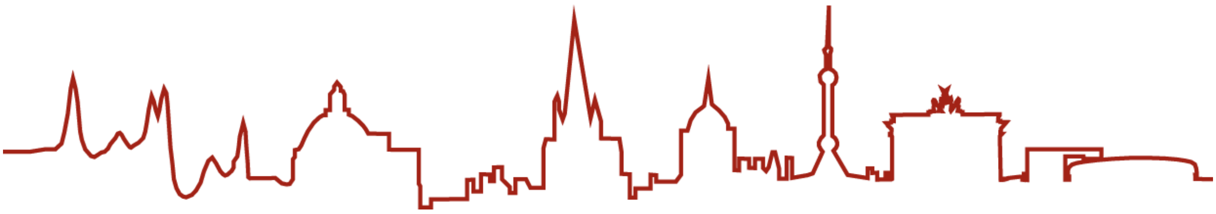

# 6th Annual Ambient pressure X-ray Photoelectron Spectroscopy Workshop 2019

## Full program

10th-13th December 2019

Lund, Sweden

**The APXPS-2019 workshop** is hosted by the MAX IV laboratory and brings together scientists from different fields including catalysis, electrochemistry, and environmental science in Lund, Sweden, to focus on the latest developments in the application of Ambient Pressure XPS.

The workshop features plenary and invited speakers by experts in various fields, contributed oral presentations, and sponsored commercial talks. The talks on Tuesday (10th of December) afternoon focus on recent developments of the APXPS technique, while the program on Wednesday and Thursday focuses on scientific applications of APXPS. Wednesday afternoon there is also a poster session at Skissernas museum, and the conference dinner takes place at Grand Hotel Lund, where you will have a chance to enjoy a traditional Swedish Christmas Dinner. Friday morning you will get a chance to experience Swedish Lucia and visit the MAX IV laboratory. The 2019 edition of the workshop is organised jointly by the beamline team of the SPECIES and HIPPIE beamlines and hosted by MAX IV.

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## Organizer

MAX IV

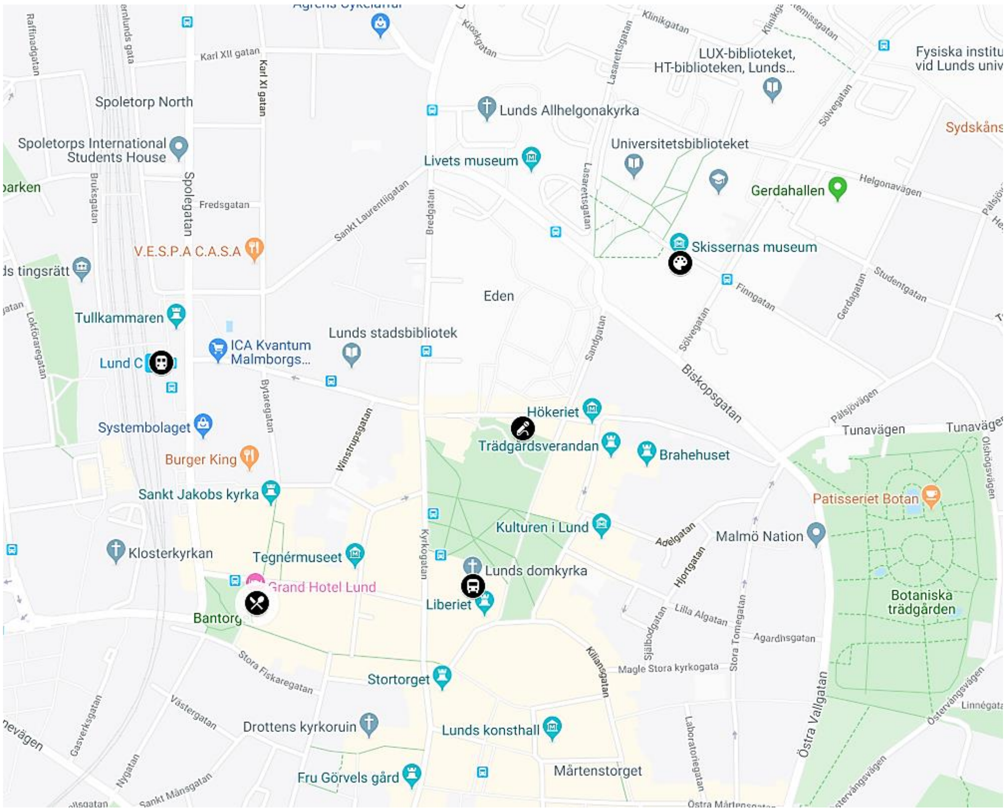
# Venue

**Oral presentations**: Palaestra et Odeum, Paradisgatan 4. *Tuesday 10th - Thursday 12th*

**Poster session**: Skissernas Museum, Finngatan 2. *Wednesday 11th 17h30-20h00*

**Conference Dinner**: Grand Hotel, Bantorget 1. *Thursday 12th from 19h00*

**Lucia Choir** and **MAX IV visit**: MAX IV, Fotongatan 2. *Friday 13th 8h00-11h00.*



On **Friday 13th** the bus departs at 7h45 from the Lund Cathedral (Lund Domkyrka, Kyrkogatan 6) to MAX IV and comes back at 11h15 from MAX IV to the Cathedral.

If you lose the organized bus you can take the public bus (green) n. 20 departing from the train station every 12 minutes (7h41, 14 min travel time). Tickets on-board, only by card or APP (Skånetrafiken)

**Lucia Choir** starts at 8h15, breakfast is served.

From 9h30 to 11h there is the MAX IV tour.

## Contact

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APXPS2019@maxiv.lu.se

## Scientific Advisory Committee

**Luca Artiglia** Paul Scherrer Institute, Switzerland
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**Mikko-Heikki Mikkelä** MAX IV Laboratory
**Esko Kokkonen** MAX IV Laboratory
**Helena Ullman** MAX IV Laboratory
**Robin Ollivander** MAX IV Laboratory

## Invited Speakers

**Bernd Winter**, Helmholtz Zentrum Berlin and BESSY II, Germany (**Plenary**)
*Photoelectron Spectroscopy from Liquid Microjets: New Developments and Opportunities*

**William Chueh**, Stanford University, USA (**Plenary**)
*Mechanistic understanding of redox reactions on cerium oxide: CO2, H2O and O2 reduction*

**Enrique Ortega**, Universidad del País Vasco, Spain
*Ignition of the catalytic CO oxidation at Pd and Pt surfaces curved around the (111) direction*

**Kees-Jan Weststrate**, Syngaschem BV, The Netherlands
*Using high resolution XPS at low and near-ambient pressures to resolve mechanistic issues in cobalt-catalyzed Fischer-Tropsch synthesis*

**Peter Amann**, Stockholm University, Sweden
*High-pressure x-ray photoelectron spectroscopy for studies of catalytic materials above atmospheric pressure*

**Qiang Fu**, Dalian Institute of Chemical Physics, China
*Catalysis and energy processes confined under 2D layers explored by near ambient pressure photoemission electron microscopy and spectroscopy (NAP-PEEM/PES)*

**Andrei Kolmakov**, NIST, USA
*From Spectromicroscopy to Nanofabrication In liquids with Soft X-rays*

**Matthias Minjauw**, Ghent University, Belgium
*In situ X-ray based characterization of atomic layer deposition*

**Fredrik Lindgren**, Uppsala University, Sweden
*The road towards operandi measurements of Li-ion battery electrodes*

**Plenary Talk** **Invited Talk** **Contributed Talk**

## Tuesday 10 December 2019

| | |
|---|---|
| **14.00 - 14.40** | **Registration & Coffee** |
| **14.40 - 14.50** | **Welcome** |

**Session: *INSTRUMENTATION 1***

| | |
|---|---|
| 14:50-15:20 | **Peter Amann**<br>*High-pressure x-ray photoelectron spectroscopy for studies of catalytic materials above atmospheric pressure* |
| 15:20-15:40 | **Slavomír Nemšák**<br>*Multimodal approach simultaneously probes structure and chemistry* |
| 15:40-16:00 | **Georg Held**<br>*Depth Profiling of Catalyst Nanoparticles* |
| **16:10 - 16:30** | **Coffee** |

**Session: *INSTRUMENTATION 2***

| | |
|---|---|
| 16:30-17:00 | **Qiang Fu**<br>*Catalysis and energy processes confined under 2D layers explored by near ambient pressure photoemission electron microscopy and spectroscopy (NAP-PEEM/PES)* |
| 17:00-17:20 | **Andreas Thissen**<br>*Chemical reactions, corrosion and electrochemistry at solid-liquid interfaces– routine operando studies with Near Ambient Pressure XPS* |
| 17:20-17:40 | **Patrick Zeller**<br>*Spatially resolved XPS measurements of the oxidation and reduction dynamics of polycrystalline transition metals* |
| 17:40-18:00 | **Lars-Åke Näslund**<br>*The magnesium assisted oxide break-up kinetics at flux-free brazing of aluminium alloy materials* |

# Wednesday 11 December 2019

## Session: *ELECTROCHEMISTRY 1*

| | |
|---|---|
| 09:10-09:50 | **William Chueh** *Mechanistic understanding of redox reactions on cerium oxide: $CO_2$, $H_2O$ and $O_2$ reduction* |
| 09:50-10:10 | **Lorenz J. Falling** *The electronic structure of electrochemical interfaces at equilibrium and the gain from transient experiments* |
| **10:10 - 10:50** | **Coffee** |

## Session: *ELECTROCHEMISTRY AND FUEL CELLS*

| | |
|---|---|
| 10:50-11:20 | **Fredrik Lindgren** *The road towards operandi measurements of Li-ion battery* |
| 11:20-11:40 | **Kuno Kooser** *Operando HT-NAP-XPS and impedance spectroscopy study ofNi-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ solid oxide fuel cell anode* |
| 11:40-12:00 | **Simon Pitscheider** *Towards the mechanistic interpretation of the oxygen exchange reactions on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ thin film electrodes* |
| **12:00 - 13:40** | **Lunch** |

## Session: CATALYSIS *1*

| | |
|---|---|
| 13:40-14:00 | **Benjamin Hagman** *Dissociative adsorption of $CO_2$ on Cu-surfaces* |
| 14:00-14:20 | **Liping Zhong** *Using NAP-XPS to identify the optimum surface state of cobalt catalysts for CO preferential oxidation in $H_2$-rich feedstock* |
| 14:20-14:40 | **Marie Døvre Strømsheim** *Investigations of the surface dynamics of Pd-alloy surfaces under oxidation reactions* |
| **14:40 - 15:10** | **Coffee** |

## Session: CATALYSIS *2*

| | |
|---|---|
| 15:10-15:40 | **Enrique Ortega** *Ignition of the catalytic CO oxidation at Pd and Pt surfaces curved around the (111) direction* |
| 15:40-16:00 | **Kræn C. Adamsen** *Combined UHV-STM and AP-XPS study of Selective Catalytic Reduction (SCR) of NOx over a VOx/$TiO_2$ based catalyst* |
| 16:00-16:20 | **Zongfang Wu** *APXPS Study of Propylene Oxidation over $Cu_2O$ Surfaces* |
| 16:20-16:40 | **Ashley R. Head** *Chemical Warfare Agent Simulants and Atmospheric Gases: Adsorption Battles in Gas Filtration* |
| 16:40-17:00 | **Lindsay R. Merte** *Surface composition of $Pt_3Sn(111)$ during CO oxidation* |
| 17:30-20:00 | POSTER SESSION at Skissernas Museum, Lund |

# Thursday 12 December 2019

## Session: LIQUID-JETS

09:00-09:40 **Bernd Winter** *Photoelectron Spectroscopy from Liquid Microjets: New Developments and Opportunities*

09:40-10:00 **Shuzhen Chen** *Effect of a cationic surfactant on the interfacial structure of bromide oxidation by ozone*

10:00-10:20 **Robert Seidel** *Photoemission Spectroscopy from Metal-oxide / Aqueous Solution Interfaces*

**10:20 - 10:50 Coffee**

## Session: LIQUID-JETS 2 AND MEMBRANES

10:50-11:10 **François Rochet** *Electronic level alignment between a metal electrode and a solution with a known redox potential: a liquid-jet XPS study at Pleiades beamline(SOLEIL)*

11:10-11:30 **Sabrina M. Gericke** *Characterization of Model Desalination Membranes by Ambient Pressure Photoelectron Spectroscopy*

11:30-11:50 **Hendrik Bluhm** *Increased Reactivity of Subsurface Hydrogen Probed in a Membrane Reactor Cell by APXPS*

**11:50 - 13:30 Lunch**

## Session: ELECTROCHEMISTRY AND ATOMIC LAYER DEPOSITION

13:30-14:00 **Andrei Kolmakov** *From Spectromicroscopy to Nanofabrication In liquids with Soft X-rays*

14:00-14:30 **Matthias M. Minjauw** *In situ X-ray based characterization of atomic layer deposition*

14:30-14:50 **Giulio D'Acunto** *ALD of $HfO_2$ on InAs: new insight by time-resolved in-situ studies*

**14:50 - 15:20 Coffee**

## Session: CATALYSIS 2

15:20-15:50 **Kees-Jan Weststrate** *Using high resolution XPS at low and near-ambient pressures to resolve mechanistic issues in cobalt-catalyzed Fischer-Tropsch synthesis*

15:50-16:10 **Evgeniy A. Redekop** *Pt-Cu nanoparticles on 2D and 3D supports: an AP-XPS/TAP study*

16:10-16:30 **Ethan J. Crumlin** *Combining Theory with Experiments to Unravel Silver Interacts with Carbon Dioxide and Water*

16:30-16:50 **Frederic Sulzmann** *Oxygen on silver and their role in methanol oxidation*

16:50-17:10 **Zbynek Novotny** *Oxidation of Ir(001) towards IrO2 studied by ambient-pressure X-ray photoelectron spectroscopy*

17:10-17:30 **Ki-jeong Kim** *APXPS20 - 8A2 KBSI-PAL beamline at Pohang Accelerator Lab*

| | |
|---|---|
| **17:30 - 18:30** | **Workshop Discussions** |
| **19.00 - 21.00** | **Dinner at Grand Hotel, Lund** |

## Friday 13 December 2019

| | |
|---|---|
| 7.45 | Bus leaves from the Cathedral to MAX IV |
| 8.00 | Arrival MAX IV |
| 8.15 | Lucia Choir and breakfast |
| 9.30-11.00 | MAX IV tour |
| 11.15 | Bus departs from MAX IV to the Cathedral |


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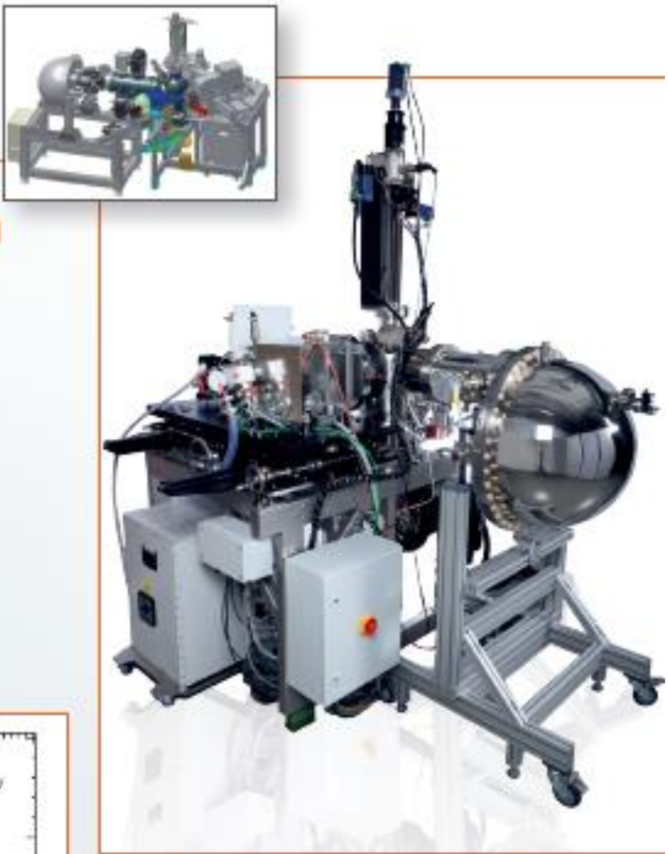

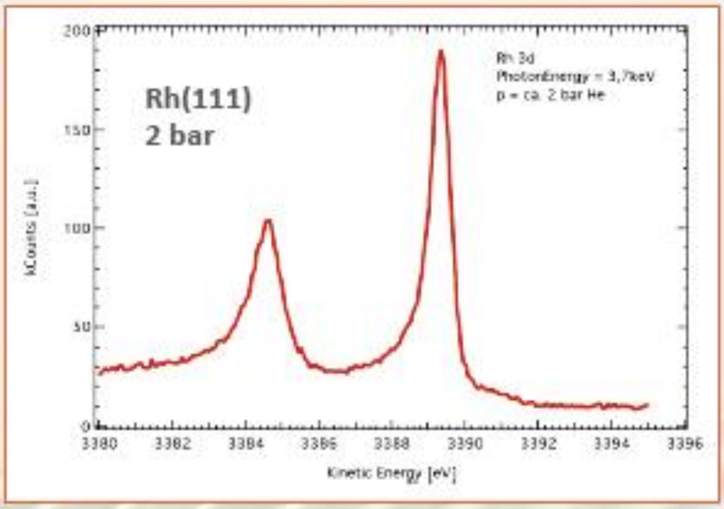
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Ion source
50 kV irradiation facility
Coated components
Helium leak detector
Mass spectrometer
Gas analyser
Rotary vane pump
Multi-stage Roots pump
Diaphragm pump

***Invited talk*** ***Tuesday 10th 15h10***

# High-pressure x-ray photoelectron spectroscopy for studies of catalytic materials above atmospheric pressure

Peter Amann[1]

[1]Department of Physics, Stockholm University, 10691 Stockholm, Sweden

In order to reach a sustainable future with net-neutral $CO_2$ emission, it is of utmost importance to find suitable catalyst materials, capable to transform anthropogentic CO and $CO_2$ into fuels and chemicals. In order to shed light into the underlying mechanism of how molecular bonds are broken and new bonds are formed, a substantial effort in instrument development has taken place, mostly with the idea to study the catalyst material under well controlled environments. In typical industrial reactors, however, related processes take place at pressures of several bars and temperatures exceeding 100 °C, which makes it difficult to examine the involved reactions from a mechanistic point of view.

Here I report on a newly developed scientific end-station called POLARIS that is capable of acquiring x-ray photoelectron spectroscopy (XPS) spectra at pressures exceeding 1 bar and temperatures up to 500 °C while the reaction takes place [1].

This instrument is currently situated at DESY research facility in Hamburg / Germany and is regularly operated at the P22 beamline. In order to enhance the signal to noise ratio, it takes advantage on a combination of developments that allow for efficient detection of photo emitted electrons of molecular species being formed during the reaction. By controlling the x-ray incidence angle with step sizes down to 2µrad, we are able to considerably enhance the surface sensitivity.

Details on the instrument will be presented. Measurement results will focus on different catalyst materials and their related reaction mechanisms.

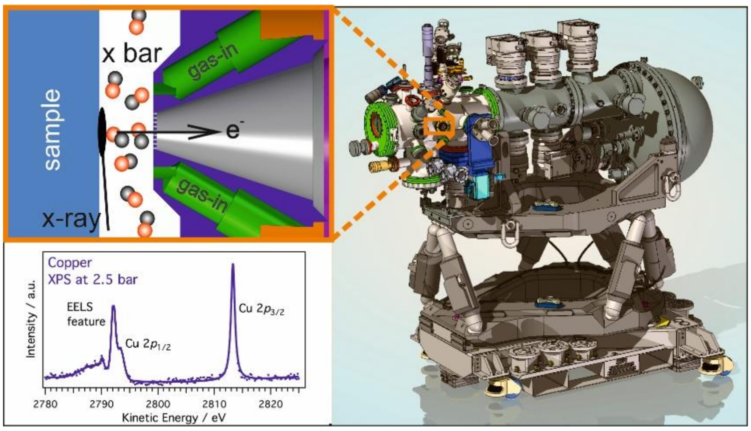

Figure 1 right: 3D model of the POLARIS end station and, top-left, a cartoon of the virtual cell. In the bottom-left Cu 2*p* data are presented that have been obtained at 2.5 bar He pressure.

[1] P. Amann et al. ‘A high-pressure x-ray photoelectron spectroscopy instrument for studies of industrially relevant catalytic reactions at pressures of several bars’, Review of Scientific Instruments 90, 103102 (2019); https://doi.org/10.1063/1.5109321

***Contributed talk*** ***Tuesday 10th 15h40***

# Multimodal approach simultaneously probes structure and chemistry

Heath Kersell[1], Hendrik Bluhm[2], Slavomír Nemšák[1]

[1]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA
[2]Fritz Haber Institute of Max Planck Society, Berlin, Germany

Ambient pressure X-ray photoemission spectroscopy (APXPS) is a powerful technique for understanding surface chemistry under operating conditions. Although it is successfully closing so-called "pressure gap", materials in operating devices often undergo structural transformations, which are connected to another - "complexity gap". Even for model systems, such as single-crystals, atomically flat surfaces can become structured and rough, exposing new active sites (e.g. boundaries and step edges) and facilitating reaction pathways unavailable on the pristine surfaces.

One successful strategy to tackle this problem is to supplement chemical probe (APXPS) with *ex-situ* structural measurements (high pressure STM, operando XRD, etc) [1,2]. Our solution to the problem goes one step further and provides simultaneous *in-situ*/*operando* chemical and structural information by coupling APXPS with ambient pressure grazing incidence X-ray scattering (AP-GIXS). The concept and the design of the newly built instrument at the beamline 11.0.2 of the Advanced Light Source will be presented. First experimental results of the Ag-behenate transformation under $O_2$ and thermal treatment will be also discussed.

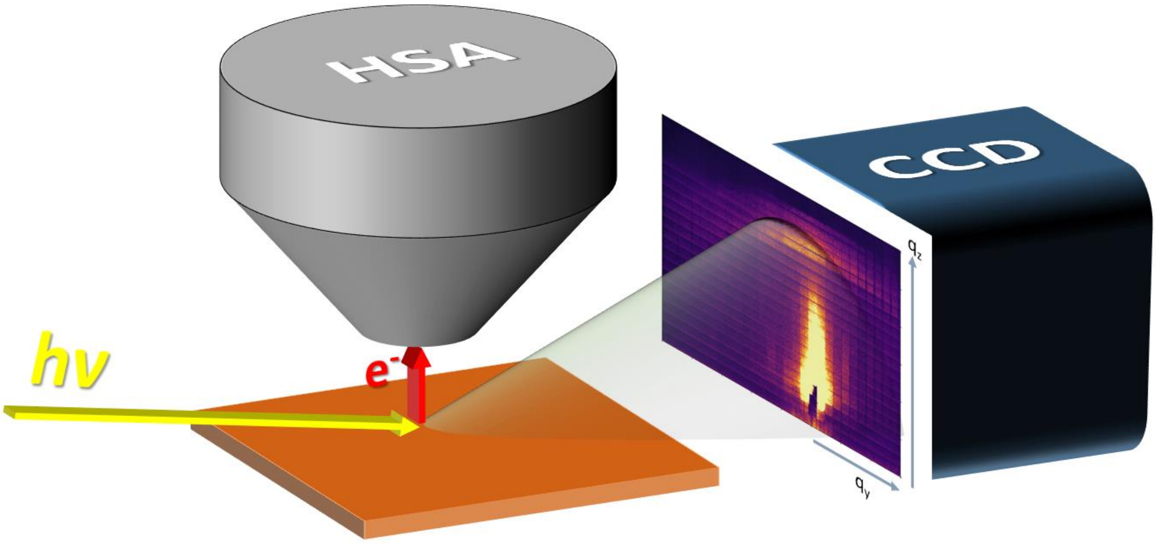

Figure 1. Experimental configuration of combined ambient pressure XPS and X-ray grazing incidence scattering setup.

[1] D.R. Butcher et al., *Chem. Comm.* **61** (2013).

[2] L. Lukashuk et al., *ACS Catalysis* **8** (2018).

***Contributed talk*** ***Tuesday 10th 16h00***

# Depth Profiling of Catalyst Nanoparticles

Georg Held[1],

[1]Diamond Light Source, Didcot, UK,

With tuneable X-ray sources, such as synchrotrons, XPS can be used depth for profiling of non-planar surfaces by making use of the variation in the photoelectron inelastic mean free path (IMFP) as function of kinetic (photon) energy. This has been used extensively in recent years in order to separate surface and bulk species in catalyst particles (see e.g. [1]). For quantification often a simple Lambert-Beer-type depth dependency is used, however, this model breaks down, when the size of the catalyst particles is of the same order of magnitude as the IMFP. We are using a spherical model to demonstrate the consequences for quantification surface-to-bulk ratios and metal loading, and apply this model to the analysis of Ni nanoparticles with organic ligand shells [2].

[1] Tao et al. Science 322 (2008) 932.

[2] Arrigo et al, (2019) submitted.

***Invited talk*** ***Tuesday 10th 16h20***

# Chemistry within 2D Nanospace Explored by Near Ambient Pressure PEEM and XPS

Qiang Fu

State Key Lab of Catalysis, Dalian Institute of Chemical Physics, CAS, Dalian 116023, China

Small spaces in nanoreactors may have big implications in chemistry, because chemical nature of molecules and reactions within nanospaces can be changed due to the nanoconfinement effect [1-3]. Two-dimensional (2D) nanospace formed under 2D materials can provide a well-defined model system to explore confined catalysis and energy storage processes [1-3]. Fundamental understanding of the confined chemistry strongly relies on in-situ surface analysis under near ambient pressure (NAP) conditions. In the first part of my talk I will mainly introduce the instrumentation for NAP surface science studies, including Environ-ESCA, Liquid-phase AFM and particularly NAP photoemission electron microscopy (NAP-PEEM) in our lab [4]. Based on the design concepts of two-stage acceleration voltage and three-stage differential pumping, we have developed a NAP-PEEM system which can work in near ambient pressure gases (> 1 mbar). Using a Hg lamp or a deep ultraviolet laser as the illumination source, a spatial resolution around 20 nm can be demonstrated at gas pressures up to 0.1 mbar. Installed with an electron gun near ambient pressure low energy electron microscopy (NAP-LEEM) can be achieved as well. In the second part, I will concentrate on operando studies in aluminium ion battery processes based on model 2D electrodes. Techniques including Raman, XPS, and AFM are successfully applied to reveal the battery mechanism and the related processes.

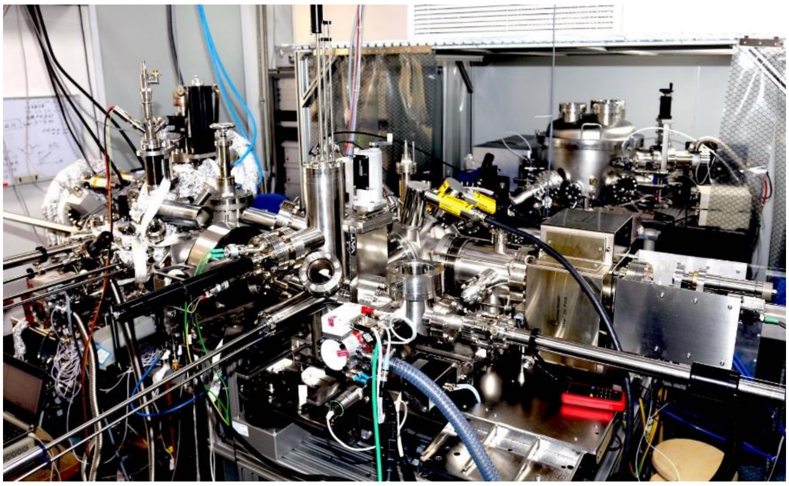

Figure 1 Picture for the NAP-PEEM system connected with XPS and Deep ultraviolet laser source (DUV).

[1] Q. Fu and X.H. Bao, ***Nat. Catal.***, 2019, 2, 834

[2] Q. Fu and X.H. Bao, ***Chem. Soc. Rev.***, 2017, 46, 1842

[3] H.B. Li, J.P. Xiao, Q. Fu, X.H. Bao, ***PNAS***, 2017, 23, 5930

[4] Y.X. Ning, Q. Fu, et al., ***Ultramicroscopy***, 2019, 200, 105

***Contributed talk*** ***Tuesday 10th 16h50***

# Chemical reactions, corrosion and electrochemistry at solid-liquid interfaces – routine operando studies with Near Ambient Pressure XPS

Paul Dietrich[1], Andreas Thissen[1]

[1]SPECS Surface Nano Analysis GmbH, Berlin, Germany

Over the last decades XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential in a wide variety of applications. Starting from operando studies of surface reactions in catalysis, the applications soon have been enhanced towards studies of processes at liquid surfaces, mainly using freezing/melting cycles, liquid jets or liquid films on rotation disks or wheels. Since more than 15 years, the need for basic studies of the fundamental chemistry at solid-liquid interfaces has attracted growing interest. Dip-and-pull experiments at synchrotrons finally also demonstrated, that in-situ and operando XPS in electrochemical experiments can be realized, mainly using synchrotron beams, significantly contributing to the basic understanding of modern energy converting or storing devices, like batteries, fuel cells, etc.

