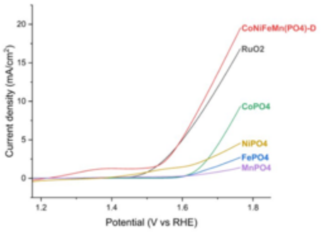
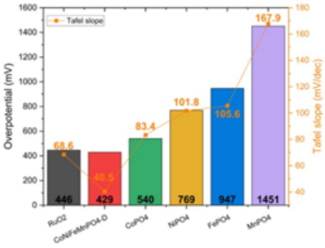
The development of efficient and cost-effective electrocatalysts is essential for sustainable hydrogen production via water electrolysis. Here, we report a novel tetrametallic phosphate ($CoNiFeMnPO_4$) synthesized via a simple, environmentally friendly precipitation method and evaluated for the oxygen evolution reaction (OER). SEM analysis revealed flake-like microstructures (4.14 × 1.21 µm) promoting high active surface area and efficient electron transport. Elemental mapping confirmed homogeneous distribution of all metals, while FT-IR and XPS analyses verified the phosphate framework and high cobalt content, contributing to crystallinity and structural stability. XPS and EDS studies done before and after electrochemical activation via cyclic voltammetry revealed an increase in atomic oxygen concentration and a decrease in phosphorus content, indicating the formation of oxide or hydroxide phases on the catalyst surface. EDS was done on the catalyst-modified carbon paper to avoid e-beam surface damage and confirmed the same atomic compositional trend. Oxygen evolution reaction (OER) electrochemical measurements, in 0.1 M KOH using a catalyst modified Glassy Carbon-Rotating Disk Electrode, demonstrated that $CoNiFeMnPO_4$ outperforms individual metal phosphates and commercial RuO_2, exhibiting a low overpotential of 429 mV at 10 mA cm^{-2} and a Tafel slope of 40.5 mV dec^{-1}. During 24-hour stability tests at a current density of 10 mA cm^{-2}, the catalyst underwent initial activation over the first 3 hours, with the OER potential decreasing to 1.63 V before stabilizing, maintaining a minimal ΔV of 0.022 V. The cooperative effects of multiple transition metals, phosphate ligand modulation, and surface oxide/hydroxide formation lead to enhanced OER performance and long-term stability, highlighting tetrametallic phosphates as promising, cost-effective catalysts for water splitting.



Map Sum Spectrum	At%
O	71.8
P	10.8
Co	9.9
Ni	3.4
Mn	2.7
Fe	1.3





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Poster 2

Operando APXPS maps active phases and promoter effects in cobalt catalysts

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Understanding how oxide catalysts reorganize under reactive atmospheres is central to linking surface chemistry with function. We present two case studies where operando (near) ambient-pressure X-ray photoelectron spectroscopy (APXPS) quantitatively resolves active phases, vacancy chemistry, and interfacial charge transfer in cobalt catalyst relevant to CO oxidation and Fischer–Tropsch (FT) synthesis.

(1) For ultrathin CoO_x films on Au(111), APXPS identifies three reaction regimes arising from coupled chemical and topographic restructuring as a function of O_2/CO stoichiometry and temperature. Under oxygen-lean feeds and ≤150 °C, partially oxidized films (CoO_x<1) containing Co^0 are efficient catalysts. Stoichiometric CoO (Co^{2+}) forms surface carbonates in CO that poison activity below 300 °C. Under oxygen-rich conditions, a more oxidized phase (CoO_x>1) with Co^{3+} forms and remains active over a wide temperature window. Resonant photoemission (ResPES) isolates the unique role of Co^{3+} sites in catalyzing CO oxidation, while density-functional theory (DFT) provides the reaction pathways and free-energy barriers across these phases.

(2) Under FT-relevant H_2/CO, Mn-promoted crystalline $CoMnO_x$ nanoparticles,with Co and Mn mixed at the sub-nanometer scale, were probed by in-situ XRD, APXPS, and XAS under H_2/CO. We observe a rapid rise of CH_x intermediates on $CoMnO_x$ that is absent without Mn. DFT shows that basic O sites in $CoMnO_x$ sequester H atoms produced by H_2 dissociation on Co^0, reducing hydrogen availability for CH_x hydrogenation and thus suppressing chain-termination, which promoting longer-chain hydrocarbons.

Together, these studies establish a structure–chemistry–function framework in which operando APXPS/ResPES quantify oxidation-state windows, carbonate formation, and promoter-induced electronic effects that control activity and selectivity.

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Poster 3

XPS investigation of KOH-induced corrosion in FeCrMnCoNi alloy

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This work studies how an equimolar FeCrMnCoNi multicomponent alloy corrodes in 1 M alkaline potassium hydroxide, with the goal of using this alloy as a corrosion-resistant coating for structural parts of alkaline water electrolyzers. Alkaline electrolysis is an efficient way to produce hydrogen on a large scale, but the high pH and applied potentials can damage structural materials, so a stable passive oxide layer is essential. We used ex-situ X-ray Photoelectron Spectroscopy (XPS) together with linear sweep voltammetry to track how the native and passive oxide layers change with applied potential. The polarization curve in 1 M KOH (Fig. 1) shows a wide passive region and almost no active region, indicating strong corrosion resistance. XPS reveals that the passive oxide composition shifts noticeably among the alloy's elements. The native surface is mainly manganese oxide with smaller amounts of chromium, iron, and cobalt oxides. Nickel oxide is absent; instead, a nickel-rich metallic layer lies beneath. Polarizing to –1.8 V (hydrogen evolution) reduces much of the manganese oxide, while +1 V (oxygen evolution) enriches the surface with Ni^{2+} and Co^{4+} oxides.

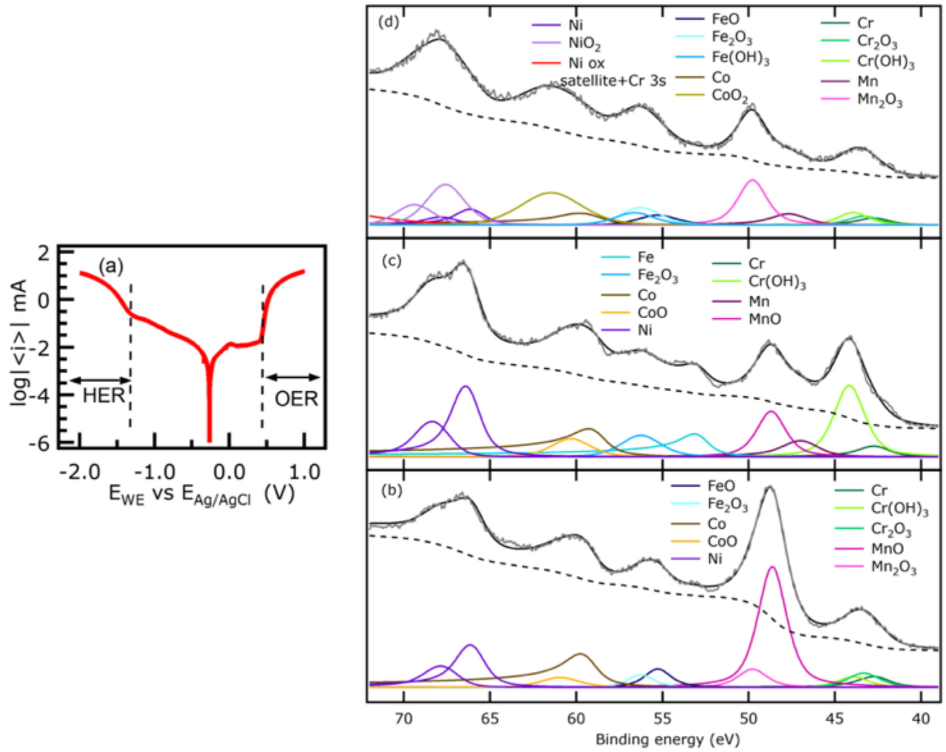

Fig. 1. Ex-situ XPS and electrochemical data for FeCrMnCoNi in 1 M KOH: (a) linear sweep voltammetry; Metal 3p spectrum of (b) native oxide; (c) after –1.8 V polarization; (d) after +1 V polarization.

