

# Monday Afternoon, October 19, 2015

## In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-MoA

### Ambient Pressure X-ray Photoelectron Spectroscopy Studies for Catalytic and Energy Materials in Gas Phase

**Moderator:** Peter Crozier, Arizona State University, Franklin (Feng) Tao, University of Kansas

2:20pm **IS+AS+SA+SS-MoA1 In situ Electron Spectroscopy for Energy Science, Robert Schlögl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany** **INVITED**

The use of volatile renewable electricity in larger amounts in our energy systems requires grid-scale technologies for integration electricity in material energy carrier streams. Several systemic options always suffer from our conceptual weakness to convert free electrons in chemical bonds. This can be achieved with accumulators for limited applications and should be done through water splitting and synthesis of solar fuels in almost unlimited applications. Complex interfacial chemistry is the underlying scientific challenge. To tackle this old challenge with new concepts it is essential to improve our ability to study chemical, electronic and geometric structures of nanoscopic objects in-situ meaning under operation conditions. A whole train of dedicated instrumentation from specimen formation, data acquisition and auxiliary analyses plus sample manipulation is necessary for this task. The presentation gives some aspects of priority challenges and uses examples of operation studies of water splitting catalysts and of CO<sub>2</sub> reduction systems to illustrate the present status of insight. In the outlook the possibilities of the novel experiment EMIL at BESSY will be discussed.

3:00pm **IS+AS+SA+SS-MoA3 Catalysis on Singly Dispersed Bimetallic Sites on Oxide Support, Luan Nguyen, University of Kansas, A. Frenkel, Yeshiva University, J. Li, Tsinghua University, China, F. Tao, University of Kansas**

Reaction events of heterogeneous catalysis occur on specific catalytic sites. Atoms of a catalytic site arrange in a specific geometric/electronic configuration for adsorbing/dissociating reactant molecules and subsequent coupling to form product molecules. Bimetallic catalysts play significant roles in chemical and energy transformations due to their tunable catalytic properties through ligand, geometric, bi-functional, or lattice strain effect.

When a bimetallic site ( $M_1A_n$ , M and A: metal elements,  $n \geq 1$ ) is one of the continuous sites on the surface of a bimetallic NP, this site is in a metallic state. However, when  $M_1A_n$  sites are *separately* anchored on a surface of a transition metal oxide support, these isolated bimetallic sites are in cationic state. Such change in electronic structure could cause these bimetallic sites to have stronger chemisorption to reactant or/and intermediate molecules, thus facilitating its dissociation and subsequent coupling. In addition, singly dispersion of metal M in  $M_1A_n$  minimizes the potential binding configurations of reactant molecules hence may enhance catalytic selectivity toward a specific reaction pathway. Here we present singly dispersed bimetallic catalyst  $Rh_1Co_3$  prepared on Co oxide support, which exhibits 100% selectivity for the production of N<sub>2</sub> in NO reduction with CO.

Preparation of isolated bimetallic sites  $Rh_1Co_3$  on  $Co_3O_4$  nanorods begins with the formation of hydroxide species  $Rh(OH)_n$  on the surface of  $Co_3O_4$ , followed by calcination at 150°C in O<sub>2</sub> to form Rh-O-Co bonds between singly dispersed  $Rh(OH)_n$  species and the surface of  $Co_3O_4$ , and concluded with a carefully controlled reduction to remove oxygen atoms between Rh and Co and thus a simultaneous formation of Rh-Co bonds. In-situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to monitor the oxidation and reduction steps and to avoid over or under-reduction.

Formation of singly dispersed Rh atoms was visualized using HAADF-STEM. The bonding environment of Rh to three Co atoms was confirmed using in-situ EXAFS. For reduction of NO with CO,  $Rh_1Co_3/CoO$  exhibits high activity at 110 °C with 100% selectivity toward N<sub>2</sub> production. In contrast, Rh-Co alloy NP/CoO has much lower activity and selectivity (10%) under the same condition. In-situ AP-XPS investigation shows that Rh atoms are at cationic state instead of metallic state. Along with this, DFT calculations suggest that a strong adsorption of intermediate N<sub>2</sub>O molecules on  $Rh_1Co_3$  site prevents its desorption as a byproduct and provides a dissociation pathway of N<sub>2</sub>O to N<sub>2</sub> with a low activation barrier (~0.21 eV), thus leading to a 100% selectivity to N<sub>2</sub> production.