The development of pure laboratory NAP-XPS systems with optimized sample environments, like special sample holders, Peltier coolers and operando liquid cells combined with full automation and process control provides possibilities for the preparation and analysis of a multitude of liquid samples or solid-liquid interfaces on a reliable daily base.

Interfaces of semiconductors with organic solvents are important for production processes and device operation. The first example presented shows the simplicity of obtaining relevant results on Silicon in different organic solvents without the need of highly sophisticated setups or special excitation sources beyond Al $K_{\square}$.

The next level of complexity is to follow the effects of corrosion in organic or inorganic acids. As an example an operando study of metal corrosion in acetic acid is shown.

Most sophisticated experiments so far have been operando electrochemistry in a classical three-electrode setup. A versatile setup is presented, allowing for studies of solid-electrolyte interfaces for example in Lithium ion batteries as a simple laboratory experiment. First experiments on a $V_2O_5$ cathode in 1 molar $LiPF_6$ in EC/DMC electrolyte solution show the operando intercalation of Lithium into the cathode and the related changes in its chemical compositions. A control experiment after air exposure of the intercalated cathode demonstrate need for intert environments during measurements.

Finally an outlook is given on the future perspective of applications and scientific contributions of general routine operando XPS.

***Contributed talk*** ***Tuesday 10th 17h10***

# Spatially resolved XPS measurements of the oxidation and reduction dynamics of polycrystalline transition metals

Patrick Zeller[1], Matteo Amati[1], Luca Gregoratti[1]

[1] Elettra - Sincrotrone Trieste S.C.p.A., Trieste, Italy

In order to get insights of relevant processes for corrosion and heterogeneous catalysis of transition metals the analysis of the oxidation and reduction behaviour and their dynamics is needed. However, real samples are typically not uniform and exhibit local structures like grain boundaries or changes in topography that affect the physical and chemical behaviour of the materials. One possible solution to overcome the so-called materials gap can be achieved by performing spatially resolved XPS measurements. Here we present investigations of polycrystalline foils of Ni and Cu using the submicrometer resolution of Scanning Photoemission Microscopy (SPEM) with a X-ray spot size down to 130 nm in combination with a special designed cell that allows *operando* measurements at NAP conditions [1, 2]. During the reactions there is a coexistence of oxidized and reduced islands highlighting the importance of the metal grain structures and their individual, different reactivity. The high spatial resolution also allows the investigations of single grain boundaries at which the oxidation occurs at lower temperatures (Figure 1). An additional feature in SPEM is the visibility of the samples topography. This allows to link the reactivity of the sample with the local roughness and to follow the topography change during the reaction. In addition, surface modifications can increase the materials properties, e.g. a graphene layer to prevent corrosion. The successful protection against oxidation was investigated with individual graphene islands on Cu which suppress oxide formation while the uncovered Cu is already fully oxidized to $Cu_2O$.[3] With increasing temperatures (starting from 340 °C) the oxygen intercalates between graphene and Cu and eventually starts the oxidation highlighting the dynamics of the graphene protection.

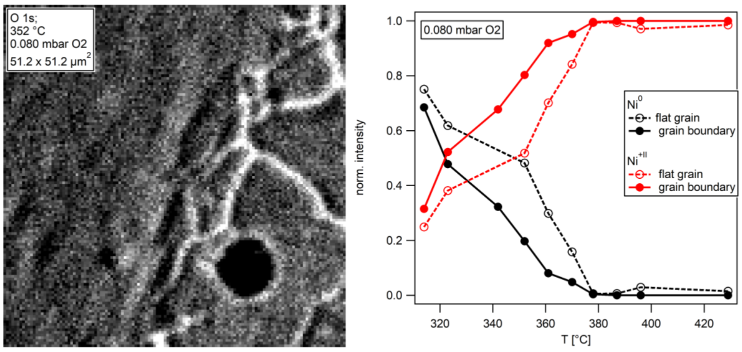

Figure 1: Left: Map showing the spatial distribution of the O 1s intensity on a polycrystalline Ni foil. The grain boundaries contain an increased amount of oxygen. Right: Quantification of the local nickel oxidation states during annealing of the sample.

[1] L. Gregoratti *et al.*, Top. Catal. **61**, (2018) 1274–1282.

[2] H. Sezen *et al.*, Surf. Interface Anal. **50**, (2018) 921-926.

[3] M. Scardamaglia *et al.*, ACS Appl. Mater. Interfaces. **11**, (2019) 29448–29457.

**Contributed talk** **Tuesday 10th 17h30**

# The magnesium assisted oxide break-up kinetics at flux-free brazing of aluminium alloy materials

Lars-Åke Näslund[1], Ning Wang[1], Martin Magnuson[2], Robert Moberg[3], Mårten Edwards[3], Torkel Stenqvist[1]

[1]Gränges AB, Finspång, Sweden, [2]Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden, [3]Uppsala Synchrotronix AB, Uppsala, Sweden

Brazing aluminium is a high-volume industrial process, mainly for automotive heat exchangers. The aluminium alloy material is a composite where a core Al-Mn alloy is clad with a layer of an Al-Si alloy that will melt at brazing temperature and flow to form joints. Presently the main process is called controlled atmosphere brazing (CAB), which occur in a furnace with a nitrogen ($N_2$) atmosphere. Prior to brazing it is necessary to break up the aluminium oxide ($Al_2O_3$) that is formed naturally on the surface. Today it is common to use a fluoride flux to break up the $Al_2O_3$, although it has some disadvantages such as being harsh for the environment and detrimental for the cooling efficiency if flux residues are left in the heat exchanger. An alternative $Al_2O_3$ break-up agent is magnesium (Mg) that conveniently can be added to the cladding alloy. Mg as an oxide break-up agent is common in vacuum brazing. However, if the nitrogen atmosphere is sufficiently pure it is possible to use Mg as the oxide break-up agent also in CAB. In this study the kinetics of the Mg diffusion into the $Al_2O_3$ is investigated using the ambient pressure X-ray photoelectron spectroscopy (AP-XPS) system at the HIPPIE beamline, which provided a sample environment not far from realistic brazing conditions, i.e. heating up to 600 °C in a pure nitrogen gas atmosphere. The samples were heated in 1 mbar $N_2$ up to 510 °C and examined in operando while the Mg enter the surface oxide.

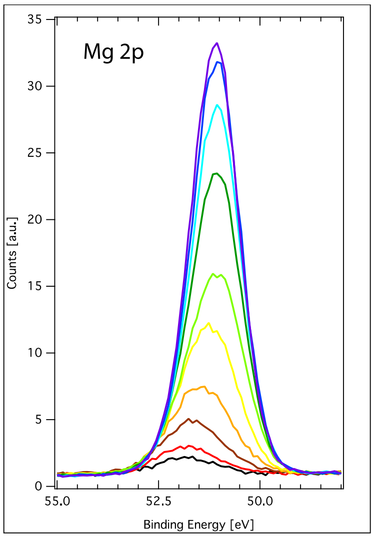

Figure 1 The Mg 2p peak intensity evolution with time at 510 °C. The photon energy is 1200 eV, which is high enough to probe through the whole oxide thickness. The black and purple spectra are the first and the last in the series that were collected during 540 s.

**PLENARY TALK** **Wednesday 11th 9h10**

# Mechanistic understanding of redox reactions on cerium oxide: $CO_2$, $H_2O$ and $O_2$ reduction

W. C. Chueh

[1]Department of Materials Science & Engineering, Stanford University, Stanford, USA

Cerium oxide (ceria) is a prototypical oxygen insertion solid, whereby oxygen can be reversibly inserted and extracted from the crystal lattice. Applications of ceria are widespread, including active catalyst support, oxygen capacitor in catalytic converters and thermochemical cycles, and electrodes in solid-oxide fuel cells and electrolysis cells. The tuneable amount of oxygen in ceria is coupled to a wide range of molecules, with the simplest being $O_2$, $H_2O$ and $CO_2$, taking place at the solid-gas interface. Over the past decade, in collaborations with the Advanced Light Source at the Lawrence Berkeley National Laboratory, we have employed ambient pressure X-ray photoelectron spectroscopy to study three aspects of the ceria-gas interface at elevated temperatures: (1) point defect chemistry, (2) electrostatic double layer, and (3) molecular reaction pathway. For defect chemistry, measurement of surface Ce oxidation state and oxygen stoichiometry as a function of temperature and oxygen partial pressure quantify the enhanced reducibility of the ceria surface relative to the bulk, leading to a large oxygen "chemical" capacitance that buffers catalytic processes. For electrostatic double layer, we analysed rigid binding energy shift to understand how polar (hydroxyl) and nonpolar (oxygen and carbonate) affect the electrostatic double layer. Finally, for reaction pathway, we employed a solid-state electrochemical cells to pump oxygen to and away from the ceria-gas interface, driving the dissociation of water, oxidation of hydrogen, deoxygenation of carbon dioxide and reduction of oxygen. In each case, monitoring the reaction intermediates, surface potential, and surface defect concentration as a function of overpotential revealed crucial details about the rate-determining step.

**Contributed talk** **Wednesday 11th 9h50**

# The electronic structure of electrochemical interfaces at equilibrium and the gain from transient experiments

Lorenz J. Falling, Travis E. Jones[1], Rik Mom[1], Juan-Jesús Velasco-Vélez[1], Detre Teschner[1], Axel Knop-Gericke[1], Robert Schlögl[1]

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## Motivation

Electrochemistry could be a key to sustainable chemistry. Driven by sustainable power sources, electrochemistry has shown the ability to be highly selective and efficient. In order to exploit its enormous potential, we need to have a thorough understanding of the electrochemical interfaces and how they change with potential.

## Technique

We developed a method to measure the electronic structure of electrochemical interfaces under wet conditions. We achieve this by permeable membranes through which water and ions can pass and a graphene blanket (representation in figure). Graphene contributes essential benefits to that approach: it serves as a current collector and an evaporation barrier, leading to a thin layer of confined electrolyte. At the same time, it is transparent to soft X-rays and photoelectrons. This special way of sample preparation in combination with a setup dedicated to in situ electrochemistry, allows surface sensitive X-ray spectroscopy of electrocatalysts under wet conditions at pressures below 1 mbar.

## Scientific Results

The communication of the results will focus on the redox transition from $\mathrm{Ir^{III}}$ to $\mathrm{Ir^{IV}}$, which is the most important redox transition for basically all applications of iridium (hydr-)oxides in electrochemistry and biosensors. On the one hand, we will show for the example of IrOOH nanosheets that thermodynamic equilibrium at a given electrochemical potential can be used to study a well-defined transition from $\mathrm{Ir^{III}}$ to $\mathrm{Ir^{IV}}$ in the identical material. On the other hand, we will show how *Potentiodynamic X-ray Absorption* (figure) helped to connect electrochemical oxidation waves with deprotonation of surface oxygen species.

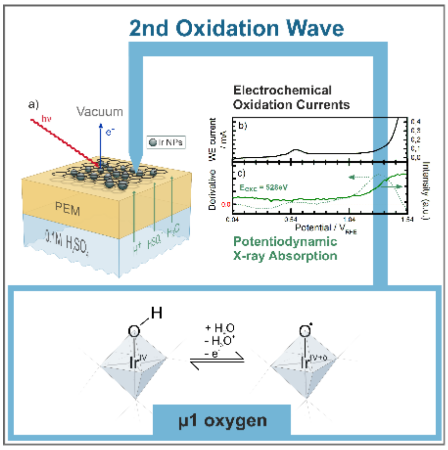

*Figure: A representation of the method (a) and synchronous in situ measurements: electrochemical currents (b) and X-ray absorption of a $\mu_1$-O species (c). This oxygen species is a radical (d) and was predicted to be the most reactive species in water oxidation.*

[1] Frevel, L. J.; Mom, R.; Velasco-Vélez, J. J.; Plodinec, M.; Knop-Gericke, A.; Schlögl, R.; Jones, T. E. *J. Phys. Chem. C* **2019**, *123* (14), 9146–9152.

***Invited talk*** ***Wednesday 11th 10h50***

# The road towards operandi measurements of Li-ion battery electrodes

Maria Hahlin[1], Fredrik Lindgren[1], Ida Källquist[1], Ming-Tao-Lee[2], Julia Maibach[3], Håkan Rensmo[1], Kristina Edström[2], Hans Siegbahn[1]

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[2]Department of Chemistry Ångström Laboratory, Uppsala, Sweden
[3] Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

The energy conversion in lithium ion batteries takes place in the functional electrochemical interfaces formed between the electrode and the electrolyte. Large research efforts are put into understanding its composition and function since they are key for developing better batteries. The interface chemistry example influences the self-discharge properties, safety and cycling stability of the battery. Much of our current knowledge of the interfaces are obtained through surface analysis using photoelectron spectroscopy, however these are always performed on post-mortem battery electrodes in an UHV environment far from that of the operating device. Moreover, half of the interface, i.e. the electrolyte, is lacking thus preventing investigations of the interaction between electrode and the electrolyte.

The development of ambient pressure photoelectron spectroscopy (APPES) has now opened for incorporating also liquids during the measurements, allowing for characterization of the full interface region that includes all components. With the development of APPES instrumentation dedicated towards batteries also it is feasible to obtain atomic level information from the interfaces in operating batteries. This is key for taking the next step in full understanding the interface functionality. Development of operando APPES measurements of battery electrodes is expected to make a strong contribution to the overall battery research community. During this talk we will present our road towards operandi measurements of Li-ion battery electrodes, including instrument development, methodology development and recent results from operandi measurements of battery electrodes at MAX IV [1-2].

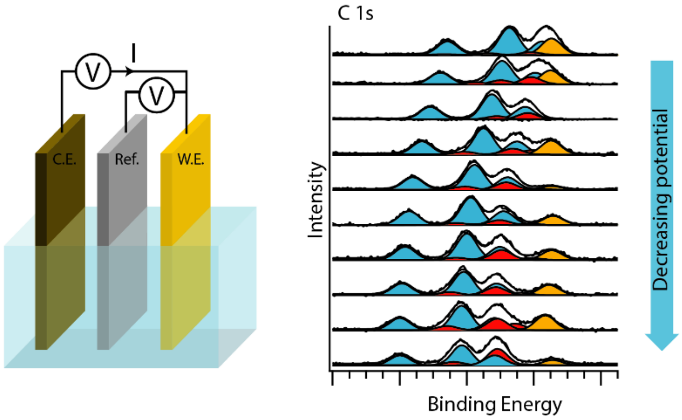

Figure 1 Schematic representation of APPES operando measurements of battery electrodes

[1] Nature Communications, 10: 3080 (2019)

[2] Review of Scientific Instruments, 2015, 85, 04410

***Contributed talk*** ***Wednesday 11th 11h20***

# Operando HT-NAP-XPS and impedance spectroscopy study of Ni-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ solid oxide fuel cell anode

Kuno Kooser[a,b], Tanel Käämbre[a], Mihkel Vestli[c], Urmas Joost[b], Samuli Urpelainen[d,e], Mati Kook[a], Fabrice Bournel[f,g], Jean-Jacques Gallet[f,g], Enn Lust[c], Edwin Kukk[b], Gunnar Nurk[c]

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[b]University of Turku, Department of Physics and Astronomy, Turku, Finland
[c]University of Tartu Institute of Chemistry, Tartu, Estonia
[d]MAX IV Laboratory, Lund University, Lund, Sweden
[e]Nano and Molecular Systems Research Unit, University of Oulu, Oulu, Finland
[f]Sorbonne Université, CNRS, Paris, France
[g]Synchrotron SOLEIL, LOrme des Merisiers, Saint-Aubin, France

Detailed chemical information concerning electrode surfaces at operating conditions is essential for rational development of solid oxide fuel cell (SOFC) electrodes. However, because of harsh operating conditions detailed understanding about mechanistic aspects of surface reactions and surface thermodynamics at SOFC electrodes under electrochemical reaction conditions is still largely missing.

Spectro-electrochemistry, i.e. spectroscopic (x-ray absorption, near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) and Raman spectroscopy) characterization of operating electrode at electrochemically controlled conditions is a promising method to characterize surface properties like oxidation states, surface polarization, surface coverage with adsorbate, etc. at real or close to real SOFC operating conditions. In this study, we present the results of operando high temperature (HT)-NAP-XPS spectro-electrochemical measurements of pulsed lased deposited thin film Ni- $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ model electrode.

In our measurements, we have used novel three-electrode dual-chamber spectro-electrochemical cell [1] developed in our previous work at different $H_2$ pressures and at different electrochemical conditions at around 650 °C. The possible redox reactions on the anode surface ($Ni^{2+} \rightarrow Ni^0$, $Ce^{4+} \rightarrow Ce^{3+}$) were investigated by HT-NAP-XPS technique simultaneously with electrochemical impedance spectroscopy measurements. The oxygen partial pressure in counter and reference electrode compartment was controlled at 0.2 bar. Changes in electronic structure of the Ce 3d and Ni 2p photoelectron spectra caused by electrode potential and $H_2$ pressure variations were observed and estimated by curve fitting procedure. The oxygen 1s and valence band photoelectron signals were used for depth probing of the chemical composition and redox changes at Ni-GDC and for studying the influence of the electrochemical polarization on the chemical state of Ni-GDC surface atoms.

As a result, changes in oxidation state of electrode surface atoms caused by electrode polarization and oxide ion flux through the membrane were detected with simultaneous significant variation of electrochemical impedance.

[1] G. Nurk et al., Journal of Power Sources **378**, 589-596 (2018)

**Contributed talk** **Wednesday 11th 11h40**

# Towards the mechanistic interpretation of the oxygen exchange reactions on $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ thin film electrodes

Simon PITSCHEIDER[1], Zixuan GUAN[2], Torben JACOBSEN[1], Hendrik BLUHM[3], Ethan J. CRUMLIN[3], William C. CHUEH[2], Mogens B. MOGENSEN[1], Christodoulos CHATZICHRISTODOULOU[1]

[1]DTU, Roskilde, Denmark, [2]Stanford University, Stanford, USA, [3]Advanced Light Source, Berkeley, USA

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) represents the state-of-the-art oxygen electrode material for solid oxide fuel and electrolysis cells (SOFC/SOEC – SOC) due to its high electronic and ionic conductivities and high activity towards the oxygen exchange reactions. The study of these reactions is complicated by the polarization dependent nature of the LSCF surface, in terms of surface composition, ionic and electronic surface defect concentrations, and varying surface potential. For this reason, advanced in situ experimental techniques are needed to study the near surface materials' properties and the electrochemical reactions in relevant operating conditions. In particular, the correlations between the overpotential of the oxygen electrode and its surface chemistry and surface potential provide valuable information in understanding the activity and the reaction mechanisms on LSCF.

In this work, both the surface chemistry and, for the first time, the surface potential variations on LSCF model thin film electrodes were studied using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) while performing electrochemical impedance spectroscopy (EIS) measurements inside the beamline chamber.

The results were compared with a simplified model of the possible oxygen exchange reaction pathways and allowed determining the most probable reaction mechanism for oxygen incorporation.

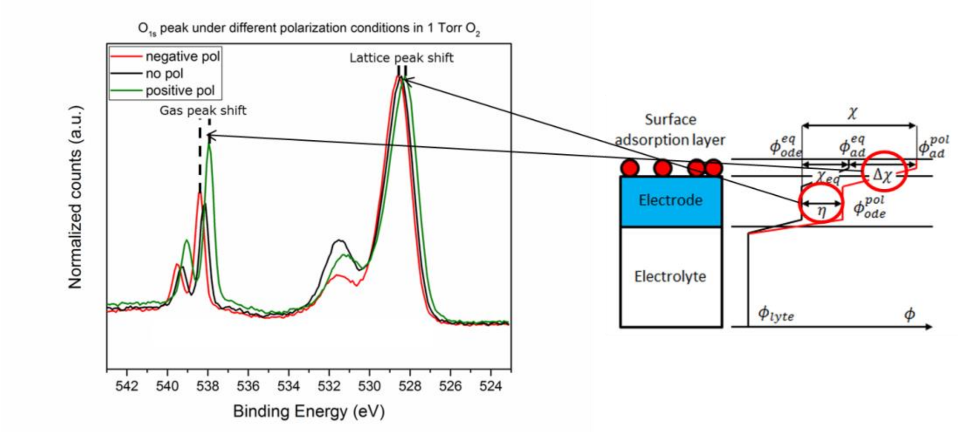


Figure 1. Correlation between $O_{1s}$ XPS peaks and investigated potential shifts (surface potential and overpotential) on the surface of LSCF electrodes.

We gratefully acknowledge financial support from ECoProbe (DFF – 4005-00129) funded by the Danish Independent Research Council, Otto Mønsteds Fond (17-70-0196) and SUNCAT in collaboration with the Danish Agency for Science and Higher Education (7032-00001B)

***Contributed talk*** ***Wednesday 11th 11h40***

# Dissociative adsorption of $CO_2$ on Cu-surfaces

Benjamin Hagman[1], Alvaro Posada-Borbón[2], Andreas Schaefer[3], Uta Hejral[1], Helen Edström[1], Kim von Allmen[1], Henrik Grönbeck[2], and Johan Gustafson[1]

[1]Synchrotron Radiation Research, Lund University, Lund, Sweden, [2]Dept. of Physics and Competence Centre for Catalysis, Chalmers University of Technology, Gothenburg, Sweden, [3]Dept. of Chemistry and Chemical Engineering and Competence Centre for Catalysis, Chalmers University of Technology, Gothenburg, Sweden

We have previously studied the dissociative adsorption of $CO_2$ on Cu(100), and the resulting oxidation of the surface [1-2]. We found that $CO_2$ adsorbs on the surface and dissociate to CO and O, where the CO will desorb leaving O behind. From a combination of AP-XPS and DFT calculations, the active site for the dissociation of $CO_2$ into CO and O is believed to be the monatomic (111) steps. Thus, to further our understanding of the interaction between $CO_2$ and Cu, we continued with investigating the adsorption of $CO_2$ on a stepped Cu(911) surface, which has (100) terraces and (111) steps every 11.5 Å. We found, as expected that the presence of the steps facilitated the adsorption of $CO_2$. Also, the behavior of $CO_2$ adsorption on Cu(911) was different than on Cu(100), see figure below, as initially the adsorbed oxygen blocked $CO_2$ adsorption but was reactivated at a more considerable oxygen coverage, followed by a slight shift in the O 1 s spectrum. The reactivation of $CO_2$ adsorption on the surface is believed to be related to the transformation of the closed-packed (111) steps to the more open (110) steps as the surface becomes oxidized.

We also plan to present preliminary results from AP-XPS experiments of $CO_2$ interaction with a curved Cu(100) crystal, in which the role of the steps in $CO_2$ dissociation is further investigated.

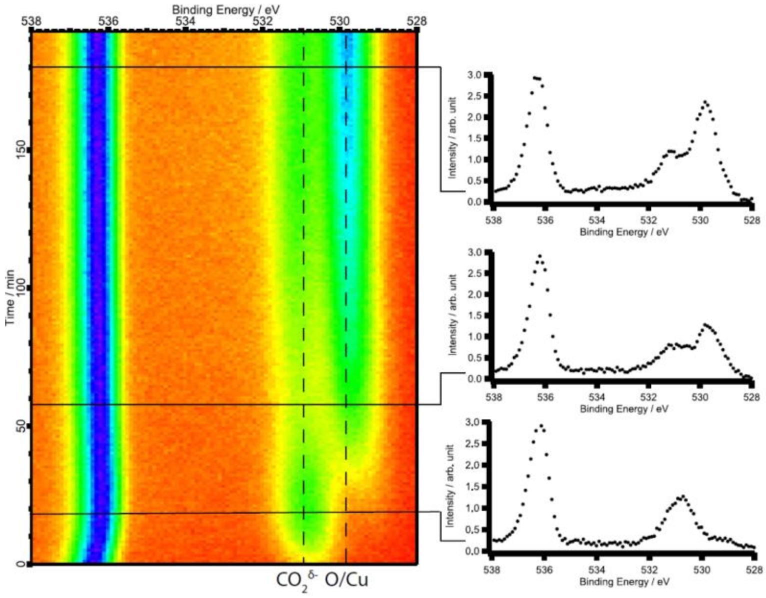


Figure 1: AP-XPS O 1s spectra as the Cu(911) surface is exposed to 0.3 Torr $CO_2$ at 75 ℃.

[1] A. Posada-Borbón et al, *Surf. Sci.*, 675 (2018), 64-89.

[2] B. Hagman et al, *J. Am. Chem. Soc.*, 140 (2018), 12974-12979.

**Contributed talk** **Wednesday 11th 14h00**

# Using NAP-XPS to identify the optimum surface state of cobalt catalysts for CO preferential oxidation in $H_2$-rich feedstock

Liping Zhong[1], Thomas Kropp[2], Detre Teschner[3], Manos Mavrikakis[2] and Spyridon Zafeiratos[1]

[1]ICPEES, UMR7515-CNRS-Université de Strasbourg, Strasbourg, France, [2]University of Wisconsin–Madison, Department of Chemical and Biological Engineering, Madison, USA, [3]Departement of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Catalytic performance is known to be influenced by several factors, with the catalysts' surface oxidation state being the most prominent of all. Cobalt appears as one of the most promising materials for preferential oxidation of carbon monoxide in hydrogen rich mixtures (COPrOx)[1]. However, the oxidation state of the active sites on cobalt-based catalysts for COPrOx is a subject of intense debate[2]. In this work we use operando NAP-XPS combined with DFT and other *in situ* and *ex situ* characterization methods to correlate COPrOx activity and cobalt oxidation state[3]. An important effort is devoted to evaluating the effect of the pressure gap between NAP-XPS measurements (0.5mbar) and realistic reaction conditions (1bar). Based on NAP-XPS we identified CoO as the optimum cobalt oxidation state, while first principal calculations provided a rational explanation of this finding. We also noted that CoO is metastable and oxidizes fast under COPrOx conditions leading to catalyst deactivation. However, NAP-XPS provided us with critical information which allowed to design a novel composite cobalt-based catalyst. Preliminary tests showed that by stabilizing the CoO phase the COPrOx catalytic activity and stability is enhanced as compared to conventional cobalt catalysts.

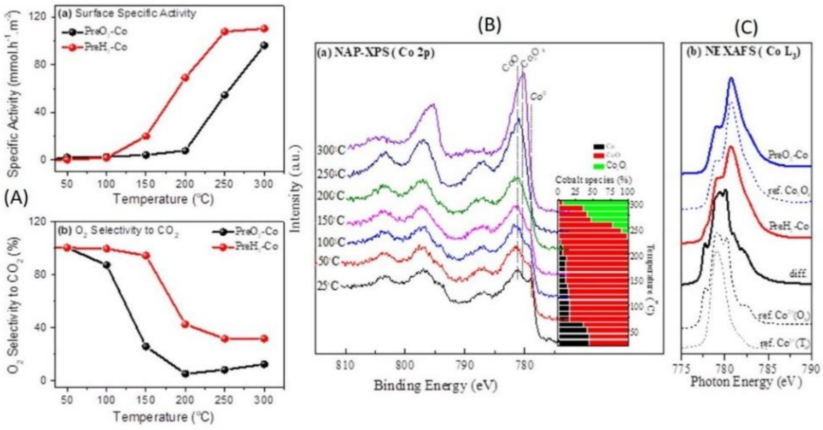


Figure 1. (A) Catalytic activity of different cobalt for CO PrOx at 1bar. (B) In situ NAP-XPS spectra and (C) NEXAFs spectra of reduced cobalt during CO PrOx at 0.5mbar.

(1) Woods, M. P.; Gawade, P.; Tan, B.; Ozkan, U. S.. *Appl. Catal. B Environ.* **2010**, *97* (1–2), 28–35.

(2) Zhong, L.; Chen, D.; Zafeiratos, S. *Catal. Sci. Technol.* **2019**, *9* (15), 3851–3867.

(3) Zhong, L.; Kropp, T.; Baaziz, W.; Ersen, O.; Teschner, D.; Schlögl, R.; Mavrikakis, M.; Zafeiratos, S. *ACS Catal.* **2019**, *9* (9), 8325–8336.