Poster 4

Oxidation and Structural Evolution of Ruthenium Nanoparticles supported on $CeO_2(111)$ and $Co_3O_4(111)$

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Understanding the dynamic interplay between metal nanoparticles and oxide supports under near-realistic conditions is crucial for advancing catalyst design and performance. Our main goal was to explore the structural and chemical evolution of ruthenium nanoparticles supported on well-defined cerium oxide and cobalt oxide surfaces upon exposure to molecular oxygen at temperatures ranging from room temperature to 400 °C. Scanning tunneling microscopy (STM), near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), and synchrotron photoelectron spectroscopy (SRPES) were used to monitor changes in morphology and oxidation states. Our results demonstrate contrasting behavior of Ru, depending on the choice of reducible metal oxide support. On $CeO_2(111)$, a temperature- and atmosphere-dependent formation of highly-oxidized Ru species is observed, followed by their sublimation at higher temperatures. On the other hand, Ru/$Co_3O_4(111)$ displayed stronger metal-oxide interaction, resulting in the formation of an ultra-thin film or highly dispersed RuO_x, resistant to sublimation. These findings provide atomic-scale insight into the dynamic nature of active sites in Ru/MO_x systems, relevant to redox catalysis.[1,2]

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Poster 5

Operando Plasma-XPS of high performance tin oxide photoresist for extreme ultra-violet photolithography

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Currently, tin oxide organometallic nanoclusters are being optimized as photoresists for extreme ultraviolet (EUV) nanolithography. Unfortunately, the chemical mechanism upon EUV irradiation that results in a solubility contrast is not well understood for these resists. The primary mechanism is thought to be homolytic cleavage of carbon-based ligands due to secondary electron generation from Sn photoabsorption.[1] Ambient pressure x-ray photoelectron spectroscopy (AP-XPS) studies further verified this suggested mechanism by showing an increase in resist sensitivity when irradiated with an O_2 overpressure due to excited O species.[2] Alternatively, plasma excitation provides another source of electrons, along with excited gaseous species, both of which can interact with the resist and further drive chemistry. Recently, plasma X-ray photoelectron spectroscopy (Plasma-XPS) has been demonstrated as a powerful platform for real-time, operando analysis during exposure to plasma.[3] Using a standard laboratory-based APXPS apparatus coupled with a cold cathode AC-driven 22 kHz plasma source, we measured XPS first in UHV, then with 1 mbar partial pressures of O_2 and H_2, respectively, followed by both respective plasmas at the same pressure. After XPS measurements, the samples were developed by dissolving the unexposed regions and revealing the x-ray spot. XPS of the C 1s in O_2 again shows a larger decrease in C relative to UHV, although this decrease remains mostly the same when exposed to O_2 plasma, suggesting no explicit benefit to O_2 plasma exposure. Alternatively, when exposed to H_2 plasma, the entire sample became completely insoluble when developed, most likely due to UV exposure from the hydrogen Lyman series lines. Still the XPS shows a substantial amount of C remains in the insoluble film. Overall, we provide further characterization of the radiolytic mechanism by identifying the chemistry when exposed to plasma relative to solely photons.

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Poster 6

Size-dependent charge transfer between nanoscale Rh species and rutile TiO_2

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A promising strategy to mitigate climate change involves utilizing carbon dioxide as a carbon source together with “green hydrogen” derived from renewable energy, enabling the production of high-value chemicals through catalytic processes. One key reaction is the Reverse Water Gas Shift (RWGS), which converts CO_2 and H_2 into syngas, a crucial precursor for diverse catalytic applications. Among the catalysts under investigation, atomically dispersed rhodium supported on titania (Rh/TiO_2) has emerged as highly active for low-temperature RWGS. However, its performance is strongly influenced by catalyst degradation, particularly Rh sintering that shifts selectivity toward methane formation. Understanding the dynamics of Rh species under working conditions is therefore essential for bridging laboratory success with industrial viability.

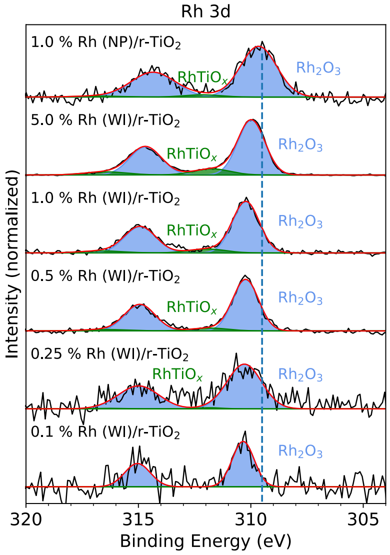

Figure 2: APXPS measurements of catalyst with different Rh particle size at 40°C in 5x10-3 mbar O_2 after annealing the catalyst in O_2 atmosphere to 400 °C for 30 min.

In this work, we investigate the evolution of Rh/TiO_2 catalysts under different gas compositions and elevated temperatures by combining ambient pressure X-ray photoelectron spectroscopy (APXPS), infrared spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM). Our results, shown in Figure 1, reveal size-dependent shifts in Rh 3d core level binding energies, providing qualitative evidence of Rh cluster growth and fragmentation. Correlating these *in situ* observations with structural changes highlights the critical role of gas environment in governing Rh stability and reactivity. Importantly, our measurements deconvolute core level shifts due to size changes from those resulting in oxidation state changes. Together, these findings advance the understanding of catalyst degradation mechanisms and establish APXPS as a valuable tool for probing the structure–function relationship in nanoscale Rh catalysts.

Poster 7

Ag(111) Remains Signficantly Reduced In Situ Under Simulared Ethylene Epoxidation Conditions

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Direct ethylene epoxidation is among the highest value processes in the chemical industry, yet the reaction mechanism remains debated. A central question is whether the unpromoted Ag catalyst used for ethylene epoxidation is metallic or oxidized under reaction conditions, as this determines the active oxidant species. Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) at chemical potentials simulating industrial conditions, we find that under oxidizing environments, nucleophilic oxygen (~0.8 ML) and some carbonate impurities (~0.2 ML) form on Ag(111). Upon switching to an industrially relevant 5:2 ethylene-to-oxygen ratio at 433 K, nucleophilic oxygen is consumed, leaving mostly surface carbonate and bare Ag. Quantification shows the Ag(111) surface maintains ~50% exposed metallic sites under these conditions. This indicates that proposed mechanisms involving a fully oxidized surface may not represent the state of the surface under relevant reaction conditions, and that bare Ag sites, which are necessary to form the oxametallacycle intermediate thought to drive selective epoxidation, are indeed available.