3:20pm **IS+AS+SA+SS-MoA4 Oxidation and Recovery of WC Thin Film Surfaces, E. Monazami, University of Virginia, J.B. McClimon, University of Pennsylvania, N. Johansson, P. Shayesteh, S. Urpelainen, J. Schnadt, Lund University, Sweden, Petra Reinke, University of Virginia**

Transition metal carbide (TMC) surfaces are coveted as catalytic materials, electrodes and hard protective coatings. A bottleneck in their use is surface oxidation, which leads to a decay in performance. Our work establishes the feasibility of surface recovery by using a carbon-rich WC layer where recarburization of the surface is initiated by an annealing step. Thin carbon-rich tungsten carbide layers are grown by co-deposition of W and C<sub>60</sub> on a MgO(001) surface at 1100 K. The MgO substrate serves as a diffusion barrier for carbon, and the films have a well-defined carbon inventory controlled by the deposition rates of the reactants. The film surfaces were studied by in-situ Scanning Tunneling Microscopy and Spectroscopy. Raman spectroscopy confirmed the presence of highly defective graphitic carbon. The oxidation-recarburization (O-R) cycles were studied in the ambient pressure endstation SPECIES at MAX-Lab (J. Synchr. Rad. 701, 19 (2012)) in a pressure of 0.3 mbar of O<sub>2</sub>. Oxidation with  $p(O_2)$  of  $10^{-5}$  mbar were performed at SPECIES for direct comparison to low  $p(O_2)$  STM experiments.

The carbon-rich WC films exhibit a relatively rough surface, which allows only in a few instances true atomic resolution, but graphite as well as graphene layers can be identified. Oxidation at  $T > 550$  K leads to etching of surface carbon and the growth of a W-oxide layer and STS maps show the oxide evolution. The oxidation in the low  $p(O_2)$  pressure regime progresses slowly and the surface carbide is recovered by annealing.

The use of the SPECIES endstation enabled a quantitative study of the O-R cycles including a detailed analysis of the respective bonding environments which are modified at different times in the O-R cycle. The oxidation in the ambient pressure environment was monitored using the ratio of W-carbide to W-oxide in the W4f core level during the reaction. The steady state thickness of oxide is a function of sample temperature and order of annealing cycles. The surface carbide concentration can be fully recovered in a subsequent annealing step, and repeated O-R cycles were performed. The O-R process is controlled by the interplay between surface oxidation, oxygen and carbon diffusion and our results will be modeled with a simple set of transport equations. We will discuss the role of different bonding environments as we move through the O-R cycle and compare UHV and ambient pressure results up to 800 K. These results clearly illustrate that carbon-rich tungsten carbide materials can be used to achieve a long term use of carbide surfaces in catalysis and fuel cell applications.

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3:40pm **IS+AS+SA+SS-MoA5 Microscopy, Spectroscopy, and Reactivity of Surfaces in Vacuum and under Ambient Reaction Pressures, Miquel Salmeron, B. Eren, Lawrence Berkeley National Laboratory** **INVITED**

The goal of surface science research is to provide atomic level understanding of the structural and dynamic properties of surfaces, a goal particularly relevant for chemical applications, including catalysis, photochemistry, batteries and fuel cells. With X-ray Photoemission Spectroscopy (XPS) and X-ray absorption Spectroscopy (XAS) we determine composition and electronic structure. With Scanning Tunneling Microscopy (STM) we image atoms and molecules as they adsorb, diffuse and react on single crystal surfaces. To study surfaces in the presence of gases, in the Torr to Atmospheres range, which is relevant to practical catalysis, new instrumentation is needed. Over the last years we developed high pressure STM, XPS and XAS, to study surfaces under high coverage of adsorbates in equilibrium with gases near ambient pressures and temperature. Using a combination of these techniques I will show how under these conditions the structure of surfaces and the adsorbed layers can be very different from that at low coverage, or even at high coverage but at low temperature. Adsorbates can induce dramatic restructuring of the surface, as I will show in the case of CO induced restructuring of Cu surfaces and the reactions with Oxygen.