**Contributed talk** **Wednesday 11th 14h20**

# Investigations of the surface dynamics of Pd-alloy surfaces under oxidation reactions

Marie Døvre Strømsheim[1], Ingeborg-Helene Svenum[1,2], Mehdi Mahmoodinia[1], Virgínia Boix[3], Jan Knudsen[3,4], Hilde J. Venvik[1]

[1]Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, [2]Sintef Industry, Trondheim, Norway, [3]Division of Synchrotron Radiation Research, Lund University, Lund, Sweden [4]MAXIV Laboratory, Lund University, Lund, Sweden

The surface dynamics of $Pd_{75}Ag_{25}(100)$ under CO oxidation were investigated using near-ambient pressure x-ray photoelectron spectroscopy (APXPS) and quadrupole mass spectrometry (QMS). The aim is to elucidate segregation behaviour under reaction conditions. Previous APXPS investigations of CO oxidation in excess oxygen ($CO:O_2$ = 1:10) over the $Pd_{75}Ag_{25}(100)$ surface reported adsorbed oxygen on the surface during high $CO_2$ formation, while the ordered $(\sqrt{5}\times\sqrt{5})R27°$ surface oxide is observed on Pd(100) under the same conditions [1]. CO coverage effects give rise to a temperature dependent hysteresis in the rate of $CO_2$ formation over Pd(100). But a reversed hysteresis was recorded for $Pd_{75}Ag_{25}(100)$, i.e. the extinction temperature for the $CO_2$ production being higher than the light-off temperature. Theoretical calculations (DFT) inferred that the reversed hysteresis could be attributed to a net segregation of Ag to the surface at high temperature [1]. However, this has not yet been confirmed experimentally. In the present work, we followed the surface dynamics as well as the segregation behaviour during CO oxidation over $Pd_{75}Ag_{25}(100)$ surface. The APXPS measurements were performed at the HIPPIE beamline at the MAXIV laboratory, Lund, Sweden. CO oxidation ($CO:O_2$ = 1:10, ~1 mbar total pressure) was performed during several temperature cycles of varying maximum temperature (450 °C and 600 °C) and varying heating rate. The Pd 3d and Ag 3d core levels were monitored and the hysteresis in the product formation was simultaneously recorded by QMS. Analysis of the segregation behaviour due to temperature cycling under CO oxidation conditions will be presented.

[1] V.R. Fernandes, M. Van den Bossche, J. Knudsen, M.H. Farstad, J. Gustafson, H.J. Venvik, H. Grönbeck, A. Borg, Reversed Hysteresis during CO Oxidation over Pd 75 Ag 25 (100), ACS Catal. 6 (2016) 4154–4161. doi:10.1021/acscatal.6b00658.

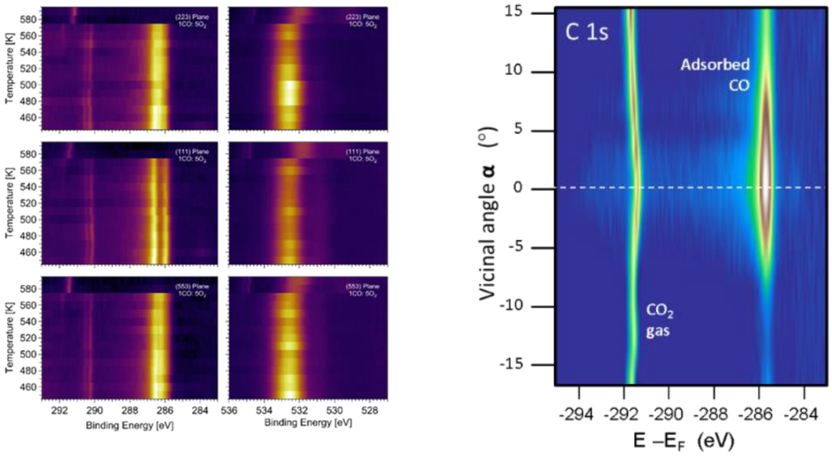
**Invited talk** **Wednesday 11th 15h10**

# Ignition of the CO oxidation at curved Pd and Pt surfaces

F. García[a], M. Ilyn[a], V. Pérez-Dieste[b], C. Escudero[b], C. Huck-Iriart[b], A. L. Walter[c], I. Waluyo[c], B. Hagman[d], S. Blomberg[d], J. Zetterberg[d], J. Gustafson[d], E. Lundgren[d], F. Schiller[a] , and J. E. Ortega[a,e,f]

*[a] Centro de Física de Materiales San Sebastian (Spain), [b]ALBA Synchrotron, Barcelona (Spain), [c]National Synchrotron Light Source, Brookhaven (USA), [c]Department of Physics, Lund Univ. (Sweden), [e] Depto. Física Aplicada, Univ. del País Vasco, San Sebastian (Spain), [f] Donostia International Physics Centre DIPC, San Sebastian (Spain)*

For many years, the study of chemical reactions on single metal surfaces has been aimed at identifying active sites at crystal planes that feature nanoparticles[1]. However, nanocrystal facets coexist in a reduced space, and are expected to simultaneously undergo chemical and structural transformations during catalytic reactions[2]. Using multi-facet samples, such as cylindrical crystals, makes it easy to compare the catalytic activity of different surfaces submitted to the same reaction conditions[3]. Within this approach, we have studied the CO oxidation reaction on cylindrical sections of Pt and Pd single crystals. Our interest is focused in the simultaneous evolution of the surface species around the ignition temperature at the different vicinal planes. Using near-ambient pressure X-ray photoemission (NAP-XPS), we first perform temperature scans at fixed crystal directions, and then map the reaction stage across the curved surface at fixed temperature above and below the ignition point. Shockingly we find that Pd and Pt behave in a radically different way. Pd shows a sequential activation of the reaction across the curved surface, whereas the CO oxidation lits at all Pt crystal planes simultaneously. Chemical analysis by XPS unveils the reason for such different behavior.



*Left, temperature scan of the O1s peak at the flat (111) and stepped (223) and (553) planes. The CO oxidation reaction is simultaneous at 505 K. Right, C1s and O 1s scans over the Pd curved surface at 485 K. The reaction is in the active stage at stepped edges, while it remains CO-poisoned around the (111) center.*

*Acknowledgements.* This work has been supported by the Spanish Ministry of Economy (MAT-2017-88374-P) and Basque Government (IT621-13).

[1] *Introduction to Surface Chemistry and Catalysis*. John Wiley & Sons (2010).
[2] Vendelbo, S. B et al. Nat Mater **13**, 884–890 (2014).
[3] Walter, A. et al. Nat Comm **6**, (2015); F. Schiller et al. JACS **140**, 16245−16252 (2008).

***Contributed talk*** ***Wednesday 11th 15h40***

# Combined UHV-STM and AP-XPS study of Selective Catalytic Reduction (SCR) of $NO_x$ over a $VO_x/TiO_2$ based catalyst.

Kræn C. Adamsen, Tao Xu, Stefan Wendt, Jeppe V. Lauritsen

Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark

Fundamental understanding of catalytic processes for $NO_x$ removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, $NO_x$ is known to react from gas-phase on adsorbed ammonia on $VO_x/TiO_2$ based catalysts [1]. Here we present a fundamental study of a partially $VO_x$ covered anatase-$TiO_2$ (101), the predominant facet on anatase-$TiO_2$ nanoparticles. Here is presented how $VO_x$ particles supported on the anatase- $TiO_2$ (101) interacted with $H_2O$, $NH_3$ and NO. The molecular interactions were studied at UHV conditions by Scanning Tunnelling Microscopy (STM). No SCR-activity is observed at UHV conditions; only by increasing the partial pressure of the gasses, we are able to observe SCR-activity. We follow the oxidation-state of vanadium and identify adsorped surface species by Near Ambient Pressure (NAP)-XPS. Figure 1 shows the development of the N1s- and O1s-peak with increasing temperature under NAP-conditions. This set of spectra, shows that the surface goes from being covered by mainly ammonium ($NH_4$) to a mainly ammonia covered surface, with increasing temperature. The O1s spectra shows the amount of hydroxylation first decrease, with the desorption of water and later and increase. The increase of hydroxylation suggest that NO and $NH_3$ is reaction and thus leaving the surface more hydroxylated. Theoretical models suggest that this hydroxylation happens together with the reduction of the vanadia particle. Examination of the V2p region indeed also shows reduction. Combining the knowledge gained from the NAP and UHV we can start to determine the active-site for SCR which has been debated for 3 decades [1][2]. We can here follow the first part of the SCR-process, namely the reduction of the $VO_x$ – particles. We are able to follow the adsorped species and follow the reduction of the vanadium.

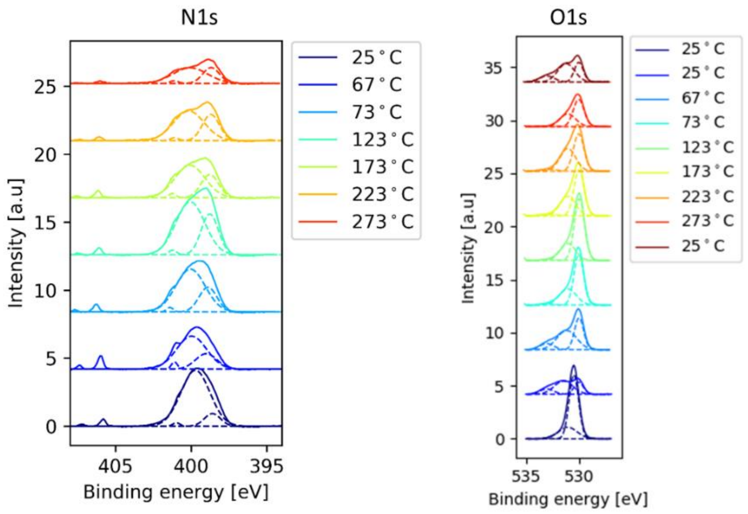


Figure 1: N1s and O1s

[1] Arnarson, Logi, et al. *Physical Chemistry Chemical Physics* 18.25 (2016): 17071-17080.

[2] Marberger, A., et al. (2016). *Angewandte Chemie Int.Ed.* **55**(39): 11989-11994.

***Contributed talk*** ***Wednesday 11th 16h00***

# APXPS Study of Propylene Oxidation over $Cu_2O$ Surfaces

Zongfang Wu[1], Chunlei Wang[1], Heloise Tissot[2], Jonas Weissenrieder[1]

[1] KTH Royal Institute of Technology, Stockholm, Sweden, [2] Centre interdisciplinaire de Nanosciences de Marseillenstitutional, Marseille, France

Catalytic oxidation of propylene with molecular oxygen to propylene oxide and acrolein is of major industrial importance and $Cu_2O$ catalysts are actively pursued as catalysts. [1] Recent studies on well-defined $Cu_2O$ powders have shown that $Cu_2O$ nanoparticles of different crystalline termination exhibit remarkably different activity and selectivity in the propylene oxidation reaction. [2] However, the adsorption sites, reaction pathway, and reaction intermediates are presently not known. Using the well-defined $Cu_2O$(110) and (100) single crystal surfaces as templates, we have studied the propylene oxidation reaction by a combination of ambient pressure X-ray photoelectron spectroscopy and mass spectrometry. The surface geometry (atomic structure), the oxidation state of copper species as well as the presence of surface modifiers such as hydroxyl groups are proved to influence the interaction of propylene with the $Cu_2O$ surface (figure 1). Variation of the reactant gas composition alternates the distribution of the oxidation gas products at elevated temperatures. This is correlated with the change of the chemical composition of the catalysts where the structure-dependent redox property of $Cu_2O$ surfaces plays an important role. The result deepens the fundamental understanding of the propylene oxidation reaction.

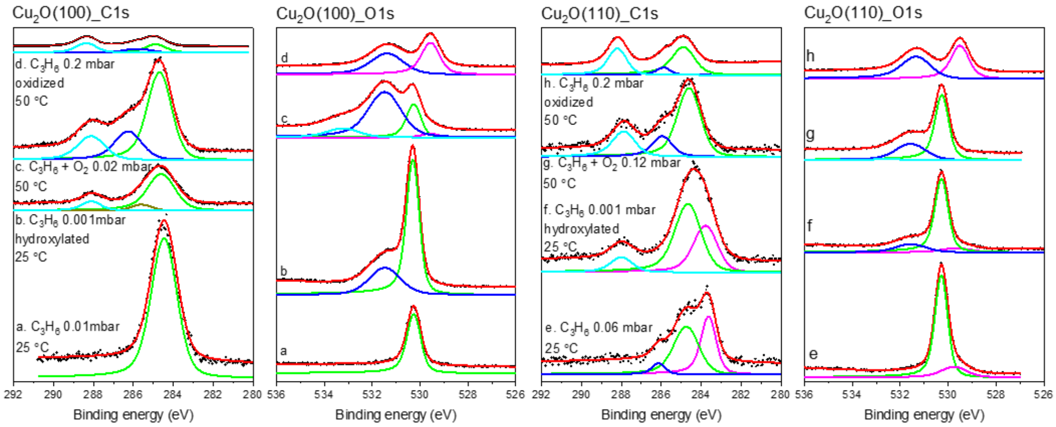


Figure 1 Ambient pressure XPS results. C 1s and O 1s from $Cu_2O$(100) and $Cu_2O$(110), respectively, in propylene and mixed propylene and oxygen ambient (denoted as a-h). The hydroxylated in a to h indicates a $Cu_2O$ surface covered with hydroxyl groups; the oxidized denotes a $Cu_2O$ surface covered with CuO layer. The O 1s and C 1s spectra were all collected at hv = 750 eV.

[1] T. A. Nijhuis, M.Makkee, J.A.Moulijn, B.M. Weckhuysen, The Production of Propene Oxide: Catalytic Processes and Recent Developments, Ind. Eng.Chem. Res. 2006, 45,3447–3459.

[2] Hua, Q.; Cao, T.; Gu, X.-K.; Lu, J.; Jiang, Z.; Pan, X.; Luo, L.; Li, W.-X.; Huang, W., Crystal-Plane-Controlled Selectivity of $Cu_2O$ Catalysts in Propylene Oxidation with Molecular Oxygen. Angew. Chem. Int. Ed. 2014, 53 (19), 4856-4861.

***Contributed talk*** ***Wednesday 11th 16h20***

# Chemical Warfare Agent Simulants and Atmospheric Gases: Adsorption Battles in Gas Filtration

Ashley R. Head,[1] Lena Trotochaud,[2] Roman Tsyshevsky,[3] Burcu Karagoz,[1] Bryan Eichhorn,[4] Maija Kuklja,[2] Hendrik Bluhm[5,6,7]

[1]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, United States
[2]Center for WaSH-AID, Duke University, Durham, NC, United States
[3]Materials Science and Engineering Department and [4]Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, United States
[5]Chemical Sciences Division and [6]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, United States
[7]Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Organophosphonates, including chemical warfare agents (CWAs), are known to bind to metal oxides through phosphoryl and oxo groups, [1] hence their use in the commercial ASZM-TEDA gas filtration material. Less known are the organophosphonate decomposition processes on metal oxides. Furthermore, there is little study on the effect of atmospheric gases on the binding and decomposition of these molecules on the filter materials. Ambient pressure X-ray photoelectron spectroscopy is ideal to quantify adsorption and identify decomposition products in controlled gas environments. The adsorption of the CWA simulant dimethyl methylphosphonate (DMMP) on $CuO_x$ and $MoO_x$, two filter components, was studied under operando conditions with varying partial pressure conditions. The results were interpreted with the aid of density functional theory (DFT) calculations. The oxidation state of the metal was found to influence the decomposition products. In general, more reduced oxidation states generate more reduced products, including unprecedented atomic phosphorus on $Cu_2O$. The effect of atmospheric gases, including water, octane, $NO_2$, CO, and $CO_2$, on the metal oxides and implications for DMMP adsorption was also investigated. While these gases did not affect the amount of DMMP adsorption, the decomposition is decreased. These studies pave the way for the design of new materials and benchmarked DFT studies of CWA on metal oxide surfaces.

[1] M. B. Mitchell, B. N. Sheinker, and E. A. Mintz, J. Phys. Chem. B 101, 11192 (1997)

***Contributed talk*** ***Wednesday 11th 16h40***

# Surface composition of $Pt_3Sn(111)$ during CO oxidation

Harald Wallander[1], Freddy Oropeza[2], Benjamin Hagman[3], Jan Knudsen[3,4], Edvin Lundgren[3], and Lindsay R. Merte[1]

[1]Malmö University, Malmö, Sweden, [2]Eindhoven University of Technology, Eindhoven, Netherlands, [3]Lund University, Lund, Sweden, [4]MAX IV Laboratory, Lund, Sweden

Compared to pure platinum, Pt-Sn alloys show enhanced performance as catalysts in several reactions, including CO oxidation. Although a weakening of CO bonding due to alloying is generally viewed as a major contributor to the catalytic properties, a number of studies have shown that the metal is oxidized during reaction conditions, and it has been suggested that the tin oxides which form can promote catalytic activity [1-4]. We performed an AP-XPS study of a $Pt_3Sn(111)$ single crystal surface during CO oxidation at the HIPPIE beamline at MAX IV, with the goal of characterizing the surface state, with particular focus on the formation of oxides and their effects on catalytic activity. Our measurements show that tin is oxidized during the reaction, and that a higher $CO:O_2$ ratio actually promotes tin oxidation: substantial Sn(IV) was formed during CO oxidation in a 1:1 gas mixture, while only Sn(II) was detected in a 1:10 (oxygen-rich) feed. CO conversion was found to be significantly higher in the oxygen-rich feed. For initially-metallic surfaces, the turnover rate was found to decrease with time, while for a pre-oxidized surface the turnover rate was lower and constant. The results generally point toward an inhibitory effect of oxide formation, rather than a promotional effect, under these conditions.

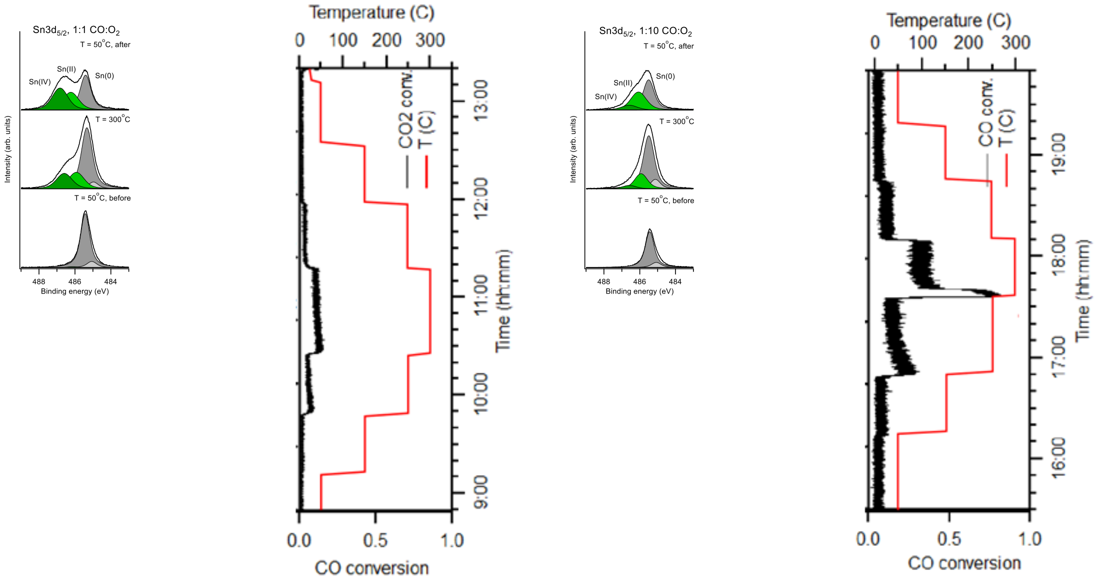


**Figure 1** AP-XPS and reactivity measurements during CO oxidation at 1 mbar in 1:1 and 1:10 mixtures of $CO:O_2$.

[1] W. D. Michalak et al., *J. Catal.* **2014**, *312*, 17 - 25.
[2] M. Vandichel et al., *ACS Catalysis*, **2017**, 7, 7431.
[3] Y. Jugnet et al., *J. Phys. Chem. Lett.* **2012**, *3*, 3707-3714.
[4] S. Axnanda et al., *J. Phys. Chem. C* **2014**, *118*, 1935-1943.

***PLENARY TALK*** ***Thursday 12th 9h00***

# Photoelectron Spectroscopy from Liquid Microjets: New Developments and Opportunities

Bernd Winter

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

Liquid microjet photoelectron spectroscopy (LJ-PES) from aqueous solutions provides unique access to electronic structure properties of solutes and solvents. This talk highlights new opportunities of soft X-ray LJ-PES enabled by the development of novel instrumentation. One example is the ability to perform PES measurements from cryogenic liquid jets, for instance from liquid ammonia close to -70 °C. Another example is the use of planar liquid jets from aqueous solutions which is a prerequisite for the study of photoelectron distributions, with respect to both the light polarization or the light propagation. The latter can be exploited to study photoelectron circular dichroism (PECD) from chiral molecules in aqueous phase, when using circularly polarized light. First results from liquid fenchone and aqueous-phase alanine near the C 1s ionization threshold, obtained at beamline P04 at PETRA III, using a unique liquid-jet PES instrument will be presented.

**Contributed talk** **Thursday 12th 9h40**

# Effect of a cationic surfactant on the interfacial structure of bromide oxidation by ozone

Shuzhen Chen[1,2], Luca Artiglia[1], Jacinta Edebeli[1,2], Xiangrui Kong[1,3], Huanyu Yang[1,2], Anthony Boucly[1], Nøne Prisle[3] and Markus Ammann[1]

[1]Paul Scherrer Institut, Villigen, Switzerland, [2]ETH Zurich, Zurich, Switzerland, [3]Univiersity of Oulu, Oulu, Finland

Oxidation of bromide to hypobromite by ozone in the dark is one of the mechanisms by which bromine activation may be initiated and subsequent ozone depletion events be triggered in the troposphere and especially in marine environments where sea water provides the source of bromide [1]. The reaction of bromide with ozone occurs through an acid catalysed mechanism which involves an intermediate $[Br{\cdot}OOO]^-$ species. Our previous work provided direct experimental evidence for the formation of the $[Br{\cdot}OOO]^-$ intermediate at the surface by liquid jet XPS of aqueous NaBr aqueous solutions exposed to ozone. $[Br{\cdot}OOO]^-$ intermediate occurs preferentially at the liquid-vapor interface and limits the reaction rate [2].

Ocean surface water and sea spray aerosol deriving from there often contain complex mixtures of organics with variable surface affinity and functionalities [3]. Surface active organics may affect multiphase chemical reactions by changing acid-base equilibria and thus the rate of acid catalyzed reactions (as e.g., for the reaction of bromide with ozone) [2,4], or by changing the interfacial activity of the halide ions [5] or of the reaction intermediate $[Br{\cdot}OOO]^-$.

Here we investigate the effect of a cationic surfactant, tetrabutylammonium (TBA) on the interfacial structure and the abundance of the bromide ions at the aqueous solution surface using the liquid jet XPS method [6] at the Swiss Light Source (SLS). In addition, we study TBA containing bromide solutions exposed to ozone to obtain the surface propensity of $[Br{\cdot}OOO]^-$ intermediate in response to the presence of TBA, and relate the information derived from photoelectron spectroscopy to the results from the kinetic experiments on the same system.

The results clearly indicate that the positively charged nitrogen group in TBA, along with its surface activity, is leading to enhanced interfacial concentration of bromide, which may be due to an ion-pairing effect. Besides, in presence of ozone, the $[Br{\cdot}OOO]^-$ concentration in the interfacial region was increased as well for TBA containing bromide containing solutions, which is consistent with the kinetic experiment that showed a strongly enhanced ozone loss rate in presence of TBA on the surface of bromide solutions.

[1] S. Wang, et al., Proc. Natl. Acad. Sci., 112, 9281-9286, 2015.

[2] L. Artiglia, et al., Nature. Comm., 8,700, 2017.

[3] C. D. O'Dowd, Nature, 2004, 431, 676-680.

[4] M.-T. Lee, et al., J. Phys. Chem. A., 2015, 119, 4600-4608.

[5] M.-T. Lee, et al., Phys. Chem. Chem. Phys., 2019, 21, 8414-8427.

[6] Brown et al., Rev. Sci. Instrum. 2013, 84, 073904.

**Contributed talk** **Thursday 12th 10h00**

# Photoemission Spectroscopy from Metal-oxide / Aqueous Solution Interfaces

Robert Seidel[1], Dennis Hein[1], Garlef Wartner[1]

[1]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

With the recent vast experimental advances photoelectron spectroscopy has now become applicable even for the investigation of solid–liquid interfaces, enabling in situ photoemission characterization of electrochemical (aqueous) systems, and in particular allowing to study chemical reactions at electrode–electrolyte interfaces.

I will first present our recent synchrotron-based liquid-jet measurements on metal oxide nanoparticle/aqueous interfaces, especially, α-$Fe_2O_3$ [1] and anatase phase $TiO_2$,[2,3] and I will demonstrate the usefulness of valence and (resonant) Auger spectroscopy to study the electronic structure and the solvation behavior of these systems. Most noteworthy, resonant photoelectron spectroscopy is shown to be sufficiently sensitive for the detection of adsorbed hydroxyl species, resulting from $H_2O$ dissociation at the nanoparticle surface in aqueous solution.

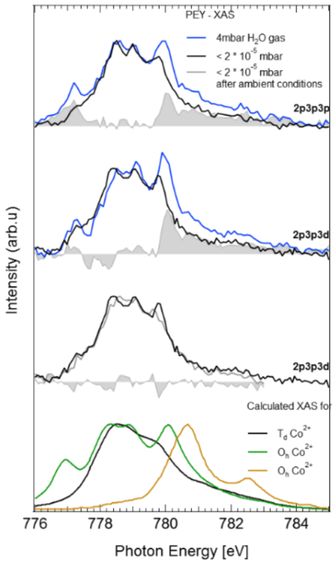


**Figure 2:** First PEY XAS spectra of supported cobalt oxide nanoparticles under vacuum and near-ambient pressure conditions, supplied by a 4-mbar water gas atmosphere. The spectral changes between both conditions reveal a change in oxidation state and coordination number of cobalt, which is reversible.

In the second part I will present our newest investigations on the multiple aspects of ambient pressure photoemission spectroscopy to supported cobalt oxide nanoparticles in contact with liquid water. This work is motivated by our recent findings that CoO shows a (reversible) phase transition between the rocksalt and the wurtzite structure at room temperature when in contact with water, which is usually only possible when applying high temperatures up to 900 degrees Celsius in the absence of water (see Figure 1).

In the last part I will give a short overview of our current work on the operando resonant XPS investigations of iron-nickel-oxyhydroxide catalysts during oxygen evolution reaction. For this experiment, we use an operando electrochemical flow cell, based on a concept pioneered at the FHI by the Schlögl group [4], where a $Si_3N_4$-supported graphene membrane separates the electrolyte from the vacuum. This membrane acts as a catalyst-coated working electrode, which is transparent for electrons and soft X-ray photons, too. Additionally to commonly used $Si_3N_4$-membranes, we also use alkaline-ionomer based membranes, because of their higher stability in a high-pH environment. Here, a water atmosphere of several mbar inside the SOL³PES main chamber is applied, to ensure a contact between the working-electrode, the catalyst and the electrolyte by the adsorbed $H_2O$ film on the membrane.

[1] *Chemical Science* 2018, 9 (19), 4511-4523
[2] *Review of Scientific Instruments* 2017, 88 (7), 073107
[3] *Journal of Materials Chemistry A* 2019**,** 7**,** 6665-6675
[4] *Angewandte Chemie International Edition* 2015, 54, 1.

***Contributed talk*** ***Thursday 12th 10h50***

# Electronic level alignment between a metal electrode and a solution with a known redox potential: a liquid-jet XPS study at Pleiades beamline (SOLEIL)

L. Perez Ramirez[1], F. Saudrais[2], C. Nicolas[3], E. Maisonhaute[4], F. Bournel[1,3], J.-J. Gallet[1,3], and F. Rochet[1,3]

[1]Sorbonne Université, CNRS, LCPMR, Paris, France [2]CEA, LIONS, Université Paris-Saclay, France [3]Synchrotron SOLEIL, France [4]Sorbonne Université, CNRS, LISE, Paris, France

The question of the electronic level alignment between an electrode and the electronic levels of water is a longstanding problem, with a renewed interest both at theoretical[1] and experimental levels.[2,3] Naturally, it is of prime importance when electrochemical systems are investigated with XPS. The model generally agreed upon is that the electrochemical potential in solutions $\tilde{\mu}^{sol}$ is equivalent of to the Fermi level in solids.[4,5] Therefore, at the interface between a metal and the solution, $\tilde{\mu}^{sol}$ aligns with the Fermi level of the metal $E_F^{metal}$ at thermal equilibrium. One could then expect that during liquid jet XPS measurements, the solution, an electrode in contact with the jet and the XPS analyzer itself will all have their "Fermi levels" (electrochemical potentials) aligned, as it is the case when one deals with solid samples. Here we present preliminary results obtained at Pleiades beamline on the measurement of the electronic structure of the so-called ZoBell solution,[6] consisting of an equimolar (3.33 $10^{-3}$ M) ferricyanide/ferrocyanide mixture in KCl (0.1 M), with a potential of 430 meV relative to the standard hydrogen electrode. Using this liquid jet procedure, we expect to work in better controlled conditions than in one of our NAP-XPS preceding work[3] on the electronic structure of NaCl solutions droplets on a gold substrate, that may have suffered from an ill-defined redox couple in the solution and from the surface contamination of the droplets.

First, we measure the O 1s, K 2p, Cl 2p and valence levels[7] in the liquid jet, allowing the referencing of the energies to gold $E_F^{metal}$. We also analyze the effects of changing the red/ox concentrations with respect to the standard Zobell solution. Second, we address the question of the solution work-function measurement. The crucial question is the measurement of the vacuum level $V_L$ in the immediate vicinity of the liquid jet surface. We show that $V_L$ determination via the ionization potential of gas phase valence levels[8] ($1b_1$) may be affected by the contact potential difference between the jet surface and the analyzer. Therefore, we determine the cutoff of the secondary electrons (SEEDC), as it is common practice for solids. We show that the rising edge of the SEEDC has a certain width, that seems intrinsic to the liquid state, and independent of the surface cleanliness of the jet (Zobell and n-butanol/Zobell solutions are compared). However, its energy position is clearly dependent of the surface dipole layer, especially when surfactants (butanol) are present at the surface. We compare the work function values and discuss our findings with those deduced from Trasatti's relationship[5]. We conclude by emphasizing the consequences of a confusion often made between the surface dipole dependent vacuum level, with the non-measurable vacuum level at infinity[9,10] that helps defining the electrochemical potential.