Poster 8

Recent Upgrades in APXPS Sample Environments at the Center for Functional Nanomaterials

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The Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory has expanded sample environments and correlative measurements for ambient pressure X-ray photoelectron spectroscopy (APXPS) in recent years. A microelectromechanical systems (MEMS) heater has been used for time-resolved APXPS data collection with 0.5 s resolution and correlative transmission electron microscopy (TEM) studies [1]. A recent upgrade of the heating system to an infrared laser has increased the accessible temperature to 1000 °C, enabling the preparation of a broader range of materials and the investigation of higher temperature processes such as catalytic growth of carbon nanotubes. Collaboration with the user community has contributed to the growth of recent capabilities. User and in-house developments have yielded graphene based-liquid cells that have been used in both APXPS and correlative X-ray absorption spectroscopy studies [2,3]. Internal CFN research has developed in situ low-frequency AC plasma and studied core level spectra of several plasmas, and users have developed methodology to characterize surfaces under plasma [4,5].

In the upcoming year, the CFN will expand capabilities further. Plans for the current system include installation of a pulse valve for continuation of time resolved studies, a Langmuir probe for direct plasma characterization, and a versatile plasma power supply to change the frequency parameters of the AC power. A new SPECS system will be installed in early 2026 with three monochromated, focused photon energies: Al K_α at1486.7 eV, Ag L_α at 2984.3 eV and Cr $K_{\alpha1}$ at 5414 eV. The system will include a manipulator for solid/liquid interface measurements.

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Poster 9

Operando XPS and NEXAFS Reveal Oxidation Dynamics and Active Oxygen Species in Iridium and Ruthenium–Iridium Oxide OER Catalysts

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Advancing water electrolysis requires a fundamental understanding of the structural and electronic transformations of oxygen evolution reaction (OER) catalysts under operating conditions. Here, we report the development of two specialized working electrode assemblies: a layered carbon-based membrane electrode and a gold-coated polycarbonate track-etched (PCTE) electrode with enhanced mass transport [1]. Both were implemented in our electrochemical flow cell [2]. These platforms enabled systematic operando X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) studies of iridium oxide catalysts with varying crystallinity. In particular, amorphous phases exhibit sequential redox transitions ($Ir^{3+} \rightarrow Ir^{4+} \rightarrow Ir^{5+}$) as a function of applied potential. By applying a novel potential-programmed NEXAFS (PP-NEXAFS) method we were able to clearly resolve μ_1-, μ_2-, and μ_3-O species, revealing an oxygen redox process that forms electrophilic oxygen without further oxidation of Ir^{5+} at near OER potential.The Au/PCTE working electrode assembly also enabled the first operando investigation of Ru–Ir mixed oxides, uncovering potential-dependent ruthenium surface segregation and $Ir^{4+/5+}$ redox transitions. Our findings refine the understanding of OER on state-of-the-art iridium-oxide based catalysts by highlighting the coupled roles of metal-centered and oxygen-ligand redox processes. The enhanced mass transport of the Au/PCTE electrode is a significant improvement for operando studies of electrochemical interfaces and enables mechanistic understanding that informs the rational design of efficient, durable, and cost-effective OER electrocatalysts for sustainable hydrogen production.

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Poster 10

Thermal Annealing Process, Water Storage, and Water Permeation Application of Graphene Oxide Membranes

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The in-situ environmental experiment is important to monitor the chemical de-oxidation and re-modification of reduced graphene oxide (rGO) due to the controllable adjustment of the surface functional groups of graphene oxide (GO). For scientific purposes, a perfect hexagonal ring of graphene (G) that exhibits various oxidation sites is crucial for inducing different chemical bonding responses and is effective for external gas molecules. A membrane composed of G/GO/rGO materials has been fabricated for potential energy and electrical applications, as described in the report. Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we observe the thermal evolution and re-oxidation behavior of thermally reduced graphene oxide (Th-rGO) under various atmospheric and humidity conditions. The thermal process was heated from room temperature to 300 °C in increments of 50 °C under ultra-high vacuum (5×10^{-6} mbar) and in simulated air (0.6 mbar, 80% N_2 / 20% O_2), in order to introduce the thermal energy and gas interaction into the GO membrane. In a vacuum environment (Th-rGO-Vac), the C–O–C and C=O groups decompose primarily as the temperature increases. Meanwhile, the C-OH and O=C–OH groups have higher ratios at lower temperatures, but these ratios decrease after reaching 150°C. In a simulated air environment (Th-rGO-Air), C–O–C, C=O, and C-OH also decompose directly, but only the O=C–OH group has a crossover behavior during the thermal annealing process. In the water storage application, following thermal annealing in ultra-high vacuum and simulated air, an increase in water gas pressure (0.1–0.6 mbar) was applied to the same Thr-GO membranes during the AP-XPS experiment. The pronounced chemical bonding and bonding transfer have been observed in both the Th-rGO membrane with rising vapor pressure, primarily through the formation of C-O-C and C–OH groups. Even at pressures as low as 0.1 mbar, the surface of Th-rGO-Air is already saturated with adsorbed water molecules, highlighting strong water–surface interactions. In contrast, the Th-rGO-Vac membrane offers higher water gas storage and better chemical bonding states than the Th-rGO-Air, making it suitable for recyclable energy applications. AP-XPS experiments were conducted using the liquid cell membrane, with the main chamber maintained under ultra-high vacuum and at three different nitrogen pressures (0.1, 0.3, and 0.6 mbar). The key aspect is to determine the rate of water molecule permeation through the GO membrane based on the pressure gradients between the main chamber and the liquid chamber. These findings reveal the crucial role of atmospheric gases and water vapor in modulating the surface chemistry and electronic properties of rGO, offering insights for sensing and electronic tuning applications.

Poster 11

The In Situ and Operando Soft X-ray Spectroscopy (IOS, 23-ID-2) Beamline at NSLS-II: Science Highlights and Future Plans

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The In Situ and Operando Soft X-ray Spectroscopy (IOS, 23-ID-2) beamline at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory provides ambient pressure X-ray photoelectron spectroscopy and soft X-ray absorption spectroscopy capabilities combined with the high brightness and superior energy resolution from the synchrotron to enable diverse and impactful energy science research. In this poster, we will show recent research results from catalysis, energy storage, and materials science to highlight our various capabilities. We will also provide an overview of ongoing short-term and long-term beamline upgrade projects to enable multi-modal ambient pressure soft X-ray spectroscopy at IOS. The installation of an energy discriminating silicon drift detector will enable ambient pressure X-ray absorption spectroscopy in partial fluorescence yield mode for a saturation-free, bulk-sensitive probe of materials, allowing the study of buried interfaces, in combination with surface sensitive studies using AP-XPS and electron yield AP-XAS. INSPIRE, an expansion of the beamline with new refocusing optics and a new multi-modal endstation will add capabilities in resonant inelastic X-ray scattering, X-ray emission spectroscopy, and infrared reflection absorption spectroscopy, as well as increasing the operating pressure. These upgrades will allow researchers to obtain comprehensive electronic and chemical information for energy materials in operating conditions at relevant time scales.