4:20pm **IS+AS+SA+SS-MoA7 Novel Solutions for Ambient Pressure and In Situ Photoelectron Spectro-Microscopy, Hikmet Sezen, M. Amati, L. Gregoratti, Elettra-Sincrotrone Trieste, Italy**

A technique based on photoelectron spectroscopy (PES) providing simultaneously spectroscopy and microscopy capabilities and being compatible with ambient pressure conditions is still missing. Ambient pressure PES (APPES), based on differential pumping of the electron energy analyzer, offers an optimal spectroscopic solution to overcome

pressure barrier for surface related studies[1]. Unfortunately, APPEs has very limited spatial resolution. On the other hand, a better than 100 nm spatial resolution scanning photoelectron microscope (SPEM), where the X-ray beam is demagnified down to a 130 nm spot by Zone Plate Fresnel optics and the sample scanned under the focused beam, is accessible from a few synchrotrons. A direct adaptation of the APPEs approach to SPEM technique is not possible because of geometric constraints, stabilities and sustainability of the x-ray optics under near ambient pressures, and mechanical stability of the photoelectron detection system under such severe pumping conditions. In this presentation we will introduce two novel solutions for near-ambient pressure SPEM with ~100 nm spatial resolution and compatible with in-situ/operando conditions operated at ESCAmicroscopy beamline at Elettra synchrotron facility.

Dynamic high pressure (DHP) is the one of our near-ambient pressure SPEM solution. The technique is based on generating high pressure pulsed gas packets directed to the sample. Under influence of gas pulses the sample feels a few mbar pressure in a burst instant, then gas packets dilute into the SPEM chamber to yield a  $1 \times 10^{-5}$  mbar background pressure. From the test results a  $10^{-3}$ - $10^{-2}$  mbar equivalent static pressure was felt by Si and Rh samples during in-situ oxidation reaction.[2] It is available for users.

Effusive cell is another solution for near-ambient pressure SPEM. The sample is encapsulated with a vacuum sealed cell and located just 30-50  $\mu\text{m}$  behind of a 200  $\mu\text{m}$  diameter size pinhole. The focused x-ray beam are scanning the sample through the pinhole. The generated photoelectrons come out from the same pinhole and are able to reach the electron energy analyzer. Due to the geometric orientation of energy analyzer and the pinhole we can achieve ca. a  $200 \times 100 \mu\text{m}^2$  aerial point of view on the sample. The pressure inside the cell can be raised up to mbar range while the pressure in the main chamber kept around  $1 \times 10^{-5}$  mbar which is the safety limit for SPEM system. An encapsulated filament is behind the sample for heating, and other electrical connections are ready for biasing of sample, and thermocouple connections.

[1] D. F. Ogletree, et al. Rev. Sci. Instrum. 73, 3872 (2002)

[2] M. Amati, et al. J. Instrum. 8, 05001 (2013)

4:40pm **IS+AS+SA+SS-MoA8 In Situ Studies of Partial Oxidation of Methanol to Hydrogen on Isolated Bimetallic Site  $\text{Pt}_1\text{Zn}_n$** , Shiran Zhang, L. Nguyen, University of Kansas, A. Frenkel, Yeshiva University, J. Liu, Arizona State University, F. Tao, University of Kansas

Partial oxidation of methanol to hydrogen and carbon dioxide offers a novel route in converting liquid fuel to hydrogen for fuel-cell systems and thus has been widely investigated in the past decade. One important category of heterogeneous catalysts for catalyzing this reaction is bimetallic nanoparticles which consist of continuous bimetallic sites in a metallic state. Isolation of such bimetallic sites through anchoring them on oxide could offer distinctly different catalytic performance in contrast to continuous sites on bimetallic nanoparticles.

Here we reported an isolated bimetallic site  $\text{Pt}_1\text{Zn}_n$  supported on ZnO which offers an extremely high catalytic activity with high selectivity for transformation of methanol to hydrogen with oxygen. It was prepared through a restructuring of singly dispersed Pt atoms on ZnO with reducing treatment. The formed isolated Pt atoms on ZnO was characterized with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along the projected [10-10] of ZnO as well as the corresponding structural model (Figure 1). The bright spots show single dispersion of Pt atoms. The offset of Pt atoms to the Zn atom row suggests Pt atoms are on the column of oxygen atoms, which indicates the bonding of Pt atom to Zn atoms. Photoemission features of Pt4f of the catalyst during catalysis were tracked with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) using monochromated Al K $\alpha$  (Figures 2). The resultant partial reduced state of Pt atoms under reaction conditions is consistent with the electronic state of Pt in  $\text{Pt}_1\text{Zn}_n$  bimetallic site.