**[1]** Bouzid, A.; Pasquarello, A. J. Chem. Theory Comput. 2017, 13 (4), 1769–1777.
**[2]** Tsiplakides, D.; Archonta, D.; Vayenas, C. G. Top. Catal. 2007, 44 (3), 469–479.
**[3]** Tissot, H. et. al. Top. Catal. 2016, 59 (5–7), 605–620. **[4]** Reiss, H. J. Phys. Chem. 1985, 89 (18), 3783–3791. **[5]** Trasatti, S. Pure Appl. Chem. 1986, 58 (7). **[6]** Nordstrom, D. K. Geochim. Cosmochim. Acta 1977, 41 (12), 1835–1841. **[7]** Seidel, R.; et. al. J. Phys. Chem. B 2011, 115 (40), 11671–11677. **[8]** Winter, B.; Faubel, M. Chem. Rev. 2006, 106 (4), 1176–1211.
**[9]** Egelhoff, W. F. Surf. Sci. Rep. 1987, 6 (6–8), 253–415. **[10]** Kahn, A. Mater. Horizons 2016, 3 (1), 7–10.

**Contributed talk** **Thursday 12th 11h10**

# Characterization of Model Desalination Membranes by Ambient Pressure Photoelectron Spectroscopy

Sabrina M. Gericke[1,2,3], Slavomir Nemšák[2], Hendrik Bluhm[2,4], Christin Büchner[2]

[1]Freie Universität Berlin, Berlin, Germany, [2]Lawrence Berkeley National Laboratory, Berkeley, CA, USA, [3]Lund University, Lund, Sweden [4]Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Saltwater is desalinated to produce water suitable for human consumption. Most modern desalination plants are based on reverse osmosis (RO) technology, where seawater is pressurized against a semi-permeable membrane, that allows water to pass but retains contaminants [1]. While RO membranes show high retention for $Na^+$ and $Cl^-$ ions, the retention for other water contaminants is poor [2]. A better understanding of the diffusion processes through the RO membranes will facilitate advances in membrane design and improvement of their performance. The goal of our research is the study of the interface chemistry of model desalination membranes, in particular specific chemical and electrostatic interactions, to shed light on the mechanism for ion selectivity in water purification.

Our model system consists of a metal-coated silicon wafer onto which the individual layers of the RO membrane are deposited using molecular layer-by-layer deposition [3]. This technique creates ultrathin RO membrane films that are sufficiently smooth to enable studies with high resolution microscopy and spectroscopy methods.

The roughness of the ultra-thin RO membrane films was investigated with atomic force microscopy. Afterwards, the membrane films were characterized using ambient-pressure X-ray photoelectron spectroscopy (APXPS) and X-ray absorption spectroscopy. This allows identifying the chemical groups of the RO membrane films, their interaction with X-rays, water and salt solutions.

In the future, the diffusion mechanisms of water contaminants through the RO membranes will be investigated using standing-wave ambient-pressure photoemission (SWAPPS). SWAPPS provides increased depth resolution to photoemission spectroscopy by locally modulating the intensity of the X-ray beam, and thus gives information on the chemical composition of a sample as a function of depth on the sub-nanometer length scale. We expect that SWAPPS studies of the RO membrane films in contact with salt solutions may pave the way to a better understanding of the diffusion mechanism through RO membranes.

[1] C. Fritzmann, J. Löwenberg, T. Wintgens, and T. Melin, “State-of-the-art of reverse osmosis desalination”, Desalination, vol. 216, pp. 1–76, 2007
[2] G. M. Geise, H.-S. Lee, D. J. Miller, B. D. Freeman, J. E. McGrath, and D. R. Paul, “Water Purification by Membranes: The Role of Polymer Science,” Journal of Polymer Science Part B: Polymer physics, vol. 48, pp. 1685–1718, 2010
[3] P. M. Johnson, J. Yoon, J. Y. Kelly, J. A. Howarter, and C. M. Stafford, “Molecular layer-by-layer deposition of highly crosslinked polyamide films,” Journal of Polymer Science, Part B: Polymer Physics, vol. 50, pp. 168–173, 2012.

**Contributed talk** **Thursday 12th 11h30**

# Increased Reactivity of Subsurface Hydrogen Probed in a Membrane Reactor Cell by APXPS

Andrey Shavorskiy[1,2], May Ling. Ng[3,4], Christoph Rameshan[3,5], Osman Karslioglu[3,6], Chloe Wang[3], Hendrik Bluhm[1,3,6]

[1]Advanced Light Source, LBNL, Berkeley, CA, USA; [2]MAX-IV Laboratory, Lund, Sweden; [3]Chemical Sciences Division, LBNL, Berkeley, CA, USA; [4]SLAC National Accelerator Laboratory, Stanford, CA, USA; [5]University of Technology, Vienna, Austria; [6]Fritz Haber Institute of the MPG, Berlin, Germany

Subsurface hydrogen has been shown to provide unique pathways and enhanced reactivity in hydrogenation reactions catalysed by transition metals. [1-5] The underlying mechanism for the enhanced reactivity of subsurface vs. adsorbed hydrogen is still under debate. Among the factors that are considered are the increased potential energy of the emerging subsurface hydrogen and changes in the electronic structure due to hydrogen-induced lattice distortions in the metal. In the case of membrane reactors, where hydrogen permeates the transition metal, increased reactivity can also be due to the absence of competition for adsorption sites between permeating hydrogen and the other reactants. Here we investigate the reactivity of hydrogen in the oxygen reduction reaction on palladium, which we have investigated in two reactor setups using APXPS. In one experiment hydrogen and oxygen were co-dosed in the same volume, in a conventional reactor scheme, with Pd foil as the catalyst (see Figure). In a second experiment we have employed a membrane reactor cell where palladium was used both for the generation of atomic, subsurface hydrogen and as catalyst for the oxygen reduction reaction. The results of these experiments show that the reactivity of subsurface hydrogen is enhanced by a factor of more than five in comparison to that of hydrogen co-dosed with oxygen in the same volume. These type of experiments could provide a platform for a broader investigation of subsurface hydrogen in other hydrogenation reactions and help to provide new experimental evidence for the underlying mechanism for the altered reactivity of this species.

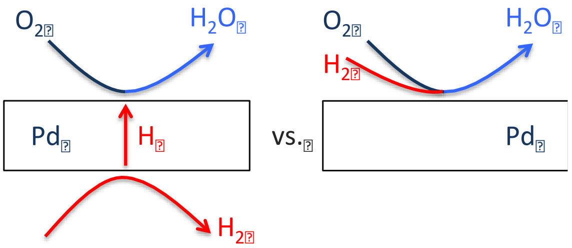


Figure 1. We have investigated the reactivity of subsurface hydrogen in a membrane reactor cell (left) and compared it to the reactivity in a conventional reactor (right).

[1] Michaelides, A., Hu, P., Alavi, V. *J. Chem. Phys*. **111**, 1343 (1999).

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[5] Teschner, D., Borsodi, J., et al. Science **320**, 86 (2008).

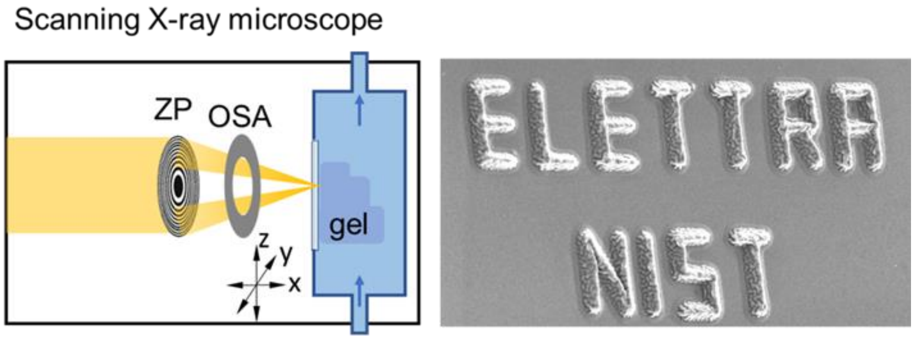
***Invited talk*** ***Thursday 12th 13h30***

# From Spectromicroscopy to Nanofabrication In liquids with Soft X-rays

Andrei Kolmakov [1]

[1]National Institute of Standards and Technology, Gaithersburg, USA

The focus of the modern high-pressure X-ray and electron spectromicroscopy studies is on the characterization of practically important interfaces under realistic (or close) operation conditions. Most of the time the beam-induced reactions in the liquid or dense gaseous media are considered as parasitic. Here we reverse this agenda and use the graphene liquid cells [1] developed for APXPS and in liquid SEM [2] to explore focused X-ray (and electron) beams induced polymer cross-linking reactions for additive nanofabrication in liquid media. The core of the technology is the employment of ultrathin electron (X-ray) transparent molecularly impermeable membranes that separate high vacuum of the X-ray or electron microscopes from a high-pressure fluidic sample. As a test media, we selected biocompatible PEGDA hydrogels which are easily functionalized porous polymeric scaffolds that found numerous applications in drug devilry, flexible (wearable/injectable) electronics, tissue engineering, soft robotics, sensorics, energy storage, etc. In particular, we report on major processes that affect the size, resolution, and degree of crosslinking of pristine and composite PEGDA hydrogels [3]. We found that cross-linking is a photon energy-dependent process that occurs at very low irradiation doses in the order of 1 e/nm$^2$. Bonds scission starts to dominate at elevated doses what has been supported with O 1s and C 1s APXPS spectra evolution. The chemically modified regions can then be selectively plasma etched what enables additional subtractive manufacturing for the gelated features with a spatial resolution of ca 50 nm. Finally, we defined the imaging and spectroscopy conditions for guest particles in composite hydrogels in its liquid state during and after the crosslinking process.



The principle of Soft X-rays beam induced cross linking in liquids (left panel) and exemplary ELETTRA/NIST logos written with 536 eV photons (right panel)

[1] A. Kolmakov *et al.*, "Graphene oxide windows for in situ environmental cell photoelectron spectroscopy," *Nature nanotechnology,* vol. 6, no. 10, p. 651, 2011.

[2] A. Kolmakov, "Membrane Based Environmental Cells for SEM in Liquids," in *Liquid Cell Electron Microscopy*, F. M. Ross, Ed. Cambridge: Cambridge University Press, 2016, pp. 78-105.

[3] T. Gupta *et al.*, "Focused Electron and X-ray Beam Crosslinking in Liquids for Nanoscale Hydrogels 3D Printing and Encapsulation," *arXiv preprint arXiv:1904.01652,* 2019.

***Invited talk*** ***Thursday 12th 14h00***

# In situ X-ray based characterization of atomic layer deposition

Matthias M. Minjauw[1], Christophe Detavernier[1], Jolien Dendooven[1]

[1]CoCooN research group, Department of Solid State Sciences, Ghent University, Ghent, Belgium.

Atomic layer deposition (ALD) is a thin film deposition technique which relies on alternating, self-limiting chemical reactions between gas-phase precursor molecules and functional groups on a solid surface. ALD is capable of producing highly conformal and pinhole free coatings with a thickness controlled at the atomic scale, which makes it of high interest for applications in microelectronics, catalysis, energy storage systems and biomedical devices.

An important part of ALD-research is in situ characterization. The alternating nature of ALD processes allows the involved growth mechanisms to be studied in situ with a wide range of characterization methods. For example, by adding a mass-spectrometer to the exhaust line of an ALD reactor, the reaction products of the ALD surface reactions can be detected for each of the precursors. By installing windows which are transparent for a specific part of the electromagnetic spectrum, one can characterize the growing film with either X-rays, IR or optical light, once the precursor molecules have been purged from the ALD-reactor.

In this talk we will focus on X-ray based in situ characterization of ALD processes. It will be demonstrated that by using a dedicated mobile ALD setup, it is possible to study an ALD process in situ at a synchrotron facility. Two examples that will be covered are grazing incidence small-angle X-ray scattering (GISAXS) and X-ray fluorescence (XRF). In addition, it will be shown that by connecting an ALD reactor to a lab-based XPS instrument, it is possible to study an ALD process in vacuo with XPS.

**Contributed talk** **Thursday 12th 14h30**

# ALD of $HfO_2$ on InAs: new insight by time-resolved *in situ* studies

Giulio D'Acunto[1], Andrea Troian[1], Esko Kokkonen[2], Sofie Yngman[1], Foqia Rehman[1], Zhihua Yong[1], Joachim Schnadt[1,2], and Rainer Timm[1]

[1]Division of Synchrotron Radiation Research, Department of Physics, and NanoLund, Lund University, Lund, Sweden, [2]MAX IV Laboratory, Lund University, Lund, Sweden

Atomic layer deposition (ALD) is a powerful technique for the deposition of thin films with atomic-scale precision. The ideal ALD scheme, which relies on the assumption of a self-limiting surface reaction during deposition [1], is of crucial importance for modern metal-oxide-semiconductor (MOS) devices. III-V semiconductors are excellent candidates for future MOS-based applications; however, defects at the semiconductor-oxide interface limit device performance. ALD of the high-k material $HfO_2$ has been shown to remove the native oxide through the so-called self-cleaning effect, but many details of the surface chemistry remain unknown and the interface quality still needs to be improved.

We studied the ALD of $HfO_2$ on InAs from tetrakisdimethylamido-hafnium (TDMA-Hf) and water fully in an *in situ* and *operando* ambient pressure X-ray photoelectron spectroscopy experiment at the HIPPIE beamline of the MAX IV Laboratory. A complete removal of As-oxides was confirmed during the first ALD half-cycle [2]. Importantly, we observed a two-step chemical reaction including molecular adsorption of the TDMA-Hf precursor prior to $HfO_2$ formation, which shows that the established ligand exchange model of ALD needs to be revised. Recent studies with improved time resolution, monitoring simultaneously As 3d, In 3d, In 4d, Hf 4f, and C 1s core-levels, reveal the time sequence of the removal of different As- and In-oxide components (Fig 1), and Hf surface chemistry. These results have significant potential to improve the performance of III-V MOS devices.

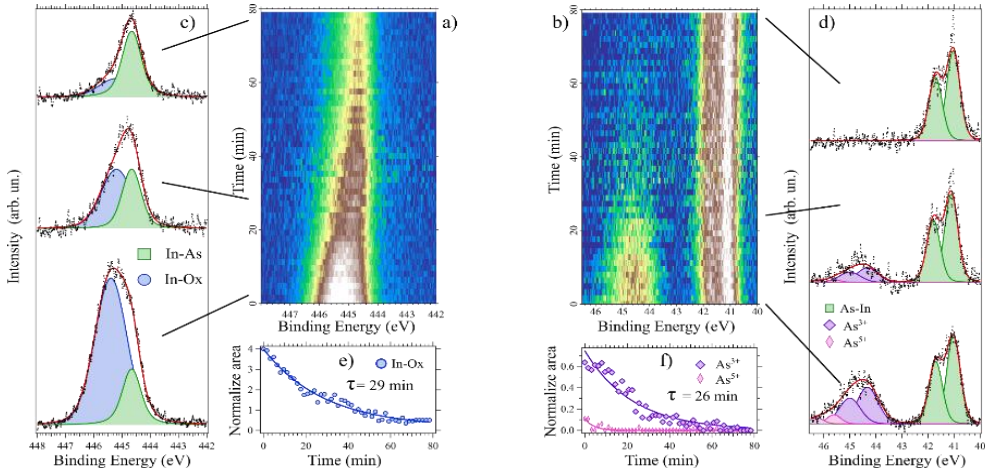


*Fig 1. Time-resolved InAs oxide removal during the first half cycle of $HfO_2$ ALD on an InAs substrate. (a) and (b) Detailed time evolution image plot showing the In $3d_{5/2}$ and As 3d AP-XP core levels. (c) and (d) Subsequent In $3d_{5/2}$ and As 3d AP-XP spectra of the time evolution image plot in (a) and (b) respectively, at 0 (bottom) and 77 (top) minutes. The middle spectrum in (c) and (d) are referred to 30 and 25 minutes, respectively. The normalised intensities relative to the bulk component are plotted in (e) and (f) for the In $3d_{5/2}$ and the As 3d lines.*

[1] F. Zaera, Coord. Chem. Rev. 257, 3177 (2013)
[2] R. Timm et al., Nature Commun. 9, 1412 (2018)

***Invited talk*** ***Thursday 12th 15h20***

# Using high resolution XPS at low and near-ambient pressures to resolve mechanistic issues in cobalt-catalysed Fischer-Tropsch synthesis

C.J. (Kees-Jan) Weststrate[1], Devyani Sharma[1,2], Daniel Garcia Rodriguez[1,2], Hans O.A. Fredriksson[1], Michael A. Gleeson[2], J.W. (Hans) Niemantsverdriet[1,3]

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Supported cobalt catalysts find their most widespread application in low temperature Fischer-Tropsch synthesis (FTS), a process in which C-C bond forming reactions produce long chain saturated hydrocarbon chains from synthesis gas, a mixture of CO and $H_2$. The versatile FTS process may very well continue to play a role in future energy scenarios: synthesis gas can be derived from biomass or $CO_2$, where $H_2$ from water electrolysis can be used to create synthesis gas via the reverse water-gas-shift reaction in the latter case. In this way, Fischer-Tropsch synthesis can provide a sustainable alternative to replace petroleum as the principal feedstock of chemicals and liquid transportation fuels.

The FTS reaction mechanism can be ranked among the most complex in the chemical industry. CO and $H_2$ get converted into long chain hydrocarbons in a sequence of bond-breaking and bond-making steps that are catalysed by metals such as cobalt, ruthenium and iron (which is active in the carbide form). As the steady state concentration of chain growth intermediates is below the detection limits of in-situ spectroscopies simplified model studies are needed to elucidate the mechanism by which long hydrocarbon chains grow on the cobalt catalyst surface. In my talk I will present a number of examples where we used a Co(0001) single crystal surface as a simple model catalyst to study elementary reaction steps relevant to Fischer-Tropsch synthesis [1-4]. By using XPS in both UHV and ambient pressure conditions in combination with other surface sensitive spectroscopies we can measure both the concentration and chemical nature of surface species and derive kinetics of elementary reaction steps.

[1] C.J. Weststrate, I.M. Ciobîcă, J. van de Loosdrecht, J.W. Niemantsverdriet, *Adsorption and Decomposition of Ethene and Propene on Co(0001): The Surface Chemistry of Fischer−Tropsch Chain Growth Intermediates,* J. Phys. Chem. C **120** *(2016), 29210–29224*

[2] C.J. Weststrate, J. van de Loosdrecht, J.W. Niemantsverdriet, *Spectroscopic insights into cobalt-catalyzed Fischer-Tropsch synthesis:A review of the carbon monoxide interaction with single crystalline surfaces of cobalt*, J. Catal. **342** (2016), 1–16

[3] C.J. Weststrate, P. van Helden, J.W. Niemantsverdriet, *Reflections on the Fischer-Tropsch synthesis: Mechanistic issues from a surface science perspective*, Catal. Today **275** (2016), 100-110

[4] A.C. Kizilkaya, J.W. Niemantsverdriet, C.J. Weststrate, *Oxygen Adsorption and Water Formation on Co(0001)*, J. Phys. Chem. C **120** (2016), 3834−3845

***Contributed talk*** ***Thursday 12th 15h50***

# Pt-Cu nanoparticles on 2D and 3D supports: an AP-XPS/TAP study

Evgeniy A. Redekop[1], Niclas Johansson[2], Esko Kokkonen[2], Maria Kalyva[1], Samuli Urpelainen[2], Spyros Diplas[1,3], and Unni Olsbye[1]

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Correlative characterization of the surface state and reactivity of catalytic materials can yield unprecedented insights into the nature of in situ catalyst evolution and structure performance relationships. Combined spectroscopic and kinetic experiments are readily available for model materials in surface science, but they are still under developped for complex catalysts. Temporal Analysis of Products (TAP) enables precise time-resolved kinetic characterization of non-model catalysts by pulse-response experiments in the Knudsen transport regime [1]. Ambient Pressure X-Ray Photoelectron Spectroscopy (APXPS) [2] offers an attractive spectroscopic counterpart to be coupled with TAP due to the similarities in their characteristic pressure regimes. However, several challenges must be overcome to take advantage of the TAP/AP-XPS synergy. Preparing samples with equivalent active sites that would be suitable for both techniques is one such challenge – while AP-XPS is optimized for conductive samples on planar (2D) supports, TAP typically utilizes high-surface area non-conductive materials. Colloidally-prepared metallic nanoparticles provide a possible avenue to bridge the disparity in sample morphology, since they can be deposited on 2D and 3D materials. Herein we report a combined APXPS/TAP study of Pt-Cu nanoparticles (NPs) supported on planar and porous silica. NPs with well-defined compositions were prepared via microwave synthesis (Figure 1A). For APXPS measurements, the NPs were spin-coated onto Si wafers. For TAP measurements, NPs were dispersed in high-surface area supports. AP-XPS measurements revealed that the organic capping agent can be efficiently removed from the NPs by heating in O2 environment to 400ºC. Cycling between O2 and CO causes alloy segregation and re-formation, respectively, with Cu being segregated to the surface in the form of CuO in oxidative environments. Based on AP-XPS data, TAP measurements were devised to probe the intrinsic reactivity of different surface states of Pt-Cu NPs prepared by CO and O2 treatments. Our findings indicate that colloidal NPs can be used as a transferable active ingredient on both planar and porous samples for the tandem TAP/AP-XPS measurements, paving the way for more systematic application of both techniques in spectro-kinetic studies of catalytic materials. In this contribution, experimental results will be presented and methodological challenges for the combined TAP/AP-XPS methodology will be discussed.

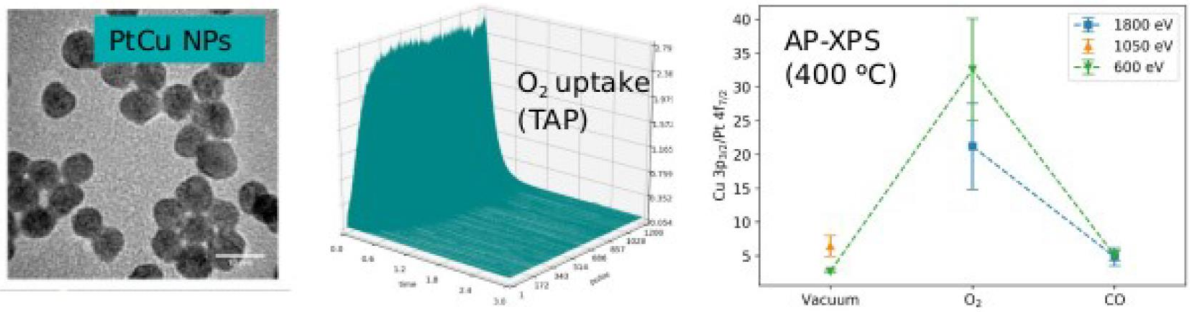

Figure 1. Structural (TEM), Chemical (TAP), and spectroscopic (AP-XPS) view of Pt-Cu NPs

[1] Gleaves et al., J. Mol. Catal. A., 315, 2010, 108-134

[2] Knudsen et al., Surface Science, 646, 2016, 160-169

***Contributed talk*** ***Thursday 12th 16h10***

# Combining Theory with Experiments to Unravel Silver Interacts with Carbon Dioxide and Water

Yifan Ye[1], Jin Qian[1,2], Hao Yang[2], Hongyang Su[1], Kyung-Jae Lee[1], Ane Etxebarria[1], Junko Yano[1], William A. Goddard III[2], Ethan J. Crumlin[1]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA, United States

[2]California Institute of Technology, Pasadena, CA, United States

Converting carbon dioxide ($CO_2$) into liquid fuels and synthesis gas is a national priority. But there is no experimental information on the initial atomic level events for $CO_2$ reduction on the metal catalysts to provide the basis for developing improved catalysts. In order to provide this experimental information, we used ambient pressure X-ray photoelectron spectroscopy (APXPS) to examine the processes as metal catalyst surfaces exposed to $CO_2$ both alone and in the presence of $H_2O$ at 298 K, the results of which we correlated with quantum mechanics density to provide definitive interpretations.[1,2]

We first investigated the interaction between $CO_2$ (+$H_2O$) with the Ag surface. On Ag we found very different gas adsorption and activation process compared to that on Cu. We found that physisorbed (*l*-) and chemisorbed (*b*-) $CO_2$ are *not* stable on pure Ag surface, but rather gaseous $CO_2$ reacts with absorbed O on Ag surface to form a chemisorbed surface species ($O{=}CO_2^{\delta-}$). Adding $H_2O$ and $CO_2$ then leads to up to four water attaching on ($O{=}CO_2^{\delta-}$) and two water attaching onto *b*-$CO_2$ on the surface.[2] Secondly, we wanted to develop a way to quantitatively connect our theory with experiments. To do this we developed a chemical reaction network (CRN) that we use to predict the time evolution of various surface chemical species concentration over a wide range of temperatures (298 – 798 K) and pressures ($10^{-6}$ to 1 Torr). Through this effort we established a good agreement with the APXPS data. Thus validating this protocol that could be useful for improving the connection between theory and data [3]

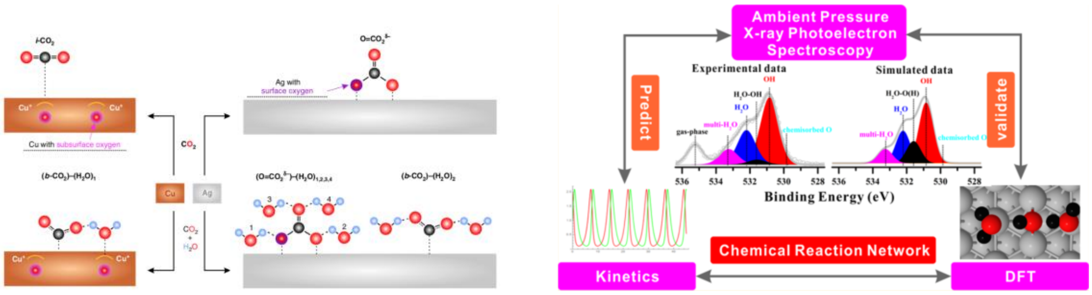

Figure 1 (left) comparison between copper and silver exposed to $CO_2$ and $CO_2 + H_2O$, (right) chemical reaction network scheme for $H_2O$ on silver

[1] Favaro, M., Xiao, H., Cheng, T., Goddard, W. A., Yano, J. & Crumlin, E. J. *Proceedings of the National Academy of Sciences of the United States of America* **114**, 6706-6711, doi:10.1073/pnas.1701405114 (2017).
[2] Ye, Y. F., Yang, H., Qian, J., Su, H. Y., Lee, K. J., Cheng, T., Xiao, H., Yano, J., Goddard, W. A. & Crumlin, E. J. *Nature Communications* **10**, 1875, doi:10.1038/s41467-019-09846-y (2019).
[3] Qian, J., Ye, Y. F., Yang, H., Yano, J., Crumlin, E. J. & Goddard, W. A. *Journal of the American Chemical Society* **141**, 6946-6954, doi:10.1021/jacs.8b13672 (2019).

***Contributed talk*** ***Thursday 12th 16h30***

# Oxygen on silver and their role in methanol oxidation

F. Sulzmann[1], E. Carbonio[3], T. Jones[1], A. Knop-Gerincke[2], R. Schlögl[1,2]

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Understanding the catalytic partial oxidation of methanol to formaldehyde is a long standing problem that is poised to face a resurgence in interest. Nowadays, formaldehyde is produced industrially by the reaction of methanol over either metal-oxide or silver based catalysts. The two catalysts require different reaction parameters and offer differing selectivity. For example, it is believed that formaldehyde is produced through both a partial oxidation and dehydrogenation pathway over silver based catalysts, while only the former seems to be important for the metal-oxide catalyst. This fact, and the simplicity of the silver based catalyst (modelled catalyst system), motivate our interest in the presented project.

The silver oxygen system has been thoroughly investigated in the last decades. When early studies on X-ray photoelectron spectroscopy (XPS) proved a powerful tool for such investigations [1].

Schlögl`s group reported of an oxygen species that is stable at high temperatures and labelled it $O_{\gamma.}$ This oxygen species, with a binding energy of 529.1 to 529.7 eV [2], is described as a subsurface oxygen forming a thin oxide-like-layer on the silver surface. Rocha et al. [2] found two oxygen species formed at 500°C in 0.25 mbar of oxygen, one denoted $O_{\gamma}$ and the other $O_{\alpha 2}$. Reichelt et al. [3] later used UHV techniques to show the strongly bound oxygen species could, in some cases, be due to Molybdenumoxide contamination on the silver surface, but the question remains as to the generality of that finding under *in situ* conditions.