Poster 12

In situ AP-HAXPES of Pt oxidation state in a hygroscopic electrochemical cell

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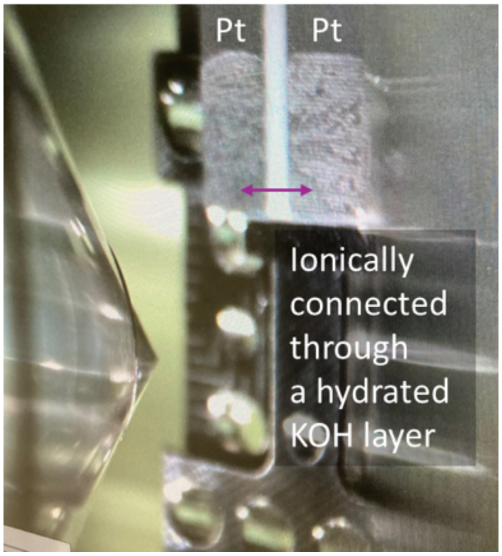
Understanding electrochemical device performance critically depends on probing the electrode/electrolyte interface. Ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) employing ultra-thin liquid films prepared by the dip-and-pull method offers one approach [1-2]; however, the use of a bulk liquid reservoir can introduce complications such as splashing, boiling, and unrepresentative current responses relative to the solid/liquid interface examined by XPS. Here, we introduce an alternative method based on *in situ* hydration of a hygroscopic electrolyte, which eliminates the need for a bulk liquid reservoir. We demonstrate the validity of this approach using the Pt/KOH(aq) interface under potential control, observing XPS binding energy shifts in the electrolyte species alongside corresponding changes in Pt oxidation states. This method is particularly suited for investigating gas- or moisture-sensitive electrochemical reactions involving hygroscopic electrolytes.



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Poster 13

Surface Analysis of Photonic-Cavity Photocatalysts via NAP-XPS: Assessing the Role of Structural Order

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Inverse opals (IOs) are photonic materials with periodic dielectric architectures that confine and manipulate light, enabling slow photon effects and enhanced local electromagnetic fields. Recent theoretical studies suggest such optical cavities may also influence chemical reactivity through interactions with quantum vacuum fluctuations, introducing the possibility of cavity quantum electrodynamic (cQED) effects in catalysis[1].

This project aims to investigate how structural order in optical cavities influences surface chemistry in photocatalytic systems. Specifically, we aim to compare ordered and disordered TiO_2/MoS_2 inverse opals to assess how variations in photonic coherence affect redox behavior and adsorbate interactions under illumination and reactive gas exposure. We adapted our synthesis from Loukopoulos et al.[2] An SEM image of a disordered IO is shown in Figure 1.

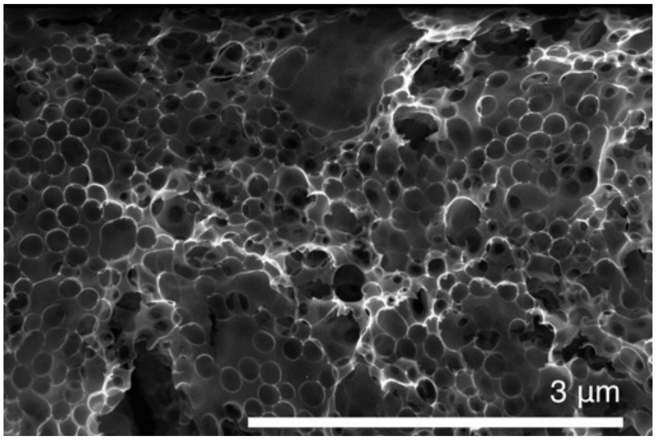

Figure 3: Immersion-mode SEM image of a disordered TiO_2/MoS_2 inverse opal, acquired using a Helios G4 UX DualBeam FIB-SEM. Image courtesy of the University of Notre Dame's Integrated Imaging Facility.

Surface-sensitive analysis under reactive conditions will be performed using NAP-XPS, supported by complementary structural and spectroscopic characterization. This study is designed to isolate the effect of photonic structuring on surface chemical processes, with an emphasis on how structural coherence modulates the behavior of active sites. Introducing disorder allows us to separate the roles of photonic coherence and geometric confinement, helping to clarify their respective impacts on photocatalytic activity.

By integrating engineered optical cavities with *in situ* surface-sensitive spectroscopy, this work contributes to emerging efforts to link design with catalytic function, potentially guiding the development of next-generation light-structured catalytic materials. In addition to its practical implications, this study may help establish experimental strategies for probing cQED-related effects in solid-state catalysis.

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Poster 14

An APXPS setup for studying atomic layer deposition

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Atomic layer deposition (ALD) is a thin film growth technique which is widely used due to its excellent ability to grow precisely controlled film thicknesses with excellent film uniformities, conformalities, and other properties. The technique relies on cyclic exposure of a substrate to constituent gas phase precursors which interact with the surface in a self-limiting manner. Often two different precursor are used in an alternating manner, which makes it possible to control the thickness of the film via the number of ALD cycles.

Many ALD reactors operate at pressures within the mbar range and substrate temperatures within a few hundred degrees C. This makes APXPS an excellent match for studying the growth dynamics in real-time using appropriate instrumentation. We have developed a custom made APXPS sample environment which mimics the properties of ALD reactors [1]. The system is designed in the cell-in-cell style, making it compact and have small internal volumes, enabling fast gas cycling. The experimental setup consists of a unique gas sending system specifically designed to pulse ALD precursors in a well-defined manner. The system has been in operation for a few years, and has been used to study the deposition of many materials including: the oxides of titanium, hafnium, zirconium, aluminum, the nitrides of gallium, aluminum, metallic platinum, copper, and others.

With APXPS it is possible to get unprecedented detail on the chemical processes governing the film growth, which is especially important in the initial stages of the growth. The initial stages often dictate the properties the film will have, and therefore it is essential to be able to understand how the individual precursor molecules interact with the substrate surface as well as the interactions with the subsequent precursors. Through APXPS we have found details on ALD chemistry which have been previously unknown: These discoveries include: the so-called self-cleaning process which happens during the exposure of a InAs substrate to a Hf-containing precursor that removes some of the surface oxide during the exposure [2,3], evidence for bimolecular reaction pathways in the deposition of Hf oxide which provides new insights into the commonly believed ligand-exchange mechanisms [4], and investigations into the thickness of a created oxide which depends on the thickness of the underlaying substrate oxide [5].

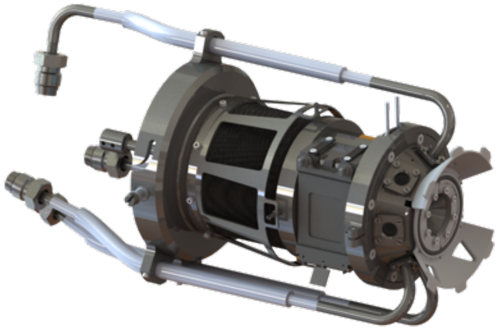

Figure 4: A schematic view of the ALD cell.