Catalytic performance of the formed isolated  $\text{Pt}_1\text{Zn}_n$  bimetallic site in partial oxidation of methanol was evaluated and compared with Pt-Zn bimetallic nanoparticle catalyst (Figure 3). Isolated  $\text{Pt}_1\text{Zn}_n$  bimetallic site catalyst exhibits much higher activity per active site and selectivity to  $\text{H}_2$  than Pt-Zn nanoparticle catalyst in transformation of methanol to hydrogen through partial oxidation. The cationic nature of these isolated bimetallic site in contrast to the metallic nature of active sites on a nanoparticle could be responsible for the differences in catalytic performance. This study illustrates that isolation of continuous bimetallic sites on a nonmetallic support is a new opportunity to tune catalytic performance of bimetallic catalysts.

5:00pm **IS+AS+SA+SS-MoA9 New Developments in Small Spot and Imaging Near Ambient Pressure XPS**, Andreas Thissen, SPECS Surface Nano Analysis GmbH

Over the last 15 years, Near Ambient Pressure (NAP-) XPS has demonstrated its promising potential in a wide variety of applications. Starting from the Catalysis and Ice paradigm, the focus has shifted towards solid-liquid interfaces, liquid jets and in-situ electrochemistry. Initially, the experiments had to be carried out using advanced synchrotron sources to reach reasonable count rates. But now, the SPECS PHOIBOS 150 NAP offers optimized transmission for electrons, even at pressures up to and above 100mbar, so researchers can now use it with conventional X-ray and UV sources in their own laboratories. Because of the widened application fields, standard XPS is now also attainable when combined with easily adjustable monochromated X-ray sources that offer stable operation, small excitation spots, and high photon flux densities, even in Near Ambient Pressure conditions. The latest designs and results are presented showing small spot performance for spot sizes < 30  $\mu\text{m}$ , while also showcasing the latest implementations of imaging NAP-XPS that uses a new concept allowing for lateral resolved measurements without a compromise in count rate and usability. Highlighting on how sample environments (in situ cells for gases and liquids, electrochemical cells, gas inlets) and integration are both absolutely essential to obtain relevant results from well-defined samples, the presentation will demonstrate the use of NAP-XPS systems for high throughput-XPS measurements, as well as a variety of applications.

5:20pm **IS+AS+SA+SS-MoA10 In Situ Measurement of the Abundances and Temperatures of the Constituents of Semiconductor Manufacturing Plasmas via Terahertz Absorption Spectroscopy: Comparison with Theoretical Models**, Yaser Helal, C.F. Neese, F.C. De Lucia, The Ohio State University, A. Agarwal, B. Craver, P.R. Ewing, P.J. Stout, M.D. Armacost, Applied Materials, Inc.

Plasmas used by the semiconductor manufacturing industry are similar in pressure, temperature, and electron density to those used for the laboratory study of astrophysical neutrals, ions, and radicals. Thus, methods developed over several decades in the submillimeter/terahertz spectral region are directly applicable. Important attributes of terahertz absorption spectroscopy are that it can provide from first principles, without need for calibration, absolute concentrations and temperatures. Furthermore, since there are no intrusive probes, terahertz observations do not impact or change the plasma under study. Such measurements provide details and insight into the interactions and reactions occurring within the plasma and their implications for semiconductor manufacturing processes. In this work, a continuous wave, 0.5 – 0.75 THz absorption spectrometer was developed and used to study the processes in a commercial inductively coupled plasma (ICP) etch chamber. Because of the relatively long wavelength of the terahertz radiation, diffraction is more serious than in the optical regime. As a result, an important part of this work was the development of optical strategies to couple this spectrometer to the plasma reactor using its existing viewports. Comparisons of the experimental results with predictions from equipment models for ICPs will also be presented for Ar/CF $_4$ /CHF $_3$  with varying pressures, powers, and gas mixture ratios. Comparisons such as this provide a basis for validating and improving models, whose development is a complex and difficult science in itself. The results presented in this talk show that terahertz rotational spectroscopy can provide unique and easy to interpret information about manufacturing plasmas and is a useful development tool for process, theoretical and physical models, and the improvement of etch methods.

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