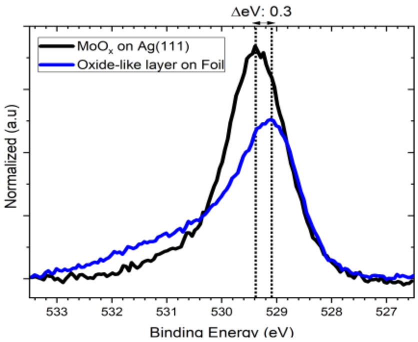


*Figure 1: The O1s spectra for $MoO_x$ and oxide-like layers at 0.25mbar $O_2$ at 500°C.*

We will now report on ways to differentiate between oxygen species attributed to silver and the ones attributed to Molybdenumoxide using synchrotron NAP-XPS in combination with X-ray absorption measurements. Furthermore, we investigated the silver oxygen system under reaction conditions for methanol oxidation.

[1] X. Bao et al. Surface Science. 1-2 (1993) 284.
[2] T. Rocha et al. Phys. Chem. Chem. Phys. 14 (2012) 14.
[3] R. Reichelt et al. J. of Physical Chemistry C 35 (2011) 115.

***Contributed talk*** ***Thursday 12th 16h50***

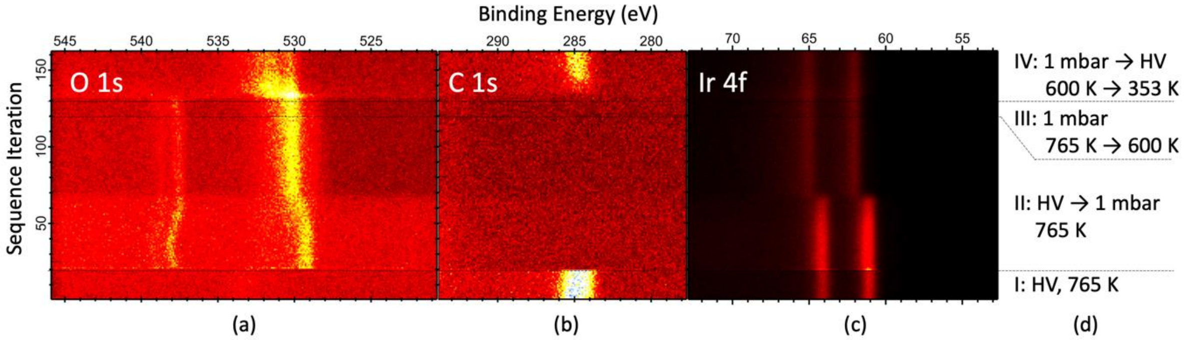
# Oxidation of Ir(001) towards $IrO_2$ studied by ambient-pressure X-ray photoelectron spectroscopy

Zbynek Novotny[1,2], Benjamin Tobler[1], Luca Artiglia[2], Jörg Raabe[2], and Jürg Osterwalder[1]

[1]Physik-Institut, Universität Zürich, Switzerland, [2]Paul Scherrer Institut, Villigen, Switzerland

The oxides of iridium are known to be a very stable electrode material for the oxygen evolution reaction and were therefore intensively studied by the electrochemical community in acidic media. Recently, $IrO_2(110)$ films were found to be an excellent catalyst for low-temperature activation of methane [1], which initiated intense research of the chemistry and properties of the $IrO_2(110)$ surface. The formation of the rutile $IrO_2$ requires the oxygen pressure in the millibar range - a pressure significantly higher than most surface sensitive techniques can operate in. The pressure-dependence of the oxide growth, its structure and the amount of oxygen within the oxide film was studied using ex-situ low energy electron diffraction and temperature-programmed desorption, finding that rotated $IrO_2(110)R27°$ films [2] can be grown by thermal oxidation at 765 K and $O_2$ pressures of 0.75 Torr, while the aligned $IrO_2(110)$ structure forms upon oxidation at 5 Torr [3]. While the structure of the as-grown oxides is well known, the kinetics of the oxide growth is still not well understood, calling for *in-situ* studies with techniques such as ambient-pressure X-ray photoelectron spectroscopy (APXPS).

We studied the thermal oxidation of single-crystalline Ir(001) films using time-lapsed APXPS. Based on the binding energy change of the Ir 4f and O1s core level peaks, we initially observe the formation of a carbon-free surface covered with a complete monolayer of chemisorbed oxygen. After a rather long nucleation period during which the oxygen coverage is nearly constant (while the work function is changing as sensed by the gas phase O 1s peaks), we observe a rapid formation of $IrO_2$ rutile phase with a thickness above 3.5 nm. Using quantitative analysis, we provide direct evidence that the oxide film is formed via an autocatalytic growth mechanism that was proposed previously for lead oxide and $RuO_2$ [4]. Finally, we will present our plans to investigate such rutile-based oxides using our electrochemical APXPS endstation that we recently built at the Swiss Light Source [5].



Spectra of (a) O 1s, (b) C 1s, and (c) Ir 4f spectra acquired using a photon energy of 653 eV. Acquisition of one cycle of O 1s, C 1s and Ir 4f regions (one line in the image) required 29.2 seconds. Panel (d) shows experimental conditions within the regions, with a dashed line (extending to panels a-c) separating regions where the conditions were changed.

[1] Liang, Z.; Li, T.; Kim, M.; Asthagiri, A.; Weaver, J. F., Science 2017, 356 (6335), 299.
[2] Li, T.; Kim, M.; Liang, Z.; Asthagiri, A.; Weaver, J. F., Top. Catal. 2018, 61 (5), 397-411.
[3] Bian, Y.; Li, T.; Weaver, J. F., J. Phys. D: Appl. Phys. 2019, 52 (43), 434002.
[4] Over, H.; Seitsonen, A. P., Science 2002, 297 (5589), 2003-2005.
[5] Novotny Z. *et al.*, Rev. Sci. Instr. *(submitted)*.

***Contributed talk*** ***Thursday 12th 17h10***

# 8A2 KBSI-PAL AP-XPS beamline for *in situ* and *operando* science at Pohang Accelerator Laboratory

Geonhwa Kim[1,2], Beomgyun Jeong[3], Youngseok Yu[1,2], Hojoon Lim[1,2], Jaeyoon Baik[2], Jouhahn Lee[3], Bongjin Simon Mun[1], Ki-jeong Kim[2]

[1] Department of Physics and Photon Science, Gwangju Institute of Science and Technology, Gwangju, Korea

[2] Beamline Research Division, Pohang Accelerator Laboratory, Pohang, Korea

[3] Advanced Nano-Surface Research Group, Korea Basic Science Institute, Daejeon, Korea

In August, 2019, a new AP-XPS endstation with dedicated beamline is commissioned at Pohang Accelerator Laboratory (PAL), Korea. The major scientific program for the beamline and endstation is *in situ* and *operando* interface science, including heterogeneous catalysis, electrochemistry, and semiconductor device. Beamline (BL) 8A is an undulator-based soft X-ray beamline and has two branches for 8A1 SPEM and 8A2 AP-XPS that share a plane undulator, the first mirror (M1) and monochromator. This beamline is aimed at high-resolution ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), soft X-ray absorption spectroscopy (soft-XAS), and scanning photoemission microscopy (SPEM) experiments. Especially, 8A2 AP-XPS beamline is operated under the collaboration with Korea Basic Science Institute (KBSI). The photon beam is switched between the two branches by changing the refocusing mirrors after the monochromator. The acceptance angle of the first mirror (M1) was kept glancing at 1.2°, and Pt is coated onto mirrors to achieve high reflectance, which insures the wide photon energy range (100 ~ 2,000 eV) with high resolution at photon flux ~ $10^{13}$ photon/sec. In this presentation, the main characteristics and performance of the beamline are reported and discussed.

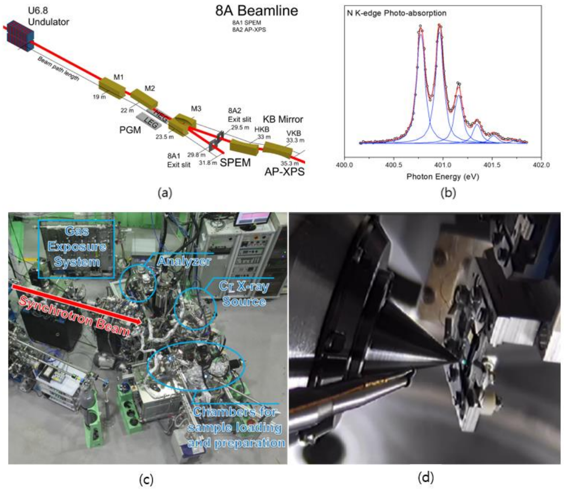


Figure 1. 8A Beamline (a) Schematic layout, (b) N K-edge absorption spectrum to estimate the photon resolution of 8A beamline, (c) Experimental system for 8A2 AP-XPS beamline and (d) Inside of sample analysis chamber.

## POSTERS Wednesday 11th 17h30-20h00

| # | PRESENTING AUTHOR | TITLE |
|---|---|---|
| P1 | Adrian Hunt | *The IOS beamline at NSLS-II: Combined APXPS and APXAS to tackle the modern catalyst* |
| P2 | Alessandro Troglia | *The Surface Stability of Components for Extreme Ultraviolet Lithography in Reactive Environments* |
| P3 | Alexander Klyushin | *APXPS and in-situ Raman study of S promotion on Ag catalysts* |
| P4 | Alexander Large | *Operando characterisation of oxide-supported bimetallic methane oxidation catalysts* |
| P5 | Carlos Escudero | *Bimetallic nanoparticles reorganize differently on nanoshaped ceria:An operando ambient pressure XPS study* |
| P6 | Chia-Hsin Wang | *In-situ study of PdZn and PdCuZn catalysts for CO2hydrogenation by Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS)* |
| P7 | Chunlei Wang | *Single-site Fe1atomsanchored on Pt(111) and Cu2O(100) for CO oxidation* |
| P8 | David Mueller | *Percolation conduction in monolithic mixed early/late transition metal perovskites* |
| P9 | Elizabeth Willneff / Andrew Britton | *Watching Paint Dry with NAPXPS* |
| P10 | Elizabeth Willneff / Andrew Britton | *Having your cake and eating it toowith NAP XPS of food* |
| P11 | Esko Kokkonen | *The APXPS branch of the SPECIES beamline at MAX IV* |
| P12 | Federica Bondino | *Stabilization and reactivity of a dense carbon monoxide layer on Pt(111) under a mixed boron nitride-graphene cover* |
| P13 | Federica Venturini / George Held | *VerSoX: a versatile Soft X-ray beamline at Diamond Light Source* |
| P14 | Felipe Lopes da Silva | *Bridging the material gap: An in-situspectroscopic study of the surface reactions for industrial selective catalytic reduction (SCR) catalysts* |
| P15 | Foqia Rehman | *Following the atomic layer deposition ofTiO2on InAs(100) inrealtime byambient pressurex-ray photoelectron spectroscopy* |
| P16 | Gregory Herman | *The Oregon State University Ambient Pressure Surface Characterization Laboratory* |
| P17 | Haiko Wittkaemper | *Spectroscopic InsightsintoLiquid Metal Solutions for Catalysis* |
| P18 | Iradwikanari Waluyo | *Oxidation and Reduction of Cu(111) in the Presence of Single Pt Atoms* |
| P19 | Jack Hart | *A Closer Look at Direct Solar Water Splitting* |
| P20 | Jesse Saari | *In situ electrochemical APXPS analysis of ALD grown Cu catalyst for CO2reduction* |
| P21 | Lucia Perez Ramirez | *The Oxidation of Aluminumat Room Temperature Studied by NAP-XPS* |
| P22 | Lukasz Walczak | *Boosted design and study of nanomaterials by HPXPS* |
| P23 | M H Mesbah Ahmed | *Migration of subsurface defects in rutile TiO2 (110) observed by XPS following exposure to water at ambient pressure(AP-XPS)* |
| P24 | Markus Ammann | *Acid and reductive dissolution of Fe at the surface of ferrihydrite* |

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|---|---|---|
| P25 | Matteo Amati | *Effusive CELLs for near ambient pressure scanning photoemission imaging and spectromicroscopy at the submicron scale* |
| P26 | Mattia Scardamaglia | *Dynamics of 2D materials protection to oxidation of copper under operando condition* |
| P27 | Michael Hävecker | *ISISS, BElChem, and CAT@EMIL: The AP-XPS facilities dedicated to catalysis research at BESSY today and in the near future* |
| P28 | Muhammad Younas | *Performance study in steady state experiments and NAP-XPS at near steady state conditions during methane oxidation over Pd based catalysts* |
| P29 | Nicolò Comini | *Probing solid-liquid interfaces with tender X-rays* |
| P30 | Nikolay Vinogradov | *Scanning Probe Microscopy capabilities for MAX IV users* |
| P31 | Petra Reinke | *Oxidation of Ni-based binary and ternary superalloys: observing the competition between NiO and chromia formation* |
| P32 | Robert Temperton | *“Dip and Pull” AP-XPSmeasurements of battery interfaces* |
| P33 | Ryo Toyoshima | *AP-XPS study of catalytic CO oxidation over Pd–Au(111) surface* |
| P34 | Tamires Gallo | *Using APXPS to measure the spatial gas composition above a catalytic active surface in the mass transfer limit* |
| P35 | Tao Xu | *WO3promoted thermal stability and reducibility of V2O5on anatase TiO2(101): anXPS study* |
| P36 | Tim Kratky | *In situ characterization of co-precipitated NiAlOx catalysts during CO2methanation* |
| P37 | Trey Diulus | *Surface Chemistry of 2-Propanoland O2Mixtures on SnO2(110) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy* |
| P38 | Virginia Boix | *Following the kinetics of confined catalysis under graphene with ambient pressure x-ray photoelectron spectroscopy* |
| P39 | Xiangrui Kong | *Reversible physisorbed and chemisorbed water on carboxylic salt surfaces at atmospheric conditions* |
| P40 | Yaw-Wen Yang | *Photoreduction of CO2with H2O on Cu2O/TiO2Heterojunction* |
| P41 | Yi Yu | *New Lab-based Ambient Pressure X-ray Photoelectron Spectroscopy for Liquid-Solid Studies in ShanghaiTech University* |
| P42 | Carlos Ostos | *Performance test of the new NAP-XPS system at the University of Antioquia, Colombia, during its application to CO oxidation study on high-quality thin film surfaces.* |

***P1*** ***Wednesday 11th 17h30-20h00***

# The IOS beamline at NSLS-II: Combined APXPS and APXAS to tackle the modern catalyst

Adrian Hunt[1], Ira Waluyo[1]

[1]National Synchrotron Light Source II, Brookhaven National Lab, Upton, NY USA

Chemical systems that underpin our modern society, such as catalysts and batteries, are complex. Understanding the redox and electrochemical processes that underpin the function of these systems is as challenging as it is important. APXPS has proven to be a vital and critical technique researchers may use to gain this understanding. At the IOS beamline at NSLS-II, APXPS is our core technique. Designed for quick switching to any energy between 250-2000 eV, IOS can access critical core levels of most of the catalytically-relevent parts of the periodic table, while allowing those catalysts to work in gas pressures ranging from UHV to 10 Torr (depending on the gas). We can provide complimentary information to APXPS using a high pressure-compatible X-ray fluorescence detector, so that one may measure APXAS spectra in partial fluorescence yield (PFY) mode. This technique is bulk-sensitive but charging-insensitive, making it viable for studying chemical systems, such as nanoparticles, that are mounted on non-conductive substrates. This is a class of material systems that is traditionally quite challenging for XPS. On a completely different front, the in situ capabilities of IOS have granted us insight into the carbon contamination of in-vacuum X-ray optics, an insidious problem plaguing soft X-ray beamlines that specialize in characterizing soft matter. However, IOS is not strictly limited to the soft X-ray regime; we can also access the tender X-ray regime; we have measured Ca 1s (~ 4000 eV), and the 2p edges of Pd and Mo, in APXAS mode. We can also reach the S 1s edge. The IOS beamline is a truly multipurpose instrument that can help researchers understand the inner workings of a wide variety of material systems, which is made possible by NSLS-II, one of the world's brightest synchrotrons.

***P2*** ***Wednesday 11th 17h30-20h00***

# The Surface Stability of Components for Extreme Ultraviolet Lithography in Reactive Environments

Alessandro Troglia[1], Roland Bliem[1]

[1]Advanced Research Centre for Nanolithography, Amsterdam, The Netherlands

Surfaces and their stability play a central role in the extreme ultraviolet (EUV) lithography process, the next generation of technology for printing structures with light of 13.5nm wavelength (corresponding to $E_{Photon}$=92 eV). The long-term performance of such a lithography device crucially depends on the surface properties and stability of various optical elements in the light path. The strong interaction of EUV light with matter requires fully reflector-based optics, based on precisely defined multilayer structures of low-absorption materials, such as Mo and Si. The resulting multilayer mirrors are usually capped by a protective layer, allowing for operation in reactive environments under the influence of high-intensity ionizing radiation. Similarly, the lithography mask, containing all the information to be printed, and the pellicle, an ultrathin protective layer for the mask, are exposed to reactive environments and require high surface stability.

The group for Materials and Surface Science for EUV Lithography focuses on understanding the elementary physical and chemical processes occurring at these surfaces in atmospheres relevant to nanolithography. Using near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS), we strive to identify the critical processes limiting the long-term performance and surface stability of essential components for EUV lithography, such as reflective multilayer structures and their protective coatings. Targeted exposures to reactive gases, ions, EUV radiation, and elevated temperatures allow us to identify crucial sources and pathways of degradation and to explore new compounds and materials concepts for future components designed to even better withstand the challenging conditions of EUV lithography. The combination with thin-film growth facilities allowing for in-vacuo transfer will open opportunities to explore the elementary interactions of mirror structures, their capping layers, and the base materials for pellicles and lithography masks with well-defined gas environments as a function of film thickness, composition, and growth conditions. Moreover, we investigate the effects of exposure to EUV light on the stability of materials in relevant gas environments: the high energy and ionizing nature of EUV radiation opens a variety of new chemical reaction pathways that need to be thoroughly investigated.

***P3*** ***Wednesday 11th 17h30-20h00***

# APXPS and in-situ Raman study of S promotion on Ag catalysts.

A.Yu. Klyushin[1,2], E. Carbonio[1,2], T. Jones[2], M. Lamoth[2], L. Zwiener[2], E. Frei[2],
M. Hävecker[3], A. Knop-Gericke[2,3], R. Schlögl[1,2,3]

[1]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany, [2]Fritz Haber Institute of the Max Planck Society, Berlin, Germany, [3] Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany

Heterogeneous catalysis is an important part of the chemical technology that is responsible for the production of the materials and fuels that drive modern society. Shortly after the discovery of the first catalytic processes, it was realized that catalyst performance can be enhanced by adding very small concentrations of additional elements; known as promoters. Empirical evidence of promotion in catalytic reactions is abundant in the literature; however, detailed mechanistic information is rarely available because of experimental limitations in determining the electronic and structural modifications that occur on the catalyst [1].

In the present work, we study the promotional effect of sulphur on silver catalyst in the ethylene epoxidation. This selective oxidation reaction is very attractive due to the economic importance of ethylene oxide as a versatile chemical intermediate. To shed light into the structure of sulphur promoters, we use a state-of-the-art in situ surface characterization technique to correlate the modifications at the silver catalyst surface induced by sulphur with the catalytic performance measured at the same time.

The catalysts were self-supported, alumina-supported silver powders and silver foil, which allow bridging a 'material' gap. In-situ XPS of the Ag catalyst under ethylene epoxidation was performed using the near ambient pressure endstation at Helmholtz-Zentrum Berlin. To prove a relevance of obtained results to industrial process in-situ Raman characterization was done at 1 bar mimicking NAP-XPS conditions. In addition, Quantum ESPRESSO40 was used for DFT calculations at the Perdew, Burke, and Ernzerhof level.

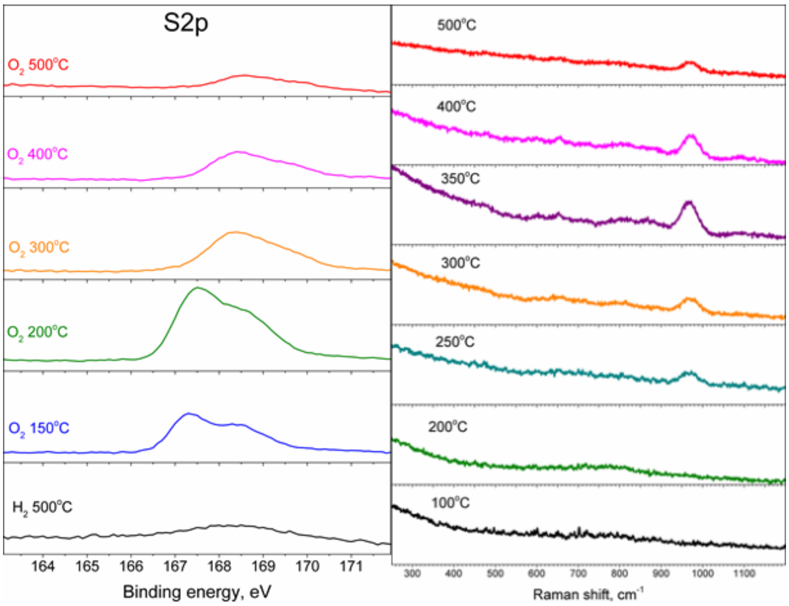

Figure 1. S2p XP spectra in 1 mbar of $O_2$ (left panel) and Raman spectra in 2% of $O_2$ in He (right panel) of Ag foil at different temperatures.

[1] T.W. Hansen, et al. Science, 294 (2001) 1508.

**P4** **Wednesday 11th 17h30-20h00**

# Operando characterisation of oxide-supported bimetallic methane oxidation catalysts

Alexander Large[1,2,3], Georg Held[1,2], Tugce Eralp-Erden[3], Roger Bennett[1] and Federica Venturini[2]

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Natural gas engines have received a lot of attention over recent years, as a cleaner alternative to traditional combustion engines. Whilst they are certainly beneficial in terms of carbon dioxide and particulate emissions, quantities of unburnt methane may be released, and so exhaust catalysts are required to convert this unburnt methane to less harmful products.

Near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) is a technique which provides quantitative chemical analysis of surfaces in gaseous conditions, bridging the "pressure gap" between traditional atmospheric pressure activity studies and ultra-high vacuum surface science studies. A range of alumina-supported monometallic and bimetallic catalysts have been prepared with total PGM loadings of up to 5 wt. %. Initial activity testing results showed that Pd catalysts outperformed Pd-Pt and Pt catalysts in oxygen rich and lean mixtures under dry conditions (see Fig. 1a). Pd catalysts showed strong deactivation in water, though this effect was decreased with the addition of Pt. It is also clear that increased oxygen concentration increases methane activation over Pd catalysts, whilst having the opposite effect on Pt catalysts. The lower activity of Pt catalysts can be attributed to the higher particle dispersion and smaller particle sizes, which were observed by CO chemisorption and TEM respectively. The smaller particles cannot activate methane as readily, and Pt suffers from strong oxygen adsorption compared to Pd. A range of catalysts have been studied using NAP-XPS, under both dry and wet conditions, to aid understanding of the activity differences and water deactivation. There is a clear difference in the ratio of Pd(0):Pd(II) (an example is given in Fig. 1b) at full conversion under dry and wet conditions, and further experiments will be performed to understand the effect that the Pd:Pt ratio has on this behaviour. Strong particle size effects were noted in previous work by this group[1], and to investigate this further model catalysts will be prepared with well-defined particle sizes.

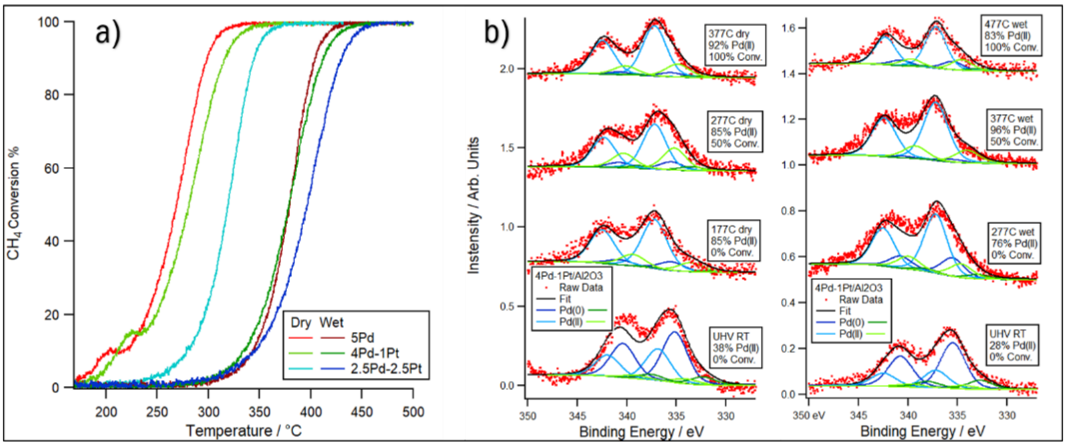

Figure 1 - Methane oxidation activity curves for various alumina-supported catalysts, under dry (methane & oxygen) and wet (methane, oxygen & water) conditions; (b) NAP-XPS data for a 4 wt.% Pd + 1 wt.% Pt on alumina catalyst under dry and wet conditions at various temperatures.

[1] R. Price, *et al.*, Top. Catal. **59**, 516-525 (2016).

**P5** **Wednesday 11th 17h30-20h00**

# Bimetallic nanoparticles reorganize differently on nanoshaped ceria: An operando ambient pressure XPS study

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The importance of nanoshaped supports has gained interest in heterogeneous catalysis since it provides a practical way to prepare novel catalysts with metal particles supported over oxide support crystallites exhibiting well-defined crystallographic planes. The role of the nanoshaped ceria support has been attributed mainly to oxygen vacancy facility formation, activation of reactants, preferential adsorption/desorption and migration of adsorbed species to the metal nanoparticles [1]. Here we provide direct evidence that the nanoshape of the support also determines the atomic reorganization and oxidation states of the metal nanoparticles under reaction conditions. To this end, we have used operando near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) using synchrotron radiation. We have studied three types of nanoshaped ceria, polycrystals, nanocubes and nanorods, and loaded them with exactly the same amount of preformed $Rh_{0.5}Pd_{0.5}$ model alloy nanoparticles with uniform size. In this way, the same number of contact points between ceria and the nanoparticles is guaranteed as well as exposed metal surface area. The reaction chosen has been the steam reforming of ethanol (ESR) aimed at producing hydrogen, $CH_3CH_2OH+3H_2O \rightarrow 6\ H_2 + 2\ CO_2$. Significant differences in the distribution of the reaction products and XP spectra are evidenced when comparing $RhPd/CeO_2$ with different nanoshapes [2,3].

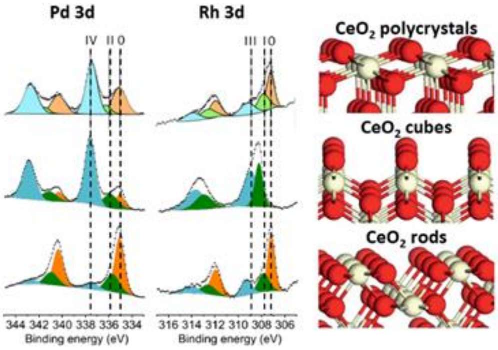

**Figure 1.** Pd 3d and Rh 3d XP spectra of $Rh_{0.5}Pd_{0.5}$ model nanoparticles supported on ceria polycrystals, cubes and rods recorded at 670 eV under 0.05 mbar of an ethanol-water mixture at 550 °C (ESR conditions).

[1] Trovarelli, A., Llorca, J. ACS Catal. 7, 4716 (2017).

[2] Divins, N.J., Angurell, I., Escudero, C., Pérez, V., Llorca, J. Science 346, 620 (2014).

[3] Soler, L., Casanovas, A., Ryan, J., Angurell, I., Escudero, C., Pérez, V., Llorca, J. ACS Catal. 9, 3641 (2019).

**P6** ***Wednesday 11th 17h30-20h00***

# In-situ study of PdZn and PdCuZn catalysts for $CO_2$ hydrogenation by Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS)

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An efficient conversion of $CO_2$ to useful low molecular-weight chemicals is an important research topic with a benefit of reducing global $CO_2$ concentration. Pd-Zn and Pd-Cu-Zn nanoparticles have been demonstrated as the potential catalysts for $CO_2$ hydrogenation. In this report, we study the PdZn and PdCuZn catalysts for $CO_2$ hydrogenation by APXPS. The PdZn and PdCuZn nanoparticles were prepared by the impregnation method using β-SiC pellets as support, and the crystallinity and particle size distribution were confirmed by X-ray diffraction and transmission electron microscopy. The surface evolution of catalytic solid was investigated in the $CO_2$ hydrogenation at the pressure of 0.5 mbar with a mixing gas by $CO_2$ and $H_2$ (1:3), and the reaction temperature was from room tempature to 573 K via APXPS at TLS BL24A. The results show that palladium oxide slightly decreased, and Zn metal was enhanced after 423 K for PdZn nanoparticles. On the other hand, palladium and palladium oxide dramatically decreased at 423K, and the surface of the trimetallic catalyst is composed mainly of Pd-Cu-Zn alloy at 573K for PdCuZn nanoparticles. This difference in surface composition for PdCuZn nanoparticles led to less carbon monoxide formation compared to PdZn catalyst. These results are consisted with the catalyst activity tests via GC-MS. The more detail will be discussed in this report.