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Poster 15

Resonant Auger-Meitner Electron Spectroscopy of nitrate ions: from crystalline powder to deliquesced solution

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Nitrate ions are the product of gas phase oxidation cycles of nitrogen oxides, and are a source of OH radicals within the particles or a source of gas phase nitrogen oxides from nitrate photolysis. Further, the heterogenous reaction of HNO_3 with aerosol particles impacts the stratospheric ozone budget, which has strong implications on the effectiveness and impacts of solar radiation modification via stratospheric aerosol injection (SAI). This impact could occur as the reaction of gaseseous HNO_3 with calcite (a solid particle candidate for SAI[1]) could lead to formation of crystalline and/or amorphous phases of calcium nitrate ($Ca(NO_3)_2$) within the particles. In addition, as aqueous aerosol particles are expected to contain high concentration of electrolyte ions at subsaturated relative humidity (RH) conditions. Thus, the detailed understanding for the coordination structure of concentrated nitrate ions is of high relevance in the condensed phase. Recent studies have shown that Resonant Auger-Meitner (AM) electron spectroscopy is an emerging and powerful spectroscopic tool to gain information on the unoccupied orbitals that are impacted by the hydrogen bonding and complex formation[2], thus provides information for the moleceular environment of the solute of interest. In this poster we aim to present the Resonant AM dataset collected with the near-ambient pressure photoelectron spectroscopy setup at the In-situ Spectroscopy (ISS) beamline of the Swiss Light Source SLS. At the ISS beamline, the Resonant AM data for $NaNO_3$,$Ca(NO_3)_2$ and $Ca(NO_3)_2•2H_2O$ were collected for samples ranging from solid powders to their deliquesced salt forms by varying the water vapor pressure and thus RH. We will discuss the collected results in the context of its potential impact on nitrate photochemistry and with the further motivation to identify crystalline and/or amorphous structure of $Ca(NO_3)_2$ relevant to SAI research.

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Poster 16

Probing Surface Chemistry of Co infiltrated Ni/YSZ Cathode Catalysts with *in situ* NAP-XPS

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Background/Objectives

Surface modification of Ni/YSZ cathode electrocatalyst via transition metals such as Co or Fe infiltration serves as an elegant approach to tune the electronic/chemical properties to reach favorable energetics of elementary steps involved in the CO_2 electroreduction at high temperatures with solid oxide cells. The surface molecular/structural transformation in these bimetallic catalysts is not yet clearly explored under reaction conditions. The current study is aimed at probing the dynamic surface chemistry of Ni(Co)/YSZ during exposure to reductive and oxidative environments, and to identify the surface carbon intermediates.

Experimental

Co infiltrated NiO/YSZ was synthesized using cobalt nitrate precursor infiltration on the sintered NiO/YSZ pellets. Bulk phases were identified with *in situ* Raman spectroscopy. NAP-XPS spectra of Ni(Co)/YSZ and references were were collected (spot size of ~1mm x 1mm) with a SPECS Ambient Pressure X-ray Photoelectron Spectroscopy system equipped with a XR 50 MF Al Kα X-ray Source. The sample holder was placed in a DeviSim AP cell (~1 mbar) with mass flow controllers for gases such as 10% O_2, 5% H_2, and pure CO_2, and heated using an e-beam from 300 to 873 K.

Results

In situ Raman spectra identifies the NiO, Co_3O_4, and YSZ phases in $Ni(Co)O_x$/YSZ under O_2 while metallic NiCo forms during reduction. Under pure CO_2, a minor amount of mixed $NiCoO_x$ spinel phase is formed in NiCo/YSZ whereas NiOx phase forms in Ni/YSZ at 700 ^{0}C. *In situ* NAP-XPS spectra under O_2 at 350 ^{0}C features surface Ni^{2+}, Co^{2+}, Y^{3+}, Zr^{4+}, lattice oxygen species while surface metallic Ni species were partially identified after reduction treatment at 600 ^{0}C in ~3nm surface region. Exposure to CO_2 (@350, 500, 600 ^{0}C) results in re-oxidation of metallic Ni with negligible changes in valence of Co. Additionally, surface carbon species (C-C, C=C) are identified in C 1s spectra. The carbon species is formed due to Boudouard reaction where CO disproportionate into CO_2 and graphitic C. Thus, bimetallic NiCo composition does not allow oxidation of Ni in pure CO_2 gas stream at technologically relevant conditions relevant to solid oxide cell operation for CO_2 electro-reduction.

Conclusions

Multiple *in situ* spectroscopic characterization techniques reveal the dynamic evolution of bulk structure, surface chemical composition of the bimetallic Ni(Co)/YSZ along with the surface intermediates under reactive conditions.

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Poster 17

Tracing Haber-Bosch Under AP-XPS Conditions: The Effect of Potassium Promotion on Iron

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Catalysis is at the heart of countless consumables that society relies on. Plastics, fuel, and fertilizer, are all crucially important to enable modern life. Yet, fertilizer production alone is responsible for substantial greenhouse gas emissions because it is largely derived from fossil fuels. Reducing these emissions by transforming the chemical industry into a renewable route is the current paradigm. This transformation can be greatly facilitated by understanding basic principles of model catalysts - as recently evidenced by our study on the nitrogen reduction over Fe and Ru model catalysts at pressures up to 1 bar, where the pressure gap was effectively overcome [1].

Using the same apparatus, we herein extend the study by closing in on the complexity gap. Instead of employing simply crystalline monometallic surfaces, we investigate the effects of K promotion over Iron under comparable conditions. Our study conclusively shows the that nitrogen dissociation is greatly enhanced over K-promoted Fe while the rapidity of the desorption of products is not significantly affected. While partially confirming theoretical expectations, the in situ observation under realistic conditions is essential, paving the way for new methods of optimizing catalysts to fit the changing landscape of the chemical industry. Future industrial solutions may require varied approaches in which pressure and temperature can be restricted and necessitate new optimization strategies. Moreover, we observed behavior that could not be evidenced by previous studies at liquid nitrogen temperatures and pressures vastly below the mbar range.

Our studies are performed at pressures up to 1 bar of reaction mixture and relevant reaction temperatures. Employing hard X-rays in the grazing incidence geometry we retain surface sensitivity in the POLARIS experiment located at P22, PETRA-III, DESY.

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Poster 18

Spin Polarization Effects in Catalysts studied with x ray Spectroscopies at Ambient Conditions (SPECTRA MSCA project)

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It is nowadays well known the urgent need of cheap, green and efficient catalysts able to convert greenhouse gases into more valuable and recyclable hydrocarbons. In this context, magnetocatalysis is an extremely promising field: in the last few years, a growing number of researchers discovered enhanced performances for electrocatalytic reactions in ferromagnetic materials [1]. The majority of these studies report empirical results, and a satisfactory explanation of the mechanism driving the spin effects is not well understood, mainly due to the lack of suitable experimental techniques. Regarding thermocatalytic reactions (such as CO oxidation or CO_2 hydrogenation), studies on the effects of applied external magnetic field and intrinsic magnetic order on the activity and selectivity of magnetic catalysts are almost completely missing. SPECTRA is a MSCA project [2] aiming to systematically unveil the mechanisms ruling the spin effects in catalytic solid/gas reactions. The main goal is to simultaneously characterize the magnetic and electronic properties of the single chemical species constituting spinel ferrites catalysts during different solid/gas reactions in *operando* conditions, with and without the presence of an applied magnetic field. This will be possible through the development and application of a reaction cell that will allow to perform Soft X-Ray Magnetic Circular Dichroism (XMCD) experiments at 1 bar and in *operando* conditions: this will be done through an upgraded version of the pre-existing *operando* Soft X-Ray NEXAFS reaction cells developed at the APE-HE beamline of Elettra Synchrotron (Fig. 1) [3]. The cell is operating at the SPECIES beamline of MAX IV Laboratory (Sweden) and the measurements are conducted exploiting the available circular polarized Synchrotron Radiation. Together with complementary techniques and offline catalytic tests, we will investigate the fundamental aspects of solid/gas magnetocatalysis ($CO+O_2$ and CO_2+H_2 reactions), building the basis for the possible development of an innovative green and cheap new type of heterogeneous catalysis.