**P7** **Wednesday 11th 17h30-20h00**

# Single-site $Fe_1$ atoms anchored on Pt(111) and $Cu_2O(100)$ for CO oxidation

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In recent years, single-atom catalysts(SACs) are supposed to bridge the homogeneous and heterogeneous catalysis due to the isolated metal atoms anchored on a support, and exhibit very unique catalytic activity as well as high selectivity in many reactions.[1] However, despite different classes of investigations on SACs, there are still considerable debate regarding the active centers and the nature of active sites in reactions for supported SACs. For instance, some studies demonstrated that the supported single atoms are the active sites for promoted CO oxidation, but some researchers attributed this reactivity to metal clusters or nanoparticles.[2] Although SAC is a very simple model to study reaction mechanism, the role from the complicated support of metal or metal oxide nanoparticles can not be ignored either. These differences in support may be from the surface reconstruction, different exposed facets for nanoparticles, the metal–support perimeters and surface defects. In addition to synthesis of single atom, the in-situ observation of active sites evolution in presence of reaction gas is also essential to understand reactions.

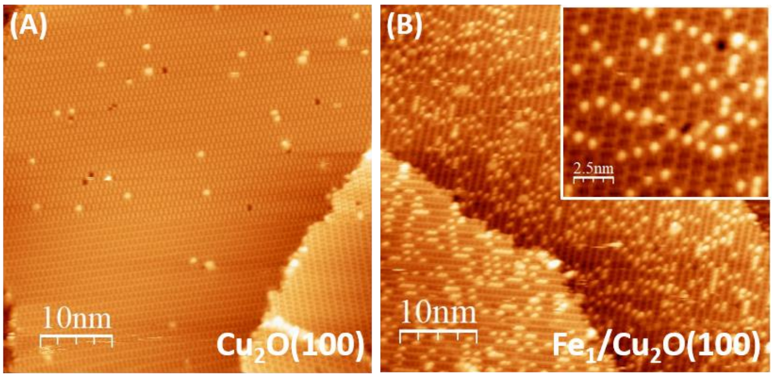

**Figure 1**. STM images of (A)clean $Cu_2O(100)$ surface and (B) with single-atom irons.

Due to the complexity of a real catalyst, one of the idea is to study the single-atom catalysts in model system under UHV, where a well-defined single crystal with isolated metal atoms on the surface is investigated by STM and other surface techniques. Thus, here We have successfully grown single-atom iron catalysts supported on Pt(111) and $Cu_2O(100)$ by means of a novel atomic layer deposition method using $FeCp_2$ and $O_2$ as precursors. In Figure 1 the isolated nature of the iron atoms on $Cu_2O(100)$ crystal was demonstrated by scanning tunneling microscopy (STM). In addition, the CO oxidation was investigated by in-situ ambient pressure XPS.

## Reference

(1) Cao, L.; Liu, W.; Luo, Q.; Yin, R.; Wang, B.; Weissenrieder, J.; Soldemo, M.; Yan, H.; Lin, Y.; Sun, Z., Atomically dispersed iron hydroxide anchored on Pt for preferential oxidation of CO in $H_2$. *Nature* **2019**, 565, 631.
(2) Sykes, E. C. H., Catalytic sites are finally in sight. *Nat Mater* **2019**, 18, 663.

(3) Wang CL et al. High-density isolated $Fe_1$ atoms on $Cu_2O(100)$ surface. J. Phys. Chem. Lett (under review)

**P8** **Wednesday 11th 17h30-20h00**

# Percolation conduction in monolithic mixed early/late transition metal perovskites

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The mixed ionic electronic conductors of the perovskite structure $ABO_3$ offer tuning of the electrochemical properties through its versatile range of compositions at the A- (typically alkaline earth metals) and B-sites. The bonding environment of the $BO_6$ building blocks, where B is typically a 3d transition metal (TM), has shown to be crucial for electrocatalytic activity towards oxygen exchange including charge and mass transport across the solid/gas interface at high temperatures. This activity governs the utility for solid state electrochemical devices such as solid oxide electrochemical cells and oxygen separation membranes (OSM). It has thus been an aim of solid state chemistry to identify A- and B-site compositions that offer favourable electronic structure for electron transfer from the oxide to the gas adsorbates, facile electronic or ionic conduction as well as reasonable thermochemical stability at high temperature operating conditions in a single phase material.

In a recent work[2], we found that substituting the B-site of an exceptionally stable early 3d TM perovskite ($SrTiO_3$) with the late 3d TM Co did not only yield an OSM of acceptable performance, but also enabled us to rationally identify the substitution level at which an ideal compromise of stability and activity is achieved: by using (*in situ*) X-Ray absorption and resonant photoemission spectroscopy we found that a percolating network of $CoO_6$-octahedra is necessary to facilitate conduction along the Co-O bonds, while charge carriers are trapped in isolated $CoO_6$ manifolds below the percolation threshold. These insights potentially open strategies for creating monolithic percolation materials, where different functionalities are designed in a single-phase material.

[1] Mueller, D. N., Machala, M. L., Bluhm, H. & Chueh, W. C., *Nat. Commun*. **6**, 6097 (2015).

[2] Liu, Y., Baumann, S., Schulze-Küppers, F., Mueller, D. N. & Guillon, O., *J. Eur. Ceram. Soc.* **38**, 5058–5066 (2018).

***P9*** ***Wednesday 11th 17h30-20h00***

# Watching Paint Dry with NAP XPS

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Understanding conservation issues of modern and contemporary works-of-art benefits from a multi-analytical interdisciplinary approach probing materials across length scales with options for *in situ* analysis under environmental control. Materials in museum collections face unique circumstances. They are required to perform longer than their typical lifespan and, in contemporary art, often in applications for which they were not envisaged. Using artists' paints and pigments as a case study, we show how NAP XPS with the SPECS EnviroESCA can be used to probe the chemistry of pigments and additives in response to environmental conditions such as humidity and temperature providing complementary information to more commonly used analytical techniques in this context.

**P10 Wednesday 11th 17h30-20h00**

# Having your cake and eating it too with NAP XPS of food

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There are endless aspects of biological materials such as foods which benefit from elemental analysis. It can provide an indicator of nutritional composition, the presence of environmental contaminants, correlations between biochemistry and shelf-life as well as the impact of industrial processing. With NAP XPS, the elemental composition can be probed virtually *in situ* by maintaining foods closer to their native, often hydrated, state. We present some recent examples of experiments in the SPECS EnviroESCA which hopefully give XPS specialists food for thought about new ways in which XPS can be used to understand these materials. Apples are one interesting case study showing how the water in the sample which is otherwise an annoyance in a UHV system can be repurposed for charge neutralisation in a NAP XPS instrument. Furthermore, one can probe the chemical fingerprint of browning in apples, identify the presence of anti-browning agents and investigate the complex chemistry of waxy surface of apple peels to distinguish garden apples from store-bought ones.

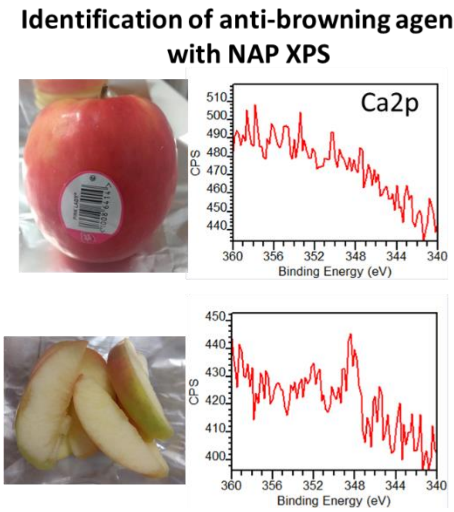
**Identification of anti-browning agents with NAP XPS**

Figure 1 Ca2p NAP XPS spectra of pre-sliced vs whole apple.

**P11** **Wednesday 11th 17h30-20h00**

# The APXPS branch of the SPECIES beamline at MAX IV

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The SPECIES beamline [1] at MAX IV Laboratory has an APXPS branch, which was transferred together with the beamline from the MAX-II storage ring to the current 1.5 GeV storage ring. The APXPS branch houses an endstation dedicated for a wide variety of experiments in the ambient pressure regime. The endstation includes a commercial SPECS analyser with a MAX IV developed AP cell. The cell is capable of pressures up to 20 mbar. Heating of the sample stage is achieved using a resistive heater which can heat up to approximately 600 °C. The endstation accommodates several cell designs for *in-operando* and *in-situ* studies: in the near-future users will have access to cells dedicated for different purposes, such as catalysis, redox chemistry, thin film growth, electrochemistry, and others.

The endstation also has typical UHV preparation tools. Sputtering and annealing is possible under UHV conditions. There are also user ports available for different types of sample preparation.

The SPECIES beamline delivers photons in the wide range from 30 eV to 1500 eV. The optical design is based on a collimated plane grating monochromator. The beamline can deliver high resolution and high flux. The synchrotron beam is delivered into the cell via a window, which can changed according to the user's needs. Both aluminium and silicon nitride windows are available. The APXPS branch at the SPECIES beamline is in general user operation in spring 2020.

[1] S. Urpelainen *et al.* "The SPECIES beamline at the MAX IV Laboratory: a facility for soft X-ray RIXS and APXPS", *Journal of Synchrotron Radiation*, **24(1)**, 344-353, (2017)

**P12** **Wednesday 11th 17h30-20h00**

# Stabilization and reactivity of a dense carbon monoxide layer on Pt(111) under a mixed boron nitride-graphene cover

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The confined space between a catalyst surface and a 2D overlayer ("cover") can be exploited for enhancing catalytic processes or performing new chemical reactions [1]. The cover can act as a barrier that confines the molecules during the reaction, it can enhance the catalytic properties of the substrate, but it can also take part in the reaction in an active way.

Although studies have been reported for molecule–catalyst interaction under pure graphene or hexagonal boron nitride (*h*-BN) [2], mixed 2D covers, such as in-plane *h*-BN–graphene (*h*-BNG) heterostructures can reveal peculiar properties. Recently we have demonstrated that this van-der-Waals layer can be easily grown on Pt(111) single crystal [3], but also on different metal foils (Pt, Ni, Fe) from a single molecular precursor [4]. Here we will present the under-cover stabilization and reactivity of the intercalated carbon monoxide molecules with the almost free standing *h*-BNG 2D layer on a Pt(111) as a model case system [5].

A densely-packed CO layer could be stabilized under the 2D cover. This result allows using standard surface science techniques to characterize such structure normally unstable under ultra-high-vacuum conditions at room temperature. The experimental results provided an evidence that the cover acted as an effective barrier confining CO since a large amount of CO found to be chemisorbed on the Pt surface under h-BNG at temperatures much higher than those of bare Pt(111). Furthermore, repeated cycles of CO intercalation and thermal desorption revealed that CO reacted with the *h*–BNG cover, at an elevated temperature, at the ternary boron nitride–graphene–platinum interface. Part of the intercalated CO molecules dissociated and the atomic oxygen reacted with boron atoms.

This research demonstrates that mixed 2D covers, such as in-plane graphene and hexagonal boron nitride heterostructure, can act not only as an effective barrier to confine gas molecules in a 2D interface, but can also significantly modulate the catalytic performance of the solid substrates underneath.

[1] P. Sutter et al. *J. Am. Chem. Soc.* 132, 23, 8175-8179 (2010); H. Zhang et al. *J. Phys. Chem. C* 113,19, 8296-8301 (2009); R. Mu et al. *Angewandte Chemie International Edition*, *51* (20), 4856-4859 (2012).

[2] H. Li, et al. Confined catalysis under two-dimensional materials. *Proceedings of the National Academy of Sciences 114* (23), 5930-5934 (2017).

[3] S. Nappini et al. *Advanced Functional Materials* 26, 7,1120-1126 (2016)

[4] S. Nappini et al. *Applied Surface Science* 479, 15 903-913 (2019)
[5] I. Píš et al. *Chem. Sci.*, 10, 1857-1865 (2019)

**P13** **Wednesday 11th 17h30-20h00**

# VerSoX: a versatile Soft X-ray beamline at Diamond Light Source

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VerSox is a Diamond Light Source bending magnet beamline that investigates the chemical nature and composition of surfaces and interfaces. The available techniques are soft X-ray photoelectron spectroscopy (XPS) and Near Edge X-ray Absorption Spectroscopy (NEXAFS) in pressure ranges that can vary from UHV to less standard Near Ambient Pressure (NAP) conditions. The beamline is able to cover a diverse range of scientific areas including heterogeneous catalysis, pharmaceuticals and biomaterials, environmental and space science studies on liquids and ices, heritage conservation, and the study of electronic and photonic materials.

***P14*** ***Wednesday 11th 17h30-20h00***

# Bridging the material gap: An *in-situ* spectroscopic study of the surface reactions for industrial selective catalytic reduction (SCR) catalysts.

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The Selective Catalytic Reduction (SCR) of nitrogen oxides converts the toxic $NO_x$ compounds into harmless nitrogen and water ($4NO + 4NH_3 + O_2 \rightarrow 6H_2O + 4N_2$) [1-2]. The most common, industrially relevant catalysts are based on the $V_2O_5$/anatase-$TiO_2$ system. Even though it has been widely used, the nature of the active $V_xO_y$ catalyst ($V^{4+}$ or $V^{5+}$) under real reaction conditions remains unsolved. In addition, the presence and role of terminal V-OH groups in the catalytic cycle leading to formation of the $V^{4+}$ oxidation state and Brøndsted acid sites needs to be investigated in detail. From the onset in Figure 1, it is possible to see that the surface V species of the industrial 3%$V_2O_5$/a-$TiO_2$ catalyst goes through a chemical shift towards higher binding energy, when exposed to 1 mbar of air. This represents the $V^{5+}$ state corresponding to the $V_2O_5$ species of the surface. However, in UHV (before and after exposure to air) the surface V species seems to be reduced to the $V^{4+}$ state, corresponding to the less active $VO_2$ species. The results in Figure 1 were obtained using a model catalyst with $V_2O_5$ evaporated onto the surface of anatase $TiO_2$ (101) single crystal. It is known that the $NH^{4+}$ species adsorbs on the Brøndsted acid sites (V-OH) while the $NH_3$* species on the lower binding energy is associated with the adsorption on the Lewis acid sites (V=O). As temperature increases, a shift on the peak region corresponding to adsorbed $NH_4^+$ can be observed, while the $NH_3$* remains constant. Our results might suggest that the $NH_4^+$ adsorbed onto Brøndsted acid sites is the one favouring the reaction with NO via an Eley-Rideal mechanism. As we elucidate the reaction mechanism in the model catalyst it is possible to compare with the industrial catalysts building evidence to reduce the material gap and highlight the importance of APXPS and *operando* studies for the industry.

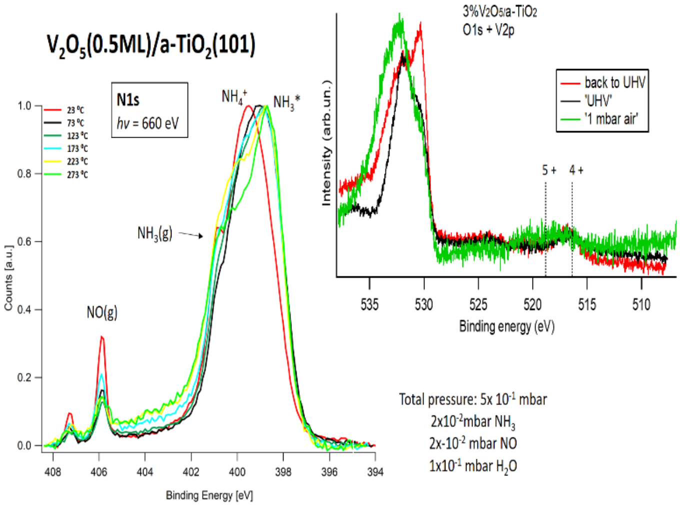

Figure 1 - N1s spectrum at $5x10^{-1}$ mbar pressure ($2x10^{-2}$ mbar of $NH_3$ and NO, $H_2O$) at different temperatures) onset: Figure 1 - O1s + V2p AP-XPS spectrum for the 3%V2O5/a-TiO2 catalyst at UHV, 1 mbar of air and back to UHV - unpublished results

[1] Janssens, V. W., *et al,* 2015. ACS Catalysis 2015 vol. 5, pp 2832-2845

[2] Rasmussen S.B., *et al,* 2018. Appl. Cat. B: Envir., vol. 224 pp 109-115.

**P15** **Wednesday 11th 17h30-20h00**

# Following the atomic layer deposition of $TiO_2$ on InAs(100) in real time by ambient pressure x-ray photoelectron spectroscopy

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Atomic layer deposition (ALD) is a thin film deposition technique for the creation of uniform and conformal layers on complex three-dimensional topographies. ALD is highly used in different fields of technology, e.g. in microelectronics and solar cell technology. In spite of the method's importance, the understanding of the surface chemical processes of ALD remains far from complete. A thorough investigation of the ALD surface chemistry for the identification and role of surface species, impurities and vapour phase reactions is much needed for the further enhancement of the technique [1].

We have applied ambient pressure x-ray photoelectron spectroscopy (APXPS) to the real-time study of ALD of $TiO_2$ on the native oxide-covered InAs(100) surface, using tetrakis(dimethylamido) titanium (TDMAT) and water as precursors. The measurements were performed with sub-second to second time resolution, as is illustrated in Fig. 1, which shows As3d spectra with the oxide signal at around 44.5 eV binding energy and the bulk As signal at around 41 eV. Here we can follow in detail how the native oxide is removed [2]. From the other spectral regions we can identify the surface chemical species during ALD: For example, the N 1s region (Fig. 2) lets us identify methyl methyleneimine, methyl methyleneamine and surface-bonded Ti-amido complex species.

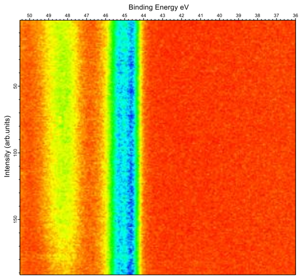

Fig. 1. As 3d spectra taken during the exposure of a native-oxide-covered InAs(100) surface to TDMAT at 70C.

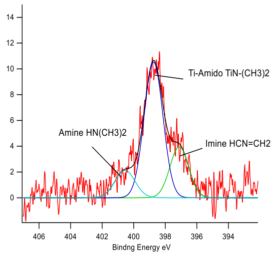

Fig. 2. N1s APXP spectrum from a N 1s time series (cf. Fig. 1), fitted with methyl methyleneimine, methyl methyleneamine Ti-amido complex components.

[1] F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013).

[2] R. Timm, A. R. Head, S. Yngman, J. V. Knutsson, M. Hjort, S. R. McKibbin, A. Troian, O. Persson, S. Urpelainen, J. Knudsen, J. Schnadt, A.Mikkelsen, Nature Commun. **9**, 1412 (2018).

***P16*** ***Wednesday 11th 17h30-20h00***

# The Oregon State University Ambient Pressure Surface Characterization Laboratory

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At Oregon State University we have developed the Ambient Pressure Surface Characterization Laboratory (APSCL, nnci.oregonstate.edu/apscl) which is part of the National Science Foundation – National Nanotechnology Coordinated Infrastructure (nnci.net) program. The core instrumentation for the APSCL is an Integrated SPECS ambient pressure X-ray photoelectron spectroscopy/ambient pressure scanning tunnelling microscopy system. Access to the equipment is available to external users through a fee based system and permanent staff are available to assist with data collection and analysis. For this presentation, two experimental studies will be reviewed. The first is the thermal oxidation of defective $MoS_2$ via water vapor. In this study, we demonstrate that defects in the $MoS_2$ surface are nucleation sites for the dissociation of water and the oxidation of Mo. The second is the thermal oxidation of 2-propanol by $SnO_2(110)$. In this study, we demonstrate the selective oxidation of 2-propanol to acetone at low $O_2$ partial pressures. Increasing the relative $O_2$ partial pressure results in the complete oxidation of 2-propanol at substantially lower temperatures.

***P17*** ***Wednesday 11th 17h30-20h00***

# Spectroscopic Insights into Liquid Metal Solutions for Catalysis

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Supported catalytically active liquid metal solutions (SCALMS) are deactivation resilient and highly active dehydrogenation catalysts for short alkanes, based on binary transition metal Gallium alloys. The remarkable properties of these catalysts, especially their good resiliency towards deactivation, are attested to the atomic dispersion of the active transition metal in liquid Gallium nano-droplets and the dynamics at the liquid metal/gas interface. The concept was pioneered at FAU and over the recent years we published findings on PdGa [1], PtGa [2] and most recently RhGa [3] alloys. Herein, we present XPS studies on macroscopic alloy droplets and model catalyst particles, including *in situ* heating and comparative near ambient pressure oxidation studies for Pd-, Pt- and RhGa alloys. In all cases transition metal enrichment at the surface is observed, the development during the oxidation however suggests that despite their similarity the chemical origin of the enrichment effects differ for the transition metals. For Platinum [4] and Rhodium we assume an incorporation of the transition metal into the oxide film, for Palladium the data points towards an enrichment at the Gallium/Gallium oxide interface. The results are supported by high resolution TEM and EDX results. Our obtained spectroscopic results were interpreted with the aid of DFT based molecular dynamics and theoretically obtained XPS shifts.

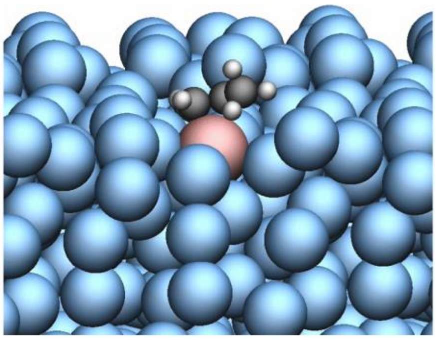

Figure 1: Snapshot from a molecular dynamics calculation showing a single transition metal atom bound to a propane molecule at the surface of a liquid gallium slab.

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**P18** **Wednesday 11th 17h30-20h00**

# Oxidation and Reduction of Cu(111) in the Presence of Single Pt Atoms

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The redox behavior of metal oxides, either as catalyst supports or as the active sites themselves, plays an important role in heterogeneous catalytic reactions. In many cases, the redox behavior of a metal oxide can be significantly affected by the presence of a dopant atom due to the introduction of additional active sites as well as new interfaces. In this talk, I will present recent results from the IOS (23-ID-2) beamline at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, in which we used AP-XPS to study the oxidation and reduction behavior of Cu(111) doped by single Pt atoms on the surface, initially forming a PtCu single-atom alloy. Complementary data from temperature-programmed desorption (TPD) experiments and results from density functional theory (DFT) calculations will also be presented. By probing the Pt 4f core level, we were able to clearly distinguish Pt atoms in different chemical and physical environments as well as monitor their evolution under oxidizing and reducing environments. XPS revealed that a mild oxidizing condition ($5 \times 10^{-6}$ Torr $O_2$ at 400 K) can result in the formation of a complete $Cu_2O$ thin film on the surface of the sample that covers the Pt atoms. TPD results show that the oxidized Pt/$Cu_2O$ surface is inert and the Pt atoms are inactive in $H_2$ dissociation. AP-XPS was used to monitor the evolution of the oxide O 1s peak in 1 Torr $H_2$ at room temperature, which revealed that the presence of a small amount of Pt, at the single atom limit, significantly accelerates the reduction of $Cu_2O$ by $H_2$, even when the Pt atoms are covered by an oxide layer. DFT calculations show that the presence of Pt atoms under the oxide layer weakens the Cu-O bonds in its immediate vicinity. This work highlights the role of the metal-oxide interface in heterogeneous catalysis in terms of its ability to influence the catalyst's ability to maintain a reduced state during a reaction.

**P19** **Wednesday 11th 17h30-20h00**

# A Closer Look at Direct Solar Water Splitting

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As the consequences of the climate crisis become ever more apparent, the need for renewable energy sources has become more urgent. To address the inherent variability of such sources, hydrogen is often touted as a potential energy carrier. The reasons for this are that hydrogen possesses a mass energy density 3-4 times higher than conventional fuels, such as petrol [1], and produces no carbon at its point of use [2].

Photoelectrochemical (solar) water splitting is a renewable and emission free technique that utilises a semiconducting electrode to generate electron/hole pairs, which catalyse the hydrogen/oxygen evolution reactions respectively. However, in order to become a viable process for hydrogen production, the semiconductor must possess several key attributes. These include, but are not limited to, a suitable band gap, good charge transport properties, fast reaction kinetics, and high stability in aqueous environments [3]. Unfortunately, no material has yet been discovered that meets these requirements simultaneously.

One promising photocatalyst, $TiSi_2$, has been little studied in the solar water splitting field. It has been found that it exhibits properties not typical of other semiconductors. For instance, the band gap of $TiSi_2$ ranges from 1.5 eV to 3.4 eV, allowing it to absorb a substantial amount of the solar spectrum [4]. However, the situation at the surface of $TiSi_2$ is complex due to its instability in water [4], which may or may not be advantageous. As a result, characterisation of $TiSi_2$ at ambient pressures of water vapour is vital to determine its' ability to split water.

Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) is uniquely positioned to study the surface of existing semiconductor catalysts, like $TiSi_2$, during water splitting. By using NAP-XPS, we gain a detailed description of how the surface of the photocatalyst changes under reaction conditions. As a result, new strategies for enhancing the efficiency of current catalysts could be found, and potentially inform the search for novel water splitting materials.

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**P20** **Wednesday 11th 17h30-20h00**

# In situ electrochemical APXPS analysis of ALD grown Cu catalyst for $CO_2$ reduction

Harri Ali-Löytty[1], Lauri Palmolahti[1], Markku Hannula[1], Jesse Saari[1], Kimmo Lahtonen[1], Hsin-Yi Wang[2], Markus Soldemo[2], Anders Nilsson[2] and Mika Valden[1]

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The grand challenge in artificial photosynthesis is to produce liquid solar fuels from water and carbon dioxide. Unfortunately, current materials solutions for a photocatalytic (PEC) solar fuel reactor lack efficiency, selectivity towards liquid fuel products, and long-term stability. Cu based catalysts are so far the most promising materials for the carbon dioxide reduction reaction ($CO_2RR$), whereas the selectivity of Cu catalyst towards liquid products is strongly affected by the exact chemical composition and structure. Recently, Eilert et al. suggested, based on in situ electrochemical APXPS measurements on Cu foil, that the high activity of oxide-derived copper towards $CO_2RR$ stems from subsurface oxygen that was proposed to increase the CO binding energy and thus enhance the production of methanol and multicarbon products [1]. This contradicts the alternative hypothesis that assigns the activity to $Cu_2O$ on the surface, albeit no copper oxide should be stable at reductive $CO_2RR$ conditions.
In this work, ALD grown Cu oxide thin film was analyzed in situ by electrochemical APXPS at the HIPPIE beamline, MAX IV Laboratory. The results, highlighted in Figure 1, show similar oxygen species on reduced ALD Cu oxide thin film to what was assigned to subsurface oxygen in Ref. [1]. Therefore, the ALD grown Cu oxide thin film is considered as a promising catalyst coating for photocathodes in PEC solar fuel reactors.

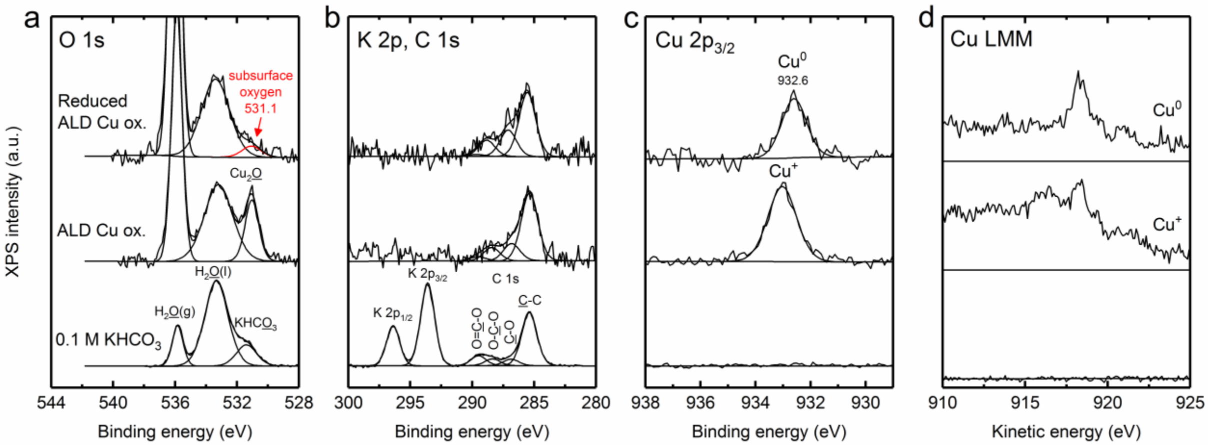

***Figure 1.*** *Oxide-derived ALD Cu electrocatalyst for $CO_2RR$ analyzed in situ by EC-APXPS. In the experiment, ALD Cu oxide thin film was electrochemically reduced in 0.1 M $KHCO_3$ inside the APXPS vacuum chamber. XPS spectra were recorded for a thick layer of 0.1 M $KHCO_3$ (bottom), for the ALD Cu oxide thin film before (middle) and after (top) electrochemical reduction. Spectral regions for a) O 1s, b) K 2p, C 1s, c) Cu $2p_{3/2}$ and d) Cu LMM transitions were recorded under equilibrium water vapor pressure of 22 mbar using 1600 eV as the excitation energy. Cu $2p_{3/2}$, Cu LMM, and K 2p spectra evidence that there is neither oxidized Cu species nor $KHCO_3$ on reduced ALD Cu oxide.*

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**P21** **Wednesday 11th 17h30-20h00**

# The Oxidation of Aluminum at Room Temperature Studied by NAP-XPS

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Fundamental understanding of the oxidation process in metals has received considerable attention during the past 50 years. This on account of the extended use and important role of thin oxides in many electronic and chemical industries. Both theoretical and experimental approaches have been used to address questions related to the mechanism behind the reaction, the oxidation kinetics and the oxygen adsorbed species, especially during the initial growth (thin film regime). Experimental studies involving the most common surface techniques (ISS, AES, UPS and XPS[1]) have been particularly devoted to aluminum among many metals due to its simple but versatile electronic structure, making it a prototypical process when discussing the Cabrera-Mott model[2]. In many cases, a prime focus has been put on the measurement of the work function due to information that can be obtained on the nature of the chemisorption sites[3]. Although the initial oxidation steps have long remained a controversial subject, many authors agree on the fact that low pressure interaction of oxygen with the aluminum surface results in a decrease of the work function, ascribed to a very fast oxygen uptake and incorporation into the subsurface region[4-6].

In the present work we show our results about the NAP-XPS study of the oxidation of the Al(111) surface. The Al2p, O1s and the secondary electron energy distribution curve related to the work function were measured as the clean surface was exposed to dry oxygen at room temperature under $O_2$ pressure ranges from $10^{-6}$ to 1 mbar. The results are compared to our previous study of the Si(111)-7×7 surface oxidation. This will help to illustrate two clearly different cases involved in the discussion of metal oxidation models.

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**P22** **Wednesday 11th 17h30-20h00**

# Boosted design and study of nanomaterials by HPXPS

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Unique features of nanomaterials make attractive in various fields such as energy conversion/storage, environment, biosensors, catalysis and nanoelectronics [1-6]. The future development prospects and challenges in the new materials can be boosted by high pressure X-ray spectroscopy (HPXPS).

Innovative and compact HPXPS platform will be presented, in order to permit design and characterization of nanomaterials in the UHV and high pressure (HP) conditions. We will report some results using HPXPS technique.

Also we will introduce EA15 HP1 and EA15 HP50 electron analysers, based on high end technology, offering a high quality and stable UHV and HP performance. The compact construction allows the connection of different techniques at versatile configurations as well as the incorporation of IR and other analysis techniques. As the platform can be used to atomic layer deposition on substrate at the different temperatures and pressures.

The HPXPS platform can be operated in the multimode by SPECTRIUM software, which can offer fully automated processes. Main features of the software will be presented.

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**P23** **Wednesday 11th 17h30-20h00**

# Migration of subsurface defects in rutile $TiO_2$ (110) observed by XPS following exposure to water at ambient pressure (AP-XPS)

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Water adsorption on reduced rutile $TiO_2$ (110) single crystal surface and afterward annealing were carried out using a near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS). In this experiment, 100% relative humidity (RH) water was exposed on highly defective single crystal rutile $TiO_2$ (110) and monitored in-situ with AP-XPS and studied the quantitative change of $Ti^{4+}$, $Ti^{3+}$, $Ti^{2+}$, and $Ti^{1+}$ intermediate oxidation states during annealing in UHV. Reduced rutile $TiO_2$ (110) surface was prepared by Argon ion bombardment. XPS measurements confirm that Argon ion sputtering causes surface and subsurface defects in rutile $TiO_2$ (110). These defects play an important role as water dissociation sites. Exposure to water at ambient pressure heals the defects in the surface [1]. O 1*s* spectra confirms the presence of OH group and adsorbed $H_2O$. Figure 1 provides information about the change of defective states as a function of the number of scans and temperature during annealing. This map shows that the Ti 2*p* spectra kept broadening up to scan 5 and after that started to shrink at lower binding energy. This process continued until ended up with clean stoichiometric rutile $TiO_2$ (110). This implies that the concentration of oxygen vacancy defects increase initially demonstrating the migration of defective sites from subsurface to surface and then all intermediate oxidation states ($Ti^{3+}$, $Ti^{2+}$, and $Ti^{1+}$) transformed into $Ti^{4+}$. Defects have a tendency to migrate from higher concentration to lower concentration (concentration gradient). In addition, according to published research, the presence of small quantities water vapor increase the diffusivity of oxygen vacancies [2]. Maybe this is the reason for $Ti^{3+}$ to a lesser extent $Ti^{2+}$ defects migration from subsurface to water healed surface. These surface migrated defects healed by adsorbed water and hydroxide group and residual water in the vacuum and transformed into $Ti^{4+}$.

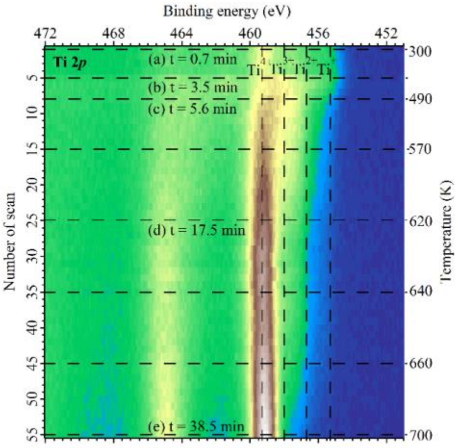

Figure 1 In situ XPS measurements of Ti 2*p* spectra during annealing of water exposed rutile $TiO_2$ (110)

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**P24** **Wednesday 11th 17h30-20h00**

# Acid and reductive dissolution of Fe at the surface of ferrihydrite

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Ferrihydrite is a metastable form of iron (Fe) (III) oxy-hydroxide that exists as nanoaggregate loosely crystalline particles [1,2]. Due to its porous nanostructure, ferrihydrite has a high specific surface area [1] and offers a high number of accessible sites for adsorption and reaction. It is also considered to be the main source of bio-available Fe and thus has a huge impact on ocean fertilization [2], which is implicated in many aspects of biogeochemistry and climate. Natural ferrihydrite mainly occurs in mineral dust particles emitted from arid and desert regions such as the Sahara. Because ocean water has a pH above 7, dissolution of Fe out of mineral dust is rather slow after deposition to the ocean. Therefore, processing of mineral dust in the atmosphere by inorganic and organic species, including acids, is a major pathway of dissolution of Fe ions from iron oxide minerals and thus for the provision of Fe ions to the ocean. In the present work we have investigated the interaction of ascorbic acid, acetic acid and citric acid with ferrihydrite powders at ambient relative humidity using ambient pressure XPS and electron yield NEXAFS at the Fe L-edge. While Fe(III) bound in ferrihydrite is stable, hydration of Fe(III) at the surface, presumably by forming Fe(III)-OH complexes, also leads to fast X-ray induced reduction to Fe(II), even under minimum X-ray exposure amenable to a useful spectroscopic analysis. Nevertheless it allows to monitor the dissolution of Fe at the surface of ferrihydrite via the change in oxidation state. The results demonstrate that already the exposure to gas phase water vapor at 60%RH leads to detectable changes at the Fe L-edge, which become even stronger at 90% RH. Furthermore, dissolution is observed in the presence of gas phase acetic acid at $10^{-2}$ mbar. When ascorbic acid was mixed with ferrihydrite, this dissolution is enhanced via direct reduction of Fe(III) in ferrihydrite to Fe (II) in solution due to its electrochemical reduction potential. In contrast, citric acid forms very strong carboxylate complexes with Fe(III) (which are highly photosensitive, even to visible light) and enhances dissolution that way. The direct reduction by ascorbic acid and non-reductive nature of citric acid assisted dissolution have been confirmed by experiments with bulk solutions in a liquid jet, where X-ray induced reduction of aqueous Fe(III) could be avoided.

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***P25*** ***Wednesday 11th 17h30-20h00***

# Effusive CELLs for near ambient pressure scanning photoemission imaging and spectromicroscopy at the submicron scale

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The authors have developed photoemission imaging and spectromicroscopy methodology based on the Scanning PhotoEmission Microscope (SPEM) to simultaneously overcome the two limitations of the XPS technique, i.e. lack of spatial resolution and UHV requirements [1]. Those solutions allow chemical and morphological analysis, providing sub micrometric information under operation conditions.

SPEM (figure) uses a direct approach to add the spatial resolution to XPS, i.e a small focused X-ray photon probe to illuminate the sample. The focusing of the X-ray beam is performed by Zone Plates lenses and samples surface is mapped by scanning the sample respect to the focused beam. X-ray beam can be downsized to a diameter of 130 nm, allowing imaging resolution of less than 50 nm with an energy resolution of 200 meV.

To overcome the UHV requirement effusive cells (figure) where high- and low-pressure regions are separated by small apertures of few hundreds micrometers, for photons delivery and photoelectrons collection, were developed. The pressure inside the cell can be raised up to the mbar regime while the pressure in the main chamber remain in high vacuum. Four isolated electrical connections are available for heating and biasing of sample.

The performances of the different effusive cell setups available for the users at the Escamicroscopy beamline@ Elettra synchrotron, like the different pressure range, the different obtainable field of view available for the spectromicroscopy measurements, and the electrical different electrical bias configurations, will be presented and discussed. In particular the differences between a cell with two pin holes [2], one for the photons and the other for electrons (figure), or with only one for both [1], will be highlighted.

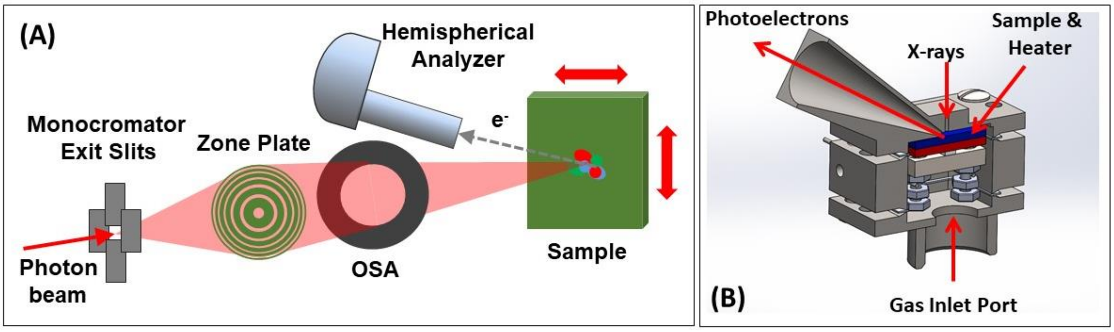

Figure: (A) SPEM Layout; (B) Effusive Cell for APXPS spectromicroscopy

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**P26** **Wednesday 11th 17h30-20h00**

# Dynamics of 2D materials protection to oxidation of copper under operando condition

Mattia Scardamaglia[1], Claudia Struzzi[1], Virginia Boix[1], Giulio D'Acunto[1], Alexey Zakharov[1], Jan Knudsen[1], Nicolas Reckinger[2], Xin Chen[3], Abhay Shivayogimath[3], Tim Booth[3], Patrick Zeller[4], Matteo Amati[4], Luca Gregoratti[4]

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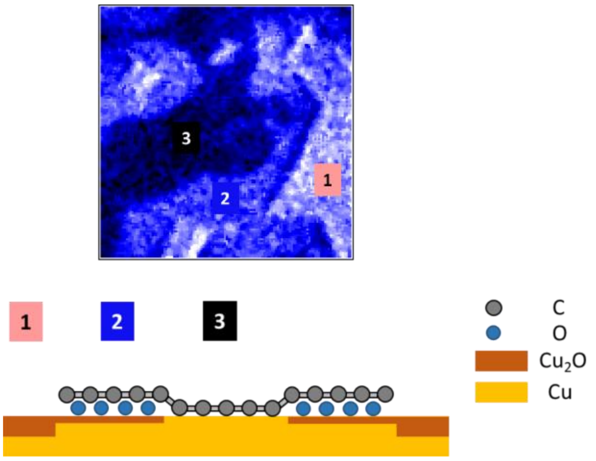

*(top) 38x38 µm² O 1s photoemission intensity map of graphene/Cu foil at 350 °C. (bottom) Sketch representation of the oxygen intercalation and graphene lifting from Cu substrate.*

The recent development of ambient pressure XPS makes accessible operando investigation of many phenomena otherwise impossible [1]. The prevention of metal corrosion is of extreme technological importance; therefore, the investigation of the protective action of 2D materials must be carefully assessed [2]. We performed ambient pressure XPS in situ experiments on copper coated by graphene and hexagonal boron nitride, in oxidation conditions ($O_2$ atmosphere). To understand the evolution of copper oxidation and the role of graphene, we investigated regions with bare copper, mono- and multi-layers graphene flakes, by using the near ambient pressure scanning photoemission microscope available at ESCAMICROSCOPY beamline (ELETTRA) [3]. Three temperature regimes were identified: (i) up to 300 °C, the amorphous carbon desorbs and the Cu under graphene remains metallic, while the bare Cu regions readily oxidized; (ii) in a short temperature range up to 360 °C, the oxygen starts to intercalate from graphene edges or defects and slightly oxidized the Cu underneath (Figure 1); (iii) at T higher than 360 °C the carbon is etched away. At HIPPIE beamline (MAX IV), we compared Cu, graphene and hBN through AP-XPS up to 5 mbar in $O_2$ atmosphere. We identified different protection thresholds, with graphene being able to protect the copper up to higher temperature with respect to hBN. These in situ experiments clearly highlight the role of 2D materials as protecting layers of copper from oxidation.

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**P27** **Wednesday 11th 17h30-20h00**

# *ISISS*, *BElChem*, and *CAT@EMIL*: The AP-XPS facilities dedicated to catalysis research at BESSY today and in the near future

Hävecker Michael[1,2], Stotz Eugen[1], Hendel Stefan[3], Koch Gregor[1], Gorgoi Mihaela[3], Trunschke Annette[1], Knop-Gericke Axel[1,2], Schlögl Robert[1,2]

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The ultimate surface and element sensitivity on the one hand and the possibility to vary the information depth on the other hand adds an extra quality to ambient pressure XPS (AP-XPS) when operated with tuneable X-ray sources like a synchrotron. The Helmholtz-Zentrum Berlin (HZB) and the FHI/MPI-CEC operate three facilities dedicated to synchrotron based AP-XPS at BESSY. These facilities are: ISISS (*Innovative Station for In Situ Spectroscopy*), BElChem (*Berlin Joint Lab for ElectroChemical Interfaces*) and CAT@EMIL (*Energy Materials In Situ Laboratory Berlin*). These laboratories combine in a unique way state of the art X-ray beamlines, ambient pressure XPS endstations, and a sophisticated, permanent infrastructure on site for experiments with a chemical background. The beamlines offer a high photon flux (up to $10^{12}$ photons/sec/0.1A ring current) and a broad energy range as shown as Figure 1. All stations are equipped with AP-XPS spectrometer designed following the same, standardised modular instrument concept. Typical methodologies like in situ secondary electron cut-off measurements to determine the work function of a material, temperature programmed XPS, and depth profiling via variation of the kinetic energy of the photoelectrons will be discussed to exemplify the characteristic of the ISISS, BElChem and CAT facilities. Finally, an outlook on future activities at these facilities like extending the available photon energy to the tender X-ray regime at CAT@EMIL will be presented.

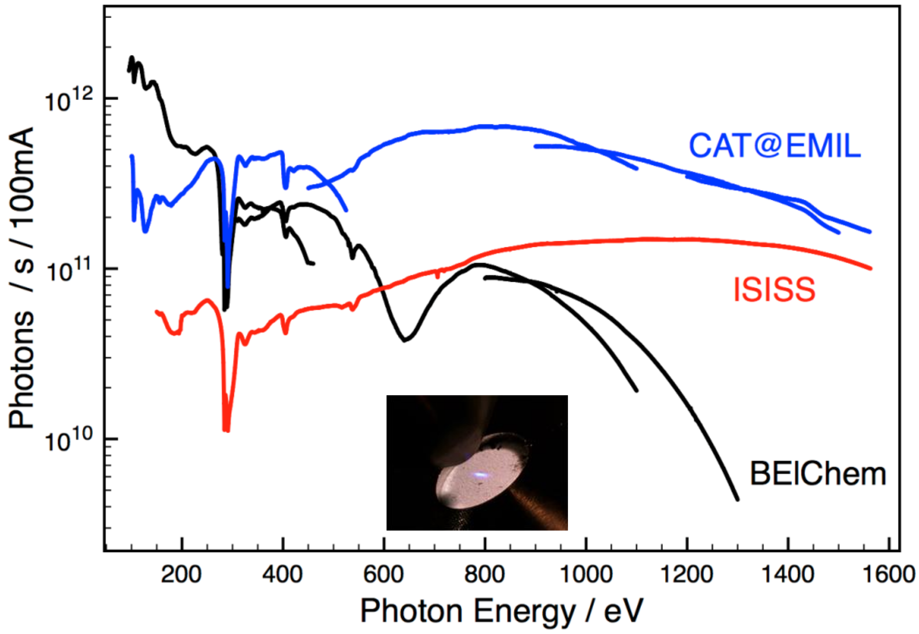

Figure 1: Photon flux at AP-XPS sample position of the beamlines CAT@EMIL, ISISS, and BElChem compared at different exit slit sizes resulting in similar spectral resolution

**P28** **Wednesday 11th 17h30-20h00**

# Performance study in steady state experiments and NAP-XPS at near steady state conditions during methane oxidation over Pd based catalysts

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Natural gas powered vehicles (NGVs) are attaining more focus due to the low carbon footprint as compared to gasoline or diesel powered engines. However, the incomplete combustion of methane in the engine makes a catalytic exhaust treatment necessary. To avoid emission of unburnt methane, Pd based catalysts are generally used for low temperature methane oxidation. It has been proposed that different forms of palladium, including metallic Pd ($Pd^0$), palladium-oxide ($PdO_x$), Pd oxide-covered metal particles, or moderately dispersed $Pd^0$ metal particles serve as active species in methane oxidation.[1,2] In this work, performance of Pd based catalysts in steady state experiments were tested for methane oxidation and almost the same process parameter were used to investigate the samples with Ambient Pressure X-rays Photoelectron Spectroscopy (AP-XPS), to understand the redox mechanism of catalysts samples and its effect on catalytic methane oxidation under realistic steady state operation. Reactant gases $CH_4$, $O_2$, and Ar as carrier gas were used for both performance study in a fixed-bed reactor as well as in the NAP-XPS to investigate the transient oxidation state of Pd species ($Pd^0$ and PdO) during methane oxidation. The XPS study revealed slow oxidation and rapid reduction (reactivation of the active sites) of the catalysts in the respective atmosphere, which shows that Pd based catalyst might perform better in the lean-burn process with the periodic short reducing pulses.

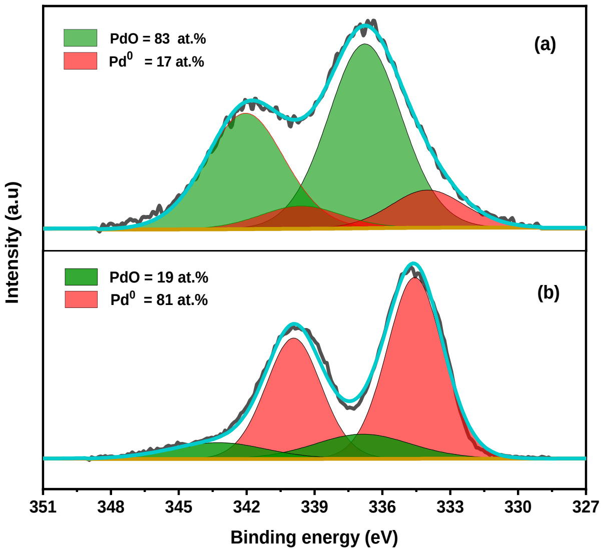

**Figure 1.** XPS spectra for Pd based catalyst (a) under lean process (6 h flow of 1500 ppm $CH_4$ balance Ar/$O_2$), room temperature (b) under reducing atmosphere (30 min flow of 2000 ppm $CH_4$ balance Ar), 500 °C.

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**P29** **Wednesday 11th 17h30-20h00**

# Probing solid-liquid interfaces with tender X-rays

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Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy of 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source (SLS) that combines ambient-pressure XPS with in-situ electrochemistry [1]. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [2], and by using tender X-rays from the Phoenix beamline at the SLS, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces. Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film (see Figure). This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and highlight our current effort to use this new endstation to probe the interface between liquid electrolytes and well-defined rutile-based metal oxides.

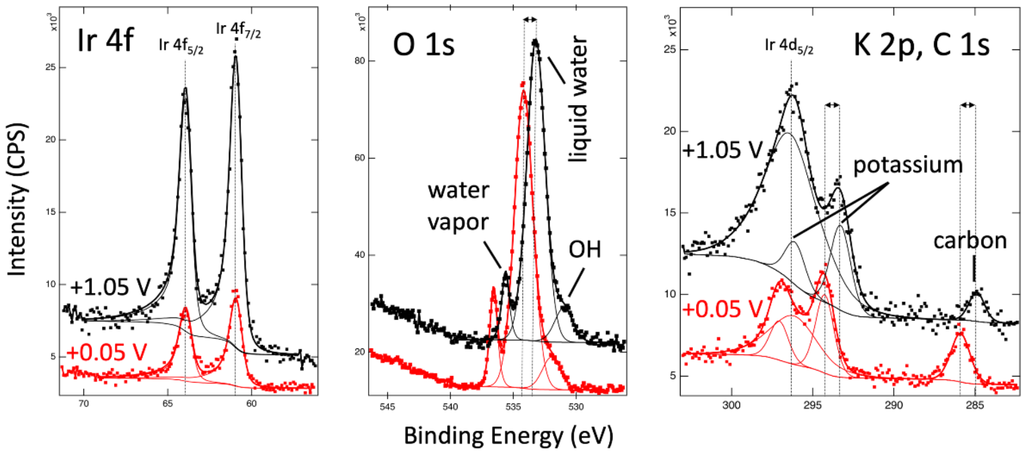

**FIGURE**. Ambient pressure XPS spectra acquired after dip&pull cycles with the Ir(001) sample and 0.1 M KOH electrolyte with an applied potential of +1.05 V vs RHE (spectra shown black color, electrolyte thickness of 21 nm) and +0.05 V vs RHE (spectra shown in red color, film thickness of 31 nm). The sample was grounded in both cases, and the potential was controlled within the thin electrolyte film. Data recorded at 12 mbar base pressure, using a photon energy of 4000 eV

[1] Z. Novotny et al., Rev. Sci. Instr. *(submitted)*.
[2] S. Axnanda, E. J. Crumlin et al., Sci. Rep. 5, 09788 (2014).

***P30*** ***Wednesday 11th 17h30-20h00***

# Scanning Probe Microscopy capabilities for MAX IV users

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A scanning probe microscopy (SPM) lab is available for all users of MAX IV. Here, by means of scanning tunneling microscopy or non-contact atomic force microscopy, morphology of samples' surfaces may be retrieved, often with atomic precision. The lab offers a broad range of tools for in situ sample preparation (leak valves, evaporators/effusion cells, sputter gun, quartz crystal microbalance, etc.) and characterization (low-energy electron diffraction set up with auger spectroscopy capabilities). We also offer all-vacuum, true UHV (around 1E-10 mbar) transfer of samples between the STM and a number of compatible beamlines (HIPPIE, FinEstBEAMS, FlexPES are tested; transfer to SPECIES and MaxPEEM is foreseen).

More info can be found at the SPM lab's webpage

https://www.maxiv.lu.se/accelerators-beamlines/beamlines/scanning-probe-microscopy-lab/

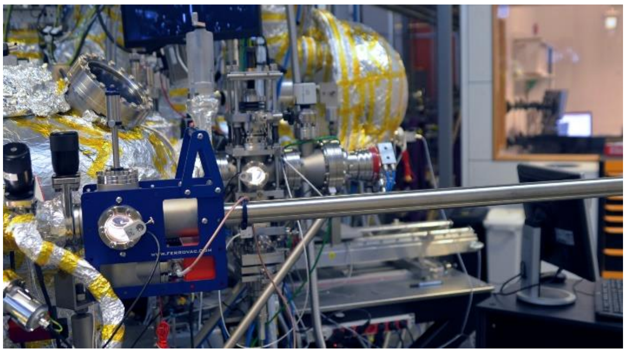

Figure 1. Vacuum suitcase mounted at experimental station of HIPPIE beamline.

**P31** **Wednesday 11th 17h30-20h00**

# Oxidation of Ni-based binary and ternary superalloys: observing the competition between NiO and chromia formation

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Ni-based superalloys are highly coveted for their unique combination of excellent mechanical properties and superb corrosion resistance which is achieved if a chromia ($Cr_2O_3$) layer is formed on the alloy surface. However, the nature of the oxide layer depends sensitively on the environmental conditions. It is known empirically that the addition of a minor alloying element such as Mo, or W leads to better performance of the protective oxide layer, and this effect is seen in dry as well as aqueous corrosion.

We will present a comprehensive study of the dry oxidation ($O_2$) of binary Ni-Cr, and ternary Ni-Cr alloys with 5-30 wt% Cr, and Mo or W admixtures (<6wt%) with AP-XPS in the pressure range from 1 to $10^{-6}$ mbar and T=200 to 500 ºC. The samples are polycrystalline, cast alloys (J. Perepezko, U. Wisconsin). The oxidation process is recorded in *operando* and alloy and oxide signal are recorded simultaneously until the oxide thickness exceeds the information depth at a few nm oxide thickness. The native oxide is removed by annealing to 800ºC and all near-surface layers are enriched with Cr. Note that this observation of Cr-segregation is in contrast to theoretical predictions [1] which indicate Ni anti-segregation for the densely packed surface. The near-surface Cr- inventory is used in the early steps of the oxidation to form chromia, which is followed by rapid nucleation and growth NiO due to cub-on-cube epitaxy.[2] The chromia layer is subsequently overgrown by NiO in a Volmer-Weber growth mode, although islanding is more extreme for higher Cr content of the alloy. We will discuss the details of the oxide evolution by comparing different alloy compositions and oxidation conditions.

The addition of W (or Mo) to the alloy promotes the formation of chromia nearly exclusively as can bee seen in Figure 1. This preference cannot solely be attributed to Cr supply and bulk diffusion, but is tentatively interpreted as a signature of modified surface chemistry, and phase separation of Cr into highly reactive bcc nodules which circumvent a more complex chromia nucleation step. No spinel is formed in the early oxidation steps, and minor contributions (<10%) of Ni(III) can be related to defects at the alloy-oxide interface. We will address the fitting the Ni2p and Cr2- core levels [3] and present a comprehensive approach to tackle this challenge.

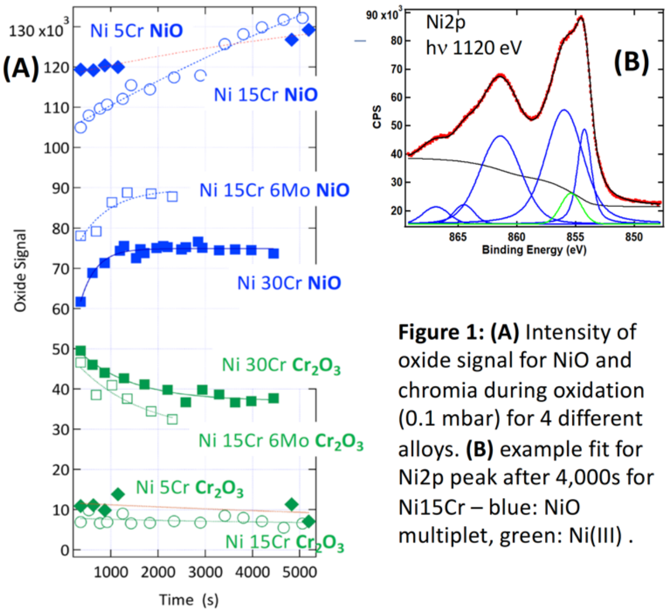

**Figure 1: (A)** Intensity of oxide signal for NiO and chromia during oxidation (0.1 mbar) for 4 different alloys. **(B)** example fit for Ni2p peak after 4,000s for Ni15Cr – blue: NiO multiplet, green: Ni(III) .