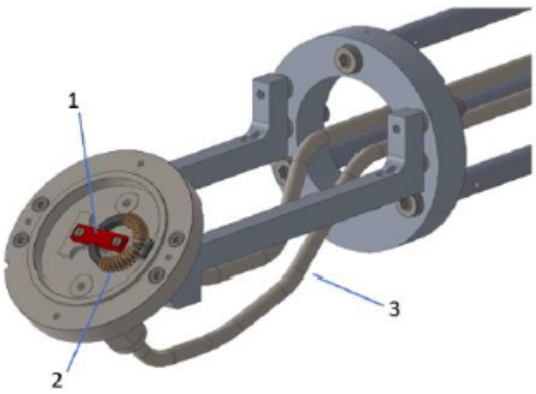

Figure 5- Ambient Pressure Soft XMCD cell design. 1) Sample; 2) Electromagnet; 3) Gas inlet.

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Poster 19

Understanding Activity, Stability, and Durability in Oxygen Electrochemistry through In Situ Detection of Reactive Oxygen Species

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Oxygen electrochemistry plays a critical role in energy conversion and environmental technologies. Beyond the conventional oxygen evolution reaction (OER), the formation of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) and ozone (O_3) can strongly influence both the oxidative performance of electrocatalysts and the long-term durability of devices such as electrolyzers and fuel cells. However, quantifying these species in situ remains difficult because of their rapid decomposition and overlapping reaction pathways.

By employing an in situ electroanalytical approach we precisely quantified the simultaneous formation of O_2, H_2O_2, and O_3 during water oxidation, aiming to clarify how activity, selectivity, and stability are interrelated in oxygen electrocatalysis.[1] A rotating ring–disk electrode (RRDE) technique was employed to deconvolute the current contributions of each oxygenated species under controlled hydrodynamic conditions across a broad pH range (1-8.3). Complementary Stationary Probe Rotating Disk Electrode coupled with and ICP-MS was used in the same conditions to track catalyst dissolution in real time, allowing direct comparison of catalytic selectivity and material stability.

The RRDE approach revealed that even conventional OER catalysts such as Pt and IrO_2 generate small but quantifiable levels of ROS, while PbO_2 exhibits markedly higher O_3 selectivity of up to 30% Faradaic efficiency in acidic media.

Combining ROS quantification with dissolution monitoring provides a unified framework to assess electrocatalyst activity, selectivity, and stability simultaneously. This integrated approach delivers mechanistic insight into performance-durability relationships and establishes design principles for advanced, long-lived materials in water oxidation, pollutant degradation, and energy conversion technologies.[2]

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Poster 20

In-situ observation of CO_2 activation in the presence of H_2 on Ni(111) and Ru(0001) surfaces by Ambient-Pressure X-ray Photoelectron Spectroscopy

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CO_2 hydrogenation is a promissing way to convert the industrial waste gas to valuable chemicals or fuels. Nickel (Ni) is the typical catalyst for CO_2 methanation with relatively high activity and selectivity. On the other hand, ruthenium (Ru) has been known as the most active catalyst for CO_2 activation [1]. There are mainly two reaction pathways: one is the direct dissociation pathway, in which CO_2 directly dissociates into CO and O on the surface, and the other is the hydrogen-assisted pathway, in which CO_2 reacts with atomic hydrogen to form formate (HCOO) or carboxyl (COOH). On Ni(111) and Ru(0001) surfaces which are the most stable facets of nanoparticles, different intermediates have been suggested depending on the experimental and calculation conditions, complicating interpretation [2,3].

In this study, the surface states and the reaction intermediates on Ni(111) and Ru(0001) surfaces have been systematically invesitgated using ambient-pressure X-ray photoelectron spectroscopy (APXPS) under 0.1 mbar CO_2 and 0.3 mbar H_2 gases. The measurements were performed at the soft X-ray beamline BL08U at NanoTerasu in Sendai, Japan [4] and the vacuum ultraviolet soft X-ray beamline BL-13B at Photon Factory in Tsukuba, Japan [5]. The photon energy was set to 1050, 490, and 730 eV for Ni 2*p*, Ru 3*d* and C 1*s*, and O 1*s* core levels, respectively. The sample temperature was changed from 300 to 570 K.

The reaction mechanisms are discussed by comparing results of the two surfaces. On a Ni(111) surface, carbonate (CO_3) and nickel oxide (NiO) due to CO_2 dissociation cover the active sites at 300 K, while above 370 K, CO and OH were observed, indicating COOH formation by H-assisted pathway. On a Ru(0001) surface, however, CO was observed from 300 to 370 K due to CO_2 dissociation. On the other hand, if H_2 was exposed to the surfaces in advance, the Ru(0001) surface was inactivated by atomic hydrogens, while COOH formation was observed even at 300 K on the Ni(111) surface. Above 470 K, carbon species accumulate on both surfaces, while the amount was much smaller on Ru(0001) compared to Ni(111) surface. The difference of reaction pathways can contribute to the unique activity and selectivity of each catalyst.

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Poster 21

Bio-inspired Surface Catalysis: Hemin Reactivity

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Catalytic processes are essential in nature, technology and chemical synthesis [1]. A new class of bio-inspired catalysts includes metal-organic frameworks and coordination networks, in which a single metal atom is embedded within an organic matrix, mimicking natural strategies for tasks such as light harvesting, chemical conversion and synthesis [2]. Here, we deposited a monolayer of Hemin (Ferriprotoporphyrin IX chloride) on Au(111). It self-assembles into an ordered structure in which two molecular species can be distinguished within the layer, corresponding to Fe-filled molecules (Hemin) and Fe-free ones (Protoporhyrin IX), reflecting the composition of the starting biological material. The structural and electronic properties of Hemin/Au(111) were characterized using Scanning Tunneling Microscopy (STM), and spectroscopy techniques from Ultra High Vacuum to Near-Ambient Pressure (NAP) conditions, revealing a mild reactivity of the layer toward 0.1 mbar O_2. When Co adatoms are co-deposited, a Co-Fe transmetalation process takes place (Figure 1, left), partially promoted by molecular oxygen exposure (Figure 1, right), further enhancing the reactivity of the system toward O_2. This work highlights the potential of functionalized bio-inspired materials, where controlled transmetalation provides a strategy to engineer active sites at atomic level, while NAP spectroscopy offers a direct access into catalytic reactions *in situ* under realistic conditions for the development of next-generation catalytic materials.

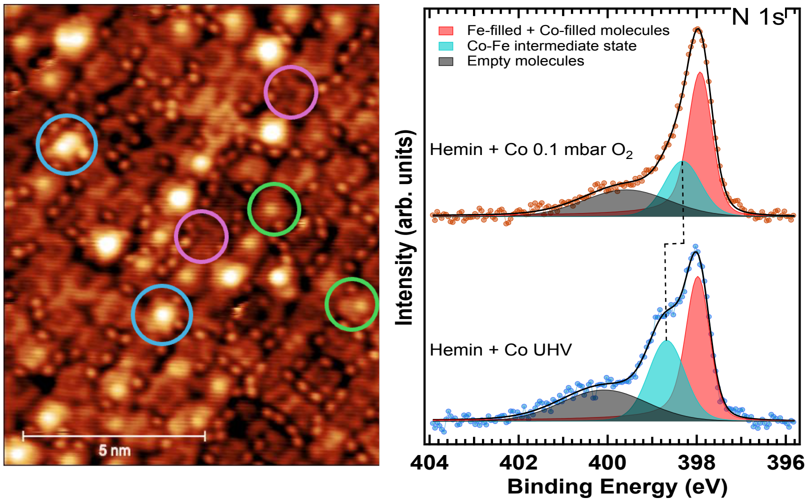

Figure 6 Left) STM image of Hemin/Au(111) after Co deposition showing Fe-filled, Co-filled molecules and Co-Fe intermediate transmetalation state (circled in pink, green and blue, respectively). Right) N 1s spectra of Hemin/Au(111) after Co deposition demonstrating that transmetalation is promoted under 0.1 mbar O_2.

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Poster 22

In-situ mapping of variables that govern Iridium electrochemical stability

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Iridium oxide is considered the benchmark catalyst for the oxygen evolution reaction (OER) due to both stability and activity. Using cyclic voltammetry and CO charge displacement, we establish potential-dependent charge states and adsorbate coverages, revealing hydrogen and hydroxyl co-adsorption at low potentials on Ir(111) and almost no Had coverage on Ir(110).1 In-situ Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) provides direct evidence of hydrogen, hydroxyl, and oxygen species and, critically, their interactions with interfacial water, which are confirmed by Density Functional Theory calculations. These insights illuminate trends in hydrogen oxidation/evolution and oxygen reduction reactions, showing that both adsorbate coverage and the hydrogen-bonding network of interfacial water determine Ir(hkl) reactivity. Additionaly, employing in-situ SPRDE-ICP-MS2 three facet-dependent dissolution processes were identified: Ir(hkl) surfaces maintain electrochemical stability up to 1.0 V in a 0.1 M perchloric acid solution, with formation of a reversible oxide.3 Notably, at higher potentials, 1.40 V, Ir(100) exhibits less reordering than Ir(111), despite dissolving five times more. After cycling Ir(100) maintains all features of the pristine surface with a slight decrease in intensity, while Ir(111) loses crystallinity, reducing the length of (111) terraces and forming (100) steps, as a result of the formation of an irreversible oxide, which is reduced to metallic iridium only at lower potential. We also explored the impact of electrochemically grown oxide on OER activity, underscoring a structural dependence on the properties of the iridium oxide. Together, these in situ measurements bridge structure–reactivity–stability relationships at the atomic scale, underscoring the central role of in situ characterization in accelerating advanced materials for energy conversion and storage.

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Poster 23

In situ and *operando* investigation of molecular layer deposition using APXPS

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Molecular Layer Deposition (MLD) is an extension of Atomic Layer Deposition (ALD), a thin film growth technique based on sequential, self-limiting reactions between gaseous precursors and a solid surface. In MLD, organic precursors can be introduced in place of or alongside inorganic ones, enabling the formation of hybrid organic–inorganic thin films. Importantly, MLD processes can be carried out in conventional ALD reactors, with the main distinction being the incorporation of organic species that add functionality to the films. Like ALD, MLD cycles consist of alternating precursor pulses and purge steps, which provide precise control over film thickness and composition at the atomic scale (cf. Fig. 1a).

Ambient pressure x-ray photoelectron spectroscopy (APXPS) is particularly well suited for *in situ/operando* characterization of ALD and MLD, as the pressure window of APXPS (up to tens of mbar) directly matches the operating conditions of ALD/MLD reactors. APXPS provides detailed insights into surface chemistry, from the initial nucleation of materials to steady-state film growth. ALD and MLD are normally carried out in dedicated reactors. The SPECIES beamline at MAX IV features a tailor-made ALD/MLD cell for APXPS investigations[1], which is similar to the standard APXPS cell design, but which is optimized for ALD/MLD by incorporating a vapor delivery system with heated lines, heated chamber walls, and ALD type pulse valves. This configuration allows real-time, time-resolved monitoring of precursor surface interactions during film growth.

The SPECIES ALD/MLD cell was used to study the MLD of *hafnicone*[2] (cf. Fig. 1), deposited using tetrakis(dimethylamido)hafnium (TDMAHf) and ethylene glycol (EG) as precursors. The APXPS data suggests that TDMAHf reacts with the Si surface following a ligand-exchange mechanism. Likewise, the ethylene glycol replaces the amido ligands by ligand exchange. Hence, the chemistry of hafnicone formation is as expected. The study highlights how APXPS can deliver mechanistic insight into MLD.

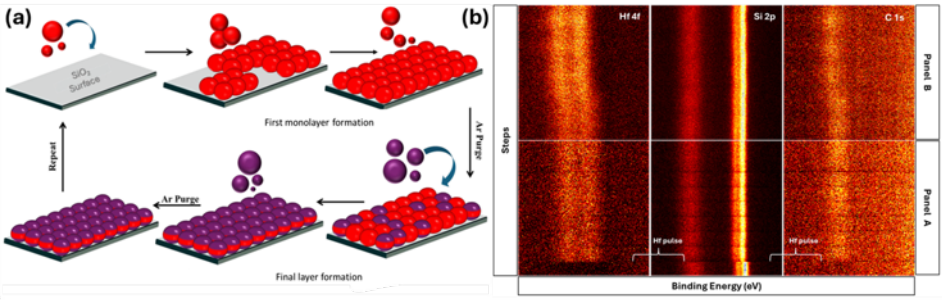

Figure 1: *(a) Schematic representation of the MLD process, (b) Time-resolved spectra showing Hafnicone formation during the MLD cycle. Panel A shows the core levels during Hf pulsing, and Panel B shows the core levels during EG pulsing. Hf 4f shifts confirm titanium incorporation, shift in the Si 2p shows the linkage of Hf to the substrate, and C 1s shift indicates Hf–O–C linkage formation, capturing the sequential chemical transformations leading to the final metalcone.*

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Poster 24

Co_3O_4 for sustainable CO_2 reduction and possible fine-tuning towards selective CO production

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Two main challenges involved in heterogeneous catalytic CO_2 reduction are: (a) decreasing the consumption of H_2 to the minimum required level with possibly the maximum CO_2 conversion, and (b) concurrently enhancing the selectivity of the desired CO, at the cost of methane. Towards meeting these two challenges, Co_3O_4 spinel has been identified as a potential catalyst and it exhibits predominant CO selectivity $\geq$ 673 K at atmospheric pressure. CO_2 conversion begins $\geq$ 523 K, with 100% CO selectivity observed $\geq$ 673 K with CO_2:H_2 = 3:2. Current work shows a sustainable catalytic CO_2 conversion to 100% CO selectivity with Co_3O_4-Nanocube (NC). Critically, CO selectivity and yield is observed to increase at the cost of methane with smaller amount of H_2. 1:1 and 3:2 CO_2:H_2 ratio exhibits 88–100% CO selectivity with 24–32.5% CO_2 conversion between 623 and 823 K. Irrespective of the input CO_2:H_2, ratio of CO_2:H_2 uptake changes from around 1:3 at 523 K to 1:1–1.5 at 823 K with concurrent production of significant methane to predominant CO, respectively. Surface electronic state changes was explored by near ambient pressure photoelectron spectroscopy, and the results suggests that Co_3O_4 is the active phase that promotes CO_2 reduction selectively to CO. Broadening observed with the vibrational feature of the CO_2 molecules at high temperature underscores the heterogeneous character of the catalyst surface, under operating conditions, due to changing electron density. By optimizing the gas hourly space velocity (GHSV), H_2-lean CO_2:H_2 ratio, and the reaction temperature/pressure, 100% CO selectivity could be broadened to a range of operating conditions.