[1] A. V. Ruban, H.L Skriver, J.K. Norskov, Phys. Rev. B **59,** 15990 (1999)
[2] W. Blades, P. Reinke, ACS Appl. Mater. Interfaces, **10**, 49 (2018)
[3] M. Biesinger et al., Surf. Interf. Anal. **41** (2009) 324

***P32*** ***Wednesday 11th 17h30-20h00***

# “Dip and Pull” AP-XPS measurements of battery interfaces

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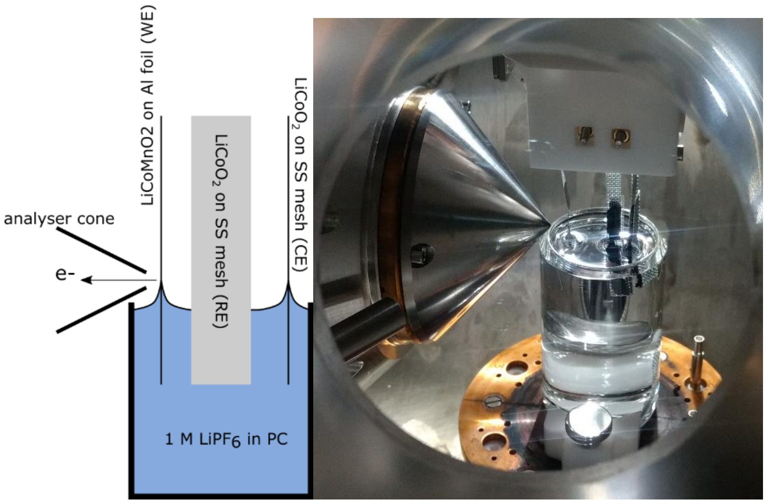
University of Nottingham, UK

Our energy landscape is rapidly becoming ever more reliant on batteries but applications like electric vehicles require improvements to battery technology for widespread adoption. A challenge in battery design is the formation of unstable “cathode-electrolyte interphases” (CEIs) [1] on Li electrodes which can reduce the capacity and worst case lead to short-circuit conditions resulting in fire. Understanding the chemistry of the CEI’s formation is therefore of great importance.

We present a commissioning experiment at the HIPPIE beamline (Max-IV Sweden) where we aimed to study the CEI growth on a “lithium rich” $LiCoMnO_2$ cathode in a model battery (see the below diagram) using the “Dip and Pull” technique. This allows in-operando XPS measurements of interface between the cathode and the liquid electrolyte solution ($LiPF_6$ in propylene carbonate) whilst under electrochemical control. This experiment was a challenge, largely due to severe radiation damage and uncontrollable wetting of the electrodes restricting access to the solid/liquid interface. This poster presents the results we did collect and discusses some of the lessons we learnt that will hopefully aid others in designing successful experiments using this exciting technique.



PC: Propylene Carbonate; SS: Stainless Steel; WE/RE/CE: Working/Reference/Counter Electrode

[1] W. Lu et al., ACS Appl. Mater. Interfaces, vol. 9, no. 22, 19313 (2017).

***P33*** ***Wednesday 11th 17h30-20h00***

# AP-XPS study of catalytic CO oxidation over Pd–Au(111) surface

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[1]Keio Univ., Yokohama Kanagawa, Japan

The catalytic conversion of chemical compounds is widely applied in the modern society (e.g. energy translation, exuberant feed stock, pollution control). Oxidation of carbon monoxide (CO) on Pt-group metal surfaces is a prototypical model system for understanding the heterogeneous catalysis. Bimetallic alloys are regarded as promising maerials for developing various functionalized catalysts. Pd–Au alloys, for example, show excellent catalytic activities for CO oxidation at lower temperature conditions.

In this work, the catalytic CO oxidation on the Pd(111) and $Pd_{70}Au_{30}(111)$ surfaces has been studied under a near realistic condition (i.e. $P_{O2}$ = 100 mTorr and $P_{CO}$ = 10 mTorr) with direct in-situ monitoring of the surfaces using AP-XPS. All the experiments were performed at the photon factory (KEK-PF), Japan [1].

The reaction behaviour on the alloy surface is clearly different from that on the monometallic one (Figure 1). Pd ensembles in the first layer of the alloy exhibit different chemical interactions with adsorbates and thus different activities; Pd monomers (labelled as m) contribute to the catalytic activity, whereas compact trimers (labelled as c) and larger ensembles are inactive. The present in-situ spectroscopic observations of the alloy surfaces enable to reveal the active ensembles for the catalytic reaction. Additionally, the in-plane aggregation of the surface Pd atoms takes place under the active conditions. Since the local Pd ensembles exhibit significantly different activities, the control of surface structure of alloys at the atomistic level will be quite important to gain a superior catalytic performance using alloy systems [2].

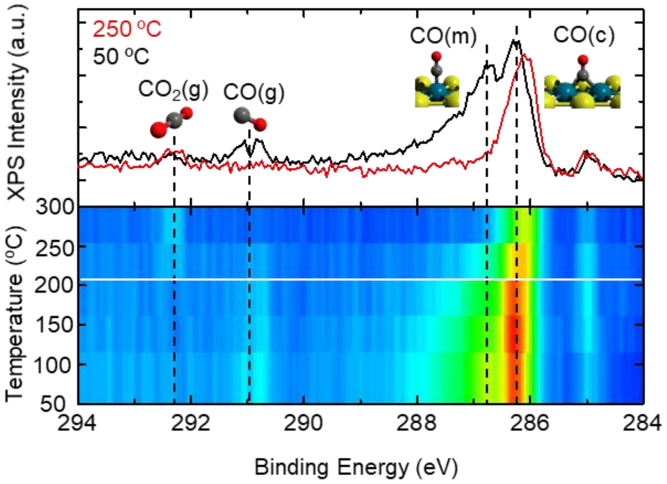

Figure 1 C 1s XP spectra taken from Pd-Au(111) surface under CO oxidation condition ($P_{O2}$=100 mTorr and $P_{CO}$=10 mTorr) as a function of temperature.

[1] Toyoshima et al. *J. Phys. Chem. C* **2012**, *116*, 18691.

[2] Toyoshima et al. *Chem. Comm.* **2017**, *53*, 12657.

**P34** **Wednesday 11th 17h30-20h00**

# Using APXPS to measure the spatial gas composition above a catalytic active surface in the mass transfer limit

Tamires Gallo[1], V. Boix[1], J. Shnadt[1,2], S. Zhu[2], A. Shavorskiy[2] and J. Knudsen[1,2]

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For many transition metal surfaces, it is possible to reach the so-called mass transfer limit (MTL) for simple reactions such as the CO oxidation reaction. Once in the MTL, the $CO_2$ production is fully determined by gas diffusion through a CO depletion layer that is formed above the catalyst surface. Recently, planar laser- induced fluorescence (PLIF) was used to simulate a typical ambient pressure X-ray photoelectron spectroscopy (APXPS) setup and measure the size of the CO depletion layer [1-2]. In this contribution, we will demonstrate how ambient pressure photoelectron x-ray spectroscopy (APXPS) can be used to measure the size of the MTL directly and probe the gas composition within it.

Our APXPS experiments was performed at the HIPPIE beamline at the MAX IV Laboratory. We moved the sample backward while recording a series of O1s and C1s spectra such that we probe a small volume determined by the overlap of the analyzer focus and the footprint of the synchrotron light. Using O, C, and volume balance one we measured the relative flow distribution through the outlet and the cone to know the total conversion for a reaction inside the cell. With this methodology, was possible to measure the spatial gas composition both with the attached QMS and directly with APXPS. The CO depletion layer is large, around 10 mm, and fills the entire cell volume at standard APXPS settings essentially.

This work it is useful for validating how true partial pressures can be obtained from APXPS gas phase data. Also important for transient studies where the inlet gas composition is changed rapidly. In the presentation, we will discuss the size of the MTL at the different flow and pressure settings of $CO/O_2$ from the APXPS and mass spectrometer data.

[1] J. Zhou, S. Blomberg, J. Gustafson, E. Lundgren and J. Zetterberg. *Catalysts*, 7, 29 (2017).

[2] V. R. Fernandes, J. Gustafsonb, M.H. Farstada, L.E. Wallea, S. Blombergb, E. Lundgrenb, H.J. Venvikc, A. Borg. *Applied Surface Science*, 313, 794 (2014).

**P35** **Wednesday 11th 17h30-20h00**

# $WO_3$ promoted thermal stability and reducibility of $V_2O_5$ on anatase $TiO_2(101)$: an XPS study

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Nitrogen oxides (NOx) from flue gas are in concern as major sources of air pollution. Increasingly stricter NOx emission control policies (e.g. Euro VI) demand innovation and better performance of NOx reduction technology. The Selective Catalytic Reduction (SCR) of NOx by vanadia supported on anatase titania, with tungsten oxide ($WO_3$) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive Raman and infrared spectroscopy studies. [1]

In this work, we use mineral a-$TiO_2$ single crystals exposing the (101) facets as the model surface and deposit $V_2O_5$ and $WO_3$ by reactive deposition and powder sublimation methods. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the atomic-scale morphology (see Figure 1) and oxidation state changes of the model catalyst upon heating. It was found that, with the presence of $WO_3$ on a-$TiO_2(101)$ surface, the migration of vanadium atoms into a-$TiO_2$ bulk at high temperature is hindered. In addition, more vanadium species exist in the 4+ state than the oxidized 5+ state with the presence of $WO_3$. The findings here suggest that the promotion effect of $WO_3$ in SCR relates to the enhanced thermal stability and reducibility of vanadia (active species in SCR). [2] It is our next step to investigate the stability and reducibility of vanadia under near ambient pressure of the reactive gases ($NH_3$, NO, $H_2O$, $O_2$).

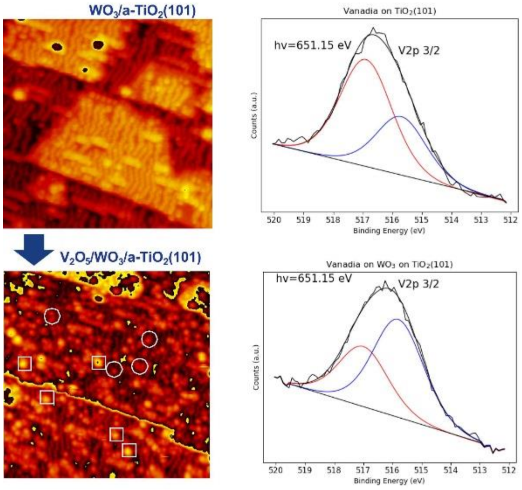

Figure 1 (left) the STM images of $WO_3$ and $V_2O_5/WO_3$ on a-$TiO_2(101)$. (right) XPS (V2p 3/2) of the as-deposited $V_2O_5$ on a-$TiO_2(101)$ with or without $WO_3$.

[1] J.-K. Lai, I. E. Wachs, *ACS Catalysis* **2018**..

[2] Manuscript in preparation.

**P36** **Wednesday 11th 17h30-20h00**

# In situ characterization of co-precipitated $NiAlO_x$ catalysts during $CO_2$ methanation

Tim Kratky[1], Tabea Gros[1], Moritz Wolf[1], Barbara A. J. Lechner[1], Thomas Burger[1], Federica Venturini[2], Georg Held[2,3], Olaf Hinrichsen[1], Sebastian Günther[1]

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[3]Department of Chemistry, University of Reading, Reading, UK

Co-precipitated $NiAlO_x$ mixed oxides proved to be the catalyst of choice for a low-cost pathway to $CO_2$ methanation as green alternative to current energy carrier formation. Such technical powder catalysts were investigated in an *in situ* study at the Diamond Light Source synchrotron facility during activation and catalytic conversion. Aiming at characterizing technical powder catalysts by APXPS problems such as surface contamination and inhomogeneous charging are encountered. While we were able to separate surface contamination from true adsorbate buildup during *in situ* catalysis, inhomogeneous charging of the industrial powder catalyst could be diminished by placing a gold grid in order to facilitate de-charging of the outermost powder crystals. Thus, elemental analysis of the outermost layers of the catalyst with a precision usually achieved only in surface science studies is possible. We were able to show that the formation of metallic Ni particles released from mixed oxide during catalyst activation in hydrogen plays the essential role of the high activity during $CO_2$ methanation. Using the activated catalyst, the $CO_2$ methanation in a 5 mbar reactive atmosphere ($CO_2$+$H_2$, 1:4) was followed *in situ* by differentially pumped QMS in addition to APXPS and yield as well as selectivity were quantified. While the reaction reached the thermodynamic limit at 450 °C, lowering the reaction temperature to 200 °C drives the catalytic reaction towards kinetic limitations. Carbon buildup is observed to be essential during the *in operando* studies at both reaction temperatures. Thermodynamic considerations proof that the coking process is inherent to the $CO_2$ methanation reaction in contrast to a pure surface contamination in a "dirty" environment. A thorough analysis proves that at intermediate pressures in the mbar regime carbon buildup is thermodynamically ruled and cannot be avoided. Lowering the reaction pressure slows down the coking process due to kinetic reasons, while at sufficiently high pressure the coking will be avoided due to thermodynamics. Thus, the peculiar situation appears that in surface science studies coking is not observed and represents the situation during catalytic performance under industrial conditions (1-10 bar). Both findings result from different reasons (kinetics versus thermodynamics) which is evidenced by *in situ* APXPS within the intermediate mbar pressure regime.

***P37 Wednesday 11th 17h30-20h00***

# Surface Chemistry of 2-Propanol and $O_2$ Mixtures on $SnO_2(110)$ Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy

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Tin dioxide ($SnO_2$) has a wide range of applications, including gas sensors, transparent conductors, and oxidation catalysts.[1] The oxidation of toxic volatile organic compounds (VOC) into less harmful molecules has recently been demonstrated using $SnO_2$, where 2-propanol was used as the probe molecule.[2] More recent studies have shown that the surface $Sn^{2+}/Sn^{4+}$ ratio strongly influences the activity of carbon monoxide oxidation.[3] In this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to study the surface chemistry of 2-propanol and $O_2$ mixtures on a well-defined $SnO_2(110)$ surface. We have prepared the stoichiometric oxidized surface and verified the Sn oxidation state with valence band spectra and the surface structure with low energy electron diffraction. AP-XPS was performed for 2-propanol pressures up to 1 mbar, various 2-propanol/$O_2$ ratios, and several temperatures. These studies allowed us to evaluate the reaction of 2-propanol on the $SnO_2(110)$ surface under a wide range of experimental conditions. The effect of surface preparation, 2-propanol/$O_2$ ratios, and sample temperature was evaluated using AP-XPS and *in-situ* mass spectrometry. Using AP-XPS valence-band spectra, we have found that the surface was reduced from $Sn^{4+}$ to $Sn^{2+}$ when the sample was heated in 2-propanol and that the main reaction product was acetone in the gas phase. This suggests that the reaction occurs through a mechanism where bridging oxygens are hydroxylated upon adsorption of 2-propanol. These bridging hydroxyl groups can then react and result in water desorption. This process results in the formation of oxygen vacancies and results in a reduced surface. For 2-propanol/$O_2$ mixtures, we found that the low temperature AP-XPS spectra (300-400 K) was nearly identical to exposures with 2-propanol and no oxygen. After increasing reaction temperatures, we found that the surface remained oxidized in 2-propanol/$O_2$ mixtures. Several new oxidation products were also observed in the gas phase. Based on these results we find that the $SnO_2$ surface is inactive for the oxidation of 2-propanol for temperatures below 500 K. With 2-propanol/$O_2$ mixtures the reactivity increased substantially at lower temperatures where oxygen is consumed by replenishing surface oxygen vacancies, leading to a reduction in acetone production. Ultimately, we propose that the oxidation of 2-propanol with $O_2$ on $SnO_2(110)$ occurs through a Mars−van Krevelen mechanism.

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[1] M. Batzill, U. Diebold, Prog. Surf. Sci. 79, 47 (2005).
[2] J. Leclercq, F. Giraud, D. Bianchi, K. Fiaty, F. Gaillard, Cat. Comm. 46, 192 (2014).
[3] Y. Inomata, K. Albrecht, K. Yamamoto, ACS Cat. 8, 451 (2018).

**P38** **Wednesday 11th 17h30-20h00**

# Following the kinetics of confined catalysis under graphene with ambient pressure x-ray photoelectron spectroscopy

*Virginia Boix, Tamires Gallo, Filippo Cavalca, Suyun Zhu, Andrey Shavorskiy, Joachim Schnadt, and Jan Knudsen*

Enhanced activity or selectivity of catalyst materials placed in confined environments have already been studied for a variety of systems [1]. Here, we focus on CO and $H_2$ oxidation performed in the confined space formed between an active Ir(111) surface and inert high quality graphene (Gr) flakes. Previously, we used x-ray photoelectron spectroscopy (XPS) to study intercalation and reactions below graphene flakes at ultra-high vacuum (UHV) conditions. With those studies, we got an atomistic understanding of the intercalation process of CO, $H_2$, and $O_2$ and the corresponding oxidation reactions performed under the Gr flakes at UHV conditions [2]. Unfortunately, our attempts to study CO and $H_2$ oxidation in the mbar regime with ambient pressure XPS (APXPS) has failed until now as we always observe complete poisoning of the surface covered by Gr flakes by one of the reactant molecules. Most likely the reason is that molecules only can diffuse in or out of the confined space at the edges of the Gr flakes. To overcome this limitation, we here take advantage of the small volume of the flow cell and the automatized gas dosing system available at the HIPPIE beamline at the Max IV Laboratory. This setup allow us to rapidly change partial gas pressures with a high degree of control. We will show how using pulses of changing partial pressures we are able to repeatedly intercalate and de-intercalate the Gr flakes and follow the kinetics of the undercover reactions. Additionally, we will demonstrate how we can use the graphene film as an extra probe to follow the undercover reactions. By monitoring the changes in the sharp and intense C 1s peak of Gr with the fast acquisition analyzer (see figure 1) and comparing its changes with the known fingerprints of intercalated species [2, 3], we demonstrate that the kinetics of confined reactions under 2D materials can be followed in detail with APXPS.

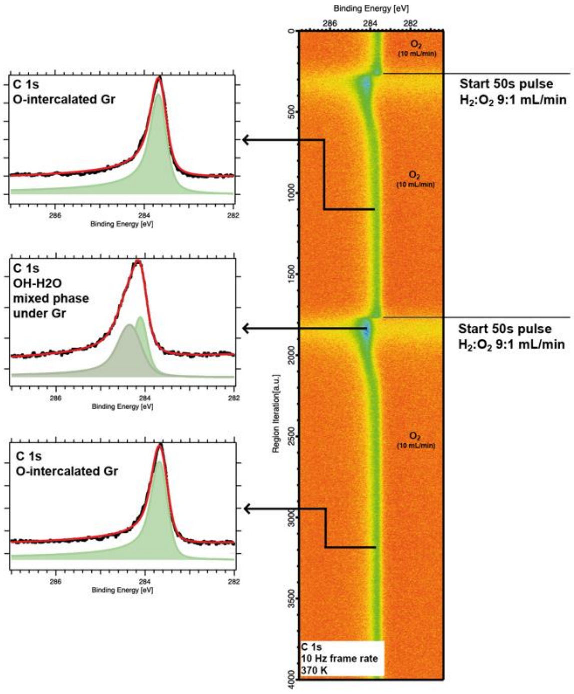

*Figure 3. C 1s image plot of 0.5 ML graphene flakes on Ir(111) at 370K acquired during two subsequent 9:1 (mL/min) $H_2$:$O_2$ pulses. In between pulses, the sample is kept at an oxygen atmosphere (10 mL/min $O_2$). Total pressure in the flow cell of 1 mbar. On the left side, three insets showing the C 1s spectra before, during and after one pulse have been included. The characteristic BE of O-intercalated Gr can be found in the spectra before and after the pulse. The C 1s components corresponding to a mixed OH-$H_2O$ phase under Gr flakes can be distinguished in the spectrum recorded during the pulse.*

[1] Q. Fu, X. Bao, Chem. Soc. Rev., 2017, 46, 1842-1874
[2] E. Grånäs, PhD thesis, Lund University (2014)

***P39*** ***Wednesday 11th 17h30-20h00***

# Reversible physisorbed and chemisorbed water on carboxylic salt surfaces at atmospheric conditions

Xiangrui Kong[1*], Dimitri Castarede[1], Anthony Boucly[2], Luca Artiglia[2], Markus Ammann[2], Erik S. Thomson[1], and Jan B.C. Pettersson[1*]

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The particle-gas interface in aerosol systems is of essential importance because it is the place where many key atmospheric processes occur. In this study, we employed ambient pressure X-ray photoelectron spectroscopy (APXPS) to investigate the surface properties and processes of an atmospherically relevant carboxylic salt, sodium acetate, at sub-deliquescence conditions. From depth profiles of the elementary ratios of sodium, oxygen and carbon, we find that after deliquescence-efflorescence cycles the salt surface is sodium-depleted. The driving force of the observed depletion is proposed to be (i) the formation of neutral aqueous acetic acid due to the nature of the basic salt; (ii) selective surface enhancement of neutral molecules; and (iii) local surface crystallization via minimization of surface free energy. When the relative humidity gradually increases and approaches the deliquescence point, both reversible water uptake and reversible sodium dissociation were confirmed by near edge X-ray adsorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge and sodium K-edge, respectively. The dissolution of sodium requires higher relative humidity than that for water adsorption, which suggests that water molecules were taken up by the surface, but dissolution of the salt surface begins only when sufficient water molecules are present, to facilitate the process. The sodium-depleted surface requires additional adsorbed water to affect and dissolve the sodium atoms in deeper regions.

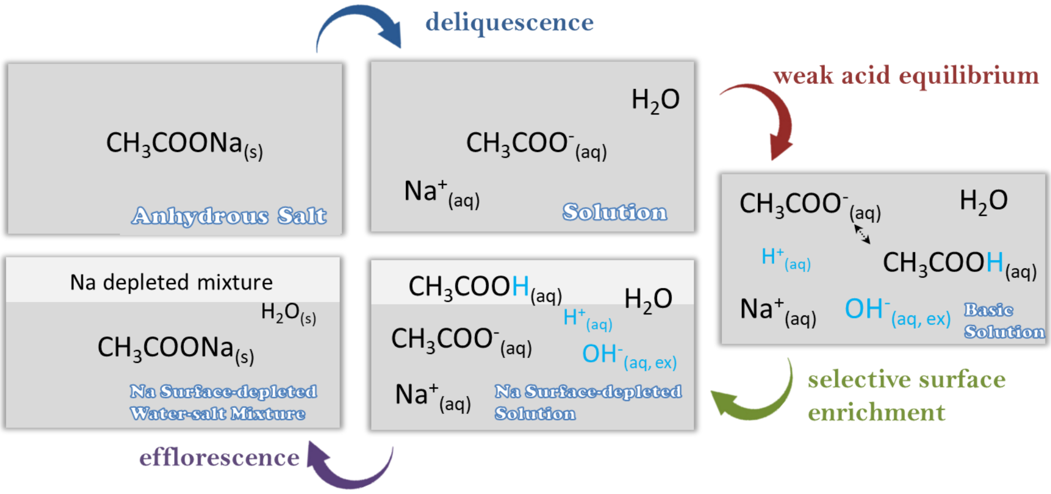

Figure 1 Proposed mechanism for formation of a sodium depleted salt surface after a deliquescence-efflorescence cycle.

**P40** **Wednesday 11th 17h30-20h00**

# Photoreduction of $CO_2$ with $H_2O$ on $Cu_2O/TiO_2$ Heterojunction

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Photocatalytic reduction of carbon dioxide, capable of turning carbon dioxide into useful commodities such as methane, methanol, carbon monoxide, etc., offers a particularly appealing advantage in reducing global $CO_2$ emission by tapping the abundant solar radiation for the energy source of conversion. Herein we report a study employing ambient pressure X-ray photoelectron spectroscopy (APXPS) to investigate the photocatalytic reduction of carbon dioxide on the semiconducting, core-shell heterojunctions fabricated with nanostructured materials of cuprous oxide (core) and titanium oxide (shell). Two types of cuprous oxide polyhedral crystallites are chosen based on the expected difference in photoreduction efficacy: the cubic structure terminated with (100) face, and the rhombic dodecahedron (r.d.) terminated with (110) face.

APXPS is specifically used to track the change of surface species during the photocatalytic reaction. The C 1s spectra strongly suggest that the $Cu_2O$(r.d.)-$TiO_2$ is more reactive than $Cu_2O$(cube)-$TiO_2$, as evidenced by a larger production of carbon species such as formate, carbonyl, aliphatic carbons on the surface. After prolonged photocatalytic reactions, the chemical identity of accumulated surface species can be revealed with an on-line quadrupole mass spectrometer by running the so-called temperature programmed reaction spectroscopy (TPRS) experiments. The production of methane and methanol at ~400 K is clearly noted.

The energy diagram relevant to the performance of photocatalysis is also obtained by XPS with a particular interest in determining band edge offsets. The larger conduction band offset found for $Cu_2O$(r.d.)-$TiO_2$ is believed to facilitate an increase of the photoreduction capability.

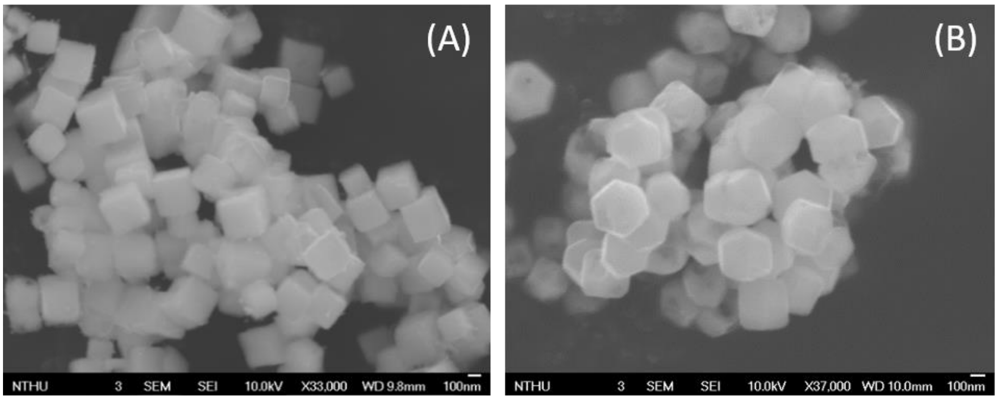

Figure 1 SEM images of (A) $Cu_2O$(cube)-$TiO_2$, and (B) $Cu_2O$(r.d.)-$TiO_2$.

**P41** **Wednesday 11th 17h30-20h00**

# New Lab-based Ambient Pressure X-ray Photoelectron Spectroscopy for Liquid-Solid Studies in ShanghaiTech University

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The electrochemical reactions occurring at the liquid-solid interface determine many processes in electrochemistry, environmental science, and corrosion. The characteristics of the interface, in particular the properties of the electric double layer, are controlling many processes. Investigations of fundamental properties, including molecular structures of the interface, specific/non-specific adsorption of ions, solvation structures, specifics at the potential of zero charge and their deviations under applied potentials, are required for a complete understanding of liquid-solid interface and the processes at this region.

In this work we will share some recent progress on the ambient pressure X-ray photoelectron spectroscopy (APXPS) facilities in China that focus on liquid-solid interfacial investigations. The lab-based APXPS system with a monochromatic Cr X-ray source is dedicated for this mission and opportunities at the APXPS endstation at the Shanghai Synchrotron Radiation Facility are being explored. Besides the “dip & pull” method, other strategies that allow probing interfacial phenomena within confined space will be briefly discussed with open questions in our understanding.

**P42** ***Wednesday 11th 17h30-20h00***

# Performance test of the new NAP-XPS system at the University of Antioquia, Colombia, during its application to CO oxidation study on high-quality thin film surfaces.

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The new near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) facility is located at the University Research Headquarters (SIU-UdeA), University of Antioquia in Medellín, Colombia. The system consists in a hemispherical PHOIBOS 150 1D-DLD electron energy analyzer and a µ-FOCUS 600 NAP X-ray monochromator (SPECS GmbH). The PE measurements were acquired at room temperature with photon energies of the Al Kα radiation (1487 eV) operated at 13kV and 100W energy power. The data were collected with a pass energy of 20eV and a step size of 0.05 eV for high-resolution data recording. The in-situ gas-pressure cell operated at 1 mbar with differential pumping scheme, which includes a three-axis manipulator with heating and cooling capability for NAP-XPS experiments. For ultra-high-vacuum XPS experiments, the system is composed of a main preparation chamber, a flood gun, an ion sputter gun and a four-axis manipulator with heating and cooling capability.

The performance test of the NAP-XPS system was evaluated during the CO oxidation experiment on (100)-highly textured Co3O4 and CoMn2O4 thin films. These materials are interesting for application in energy and environment-related areas, and thereby, high-sensitive surface spectroscopic methods have been employed to get better understanding about surface properties [1]. In this work, the measurements were carried out from RT to 573K, and reaction products were followed via RGA analyser. For fundamental understanding of catalytic mechanisms at a molecular level, a previous study to monitor surface oxidation-reduction capabilities were tested under in situ/ operando conditions using H2 and O2 atmospheres. Results suggest that highly active CoO/Co3O4 phase was obtained after the reduction process probably triggered by the formation of oxygen vacancies along the surface. During the oxidation process, the surface becomes rich in oxygen species and they promoted the formation of CO2 gas as was detected by the RGA. The kinetic activation energies of CO molecules onto the film surfaces were calculated. These results will be compared with theoretical values obtained by DFT calculations and STM measurements.

[1] B. Eren, C. Heine, H. Bluhm, G. A. Somorjai, and M. Salmeron, "Catalyst Chemical State during CO Oxidation Reaction on Cu(111) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy and Near Edge X-ray Adsorption Fine Structure Spectroscopy," J. Am. Chem. Soc., vol. 137, no. 34, pp. 11186–11190, 2015.

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