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Poster 25

Investigation of Electrochemical Dissolution Using Online Inductively Coupled Plasma Mass Spectrometry

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Electrocatalysts can experience significant changes in structure and content (material stability) and current/potential (electrochemical stability) in response to reaction conditions, prompting thorough investigation into degradation mechanisms.[1] Here, we present the stationary probe rotating disk electrode paired with inductively coupled plasma mass spectrometry (SPRDE ICP-MS),[2] a technique which enables the real-time monitoring of electrocatalyst dissolution. Through time- and potential-resolved analysis, SPRDE ICP-MS relates material stability to electrochemical stability, presenting a holistic approach to electrocatalyst stability assessments.

We demonstrate the capabilities of the SPRDE ICP-MS technique through examples relevant to electrochemical CO_2 reduction (CO_2RR). Silver-based catalysts exhibit high selectivity for CO_2 to CO conversion, thus serving as an important class of materials for cathodic dissolution analysis. IrO_x, as the leading material for the oxygen evolution reaction (OER), is often used as the anode during CO_2RR. The dynamic nature of catalysts during CO_2RR present an exciting opportunity for complementary materials characterization techniques, such as ambient pressure X-ray photoelectron spectroscopy (APXPS), to probe the surface reactions occurring during dissolution. Investigation into the stability of both the cathode and anode yields an encompassing look at CO_2RR systems and the stability challenges faced in order to inform future robust catalytic systems targeting CO_2RR.

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Poster 26

High-Precision Core Level Binding Energy Shifts of Potassium in Catalysts by Near-Ambient Pressure (NAP) XPS in the Home Laboratory

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NAP XPS system with a conventional (non-synchrotron) X-ray source allows the determination of core level BEs with unprecedented precision by taking advantage of surface charge neutralisation through electron-ion pair formation in the gas phase near the sample surface. This surface charge neutralisation technique has been used for electron-yield X-ray absorption spectroscopy since at least 1979.[1] However, its potential for core level BE measurements with extremely high precision has not been explored much. The interpretation of core level BEs depends critically on the precision of the BE measurements,[2] for which a reliable BE scale calibration is paramount. BE scale calibrations in XPS are known to be fraught with potential complications that may limit both accuracy and precision.[2] However, recent studies of Brønsted interactions by laboratory NAP XPS have demonstrated that core level BEs can be determined with extremely high precision (better than ±0.1 eV), even across different instruments.[3] The high precision is achieved by combining surface charge neutralisation with careful BE calibrations with an internal standard. BEs associated with Brønsted interactions were shown to be extremely sensitive to the electrostatic field of the protons.[3] We have extended this work to study the effects of electrostatic fields around alkali and alkaline earth metals (AAEM) cations, which are well-known promotors in economically important catalysts (water-gas shift; alcohol and ammonia synthesis). The 2p BEs of K cations change significantly as a function of chemical environment. Coordination with carbonate reduces the K 2p binding energy by several 0.1 eV compared to nitrate and chloride environments, indicating higher charge transfer (and perhaps more effective K 2p core hole screening) from the doubly charged and more polarisable carbonate anion. Studies of K_2CO_3 promotors on α-Al_2O_3 and γ-Al_2O_3 reveal that interactions with the catalyst supports also modifies the local electron density at the alkali metal centres.

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Poster 27

Preliminary study of a multimodal chamberless HAXPES and XRD system

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Hard x-ray photoelectron spectroscopy (HAXPES) is a bulk-sensitive technique with a probing depth of several tens of nanometers, utilizing high kinetic energy photoelectrons emitted by hard x-ray beams. The x-ray diffraction method typically detects a thickness of several micrometers (a bulk-sensitive technique) using a hard x-ray source and can collect data in air, vacuum, or gas conditions. The BL46XU beamline at SPring-8 has developed a system for simultaneous, chamberless HAXPES with XRD, using a single x-ray source to analyze the crystal structure, chemical state, and electronic structure of samples in atmospheric conditions. This combination allowed for a comprehensive analysis of the bulk properties within a sample. Additionally, by injecting He gas directly into the sample through a gas line, we reduced the background signal caused by atmospheric gas scattering of HAXPES spectra, leading to an improved signal-to-noise ratio. Chamberless HAXPES with XRD not only enables the simultaneous measurement of crystal and electronic structures but also introduces a new measurement paradigm for an XPS technique that can analyze samples exposed to the atmosphere.

Poster 28

Oxophilicity of Ternary Ga-Ag-Pt and Ga-Cu-Pt Liquid Metal Solutions

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Liquid alloys of Ga and a transition metal have been shown to be highly active in the propane dehydrogenation reaction.[1,2] Nevertheless, oxygen in the feed stream can deactivate the catalyst.[3] Therefore, we investigated the oxophilicity of the novel ternary liquid metal alloys GaAgPt, GaCuPt by XPS in the temperature range from 550-800 K and compared them to the original binary GaPt system. All samples were composed of 1 at.% Pt and 10 at.% coinage metal (Ag/ Cu). The onset temperature of the oxidation and the Ga-oxide layer thickness indicate that the GaCuPt system is the most oxophilic, followed by the GaAgPt system and the binary GaPt system as the least oxophilic. In addition, we report that the formation of an oxidic Pt species during oxidation at higher temperatures occurs while no oxidic Cu or Ag species were found. Furthermore, we observe an incorporation of the Pt into the Ga-oxide layer for oxidation at lower temperatures, while at higher temperatures, the Pt accumulates at the interface between the metallic Ga and the Ga-oxide. The Ga-oxide, which was formes at lower temperatures, can be thermally removed, while the layer, which formes above 700-750 K is stable even at elevated temperatures.
The results from the oxidation studies showe, that for these catalysts, temperatures above 650 K should be avoided to prevent the formation of the more stable Ga-oxide species and strong passivation by the oxide layer.

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Poster 29

Surface chemistry of Ru on ceria: a model catalyst approach

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Ruthenium supported on ceria (Ru/CeO_2) has emerged as a highly versatile catalyst owing to the unique synergy between Ru species and the oxygen storage-release capacity of ceria. This interaction promotes efficient redox processes, enhances the dispersion and stability of Ru, and enables dynamic changes in oxidation state under reaction conditions. As a result, Ru/CeO_2 plays a central role in a wide variety of reactions, including CO and hydrocarbon oxidation, the water-gas shift, CO_2 hydrogenation, the oxygen evolution reaction in water electrolysis, and ammonia synthesis and decomposition. For all these processes, a fundamental understanding of how Ru interacts with ceria, and how different environments affect the catalyst's surface structure and composition, is crucial.

In this work, we present a comprehensive investigation of Ru deposited on ceria surfaces with varying step density and degree of reduction. Using a combination of ultrahigh vacuum studies and in situ NAP-XPS and NAP-STM, we probe the surface chemistry of model Ru/CeO_2 catalysts under high vacuum and controlled gas atmosphere conditions. The results provide direct insight into the sites occupied by dispersed Ru atoms and small Ru clusters on ceria, their oxidation states, and their stability. We also demonstrate how different gas environments and temperatures influence the catalyst, revealing the mechanism of Ru redispersion reported in literature.

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