

## Surface Science Division

### Room A220-221 - Session SS+HC+PS-FrM

#### Planetary, Ambient, and Operando Environments

**Moderators:** Catherine Dukes, University of Virginia, Petra Reinke, University of Virginia

8:20am **SS+HC+PS-FrM1 Seeing is Believing: Atomic-scale Imaging of Catalysts under Reaction Conditions, Irene Groot**, Leiden University, The Netherlands, Netherlands **INVITED**

The atomic-scale structure of a catalyst under reaction conditions determines its activity, selectivity, and stability. Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra)high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra)high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts in situ under industrially relevant conditions.

In this talk, I will give an overview of the in situ imaging techniques we use to study the structure of model catalysts under industrial conditions of atmospheric pressures and elevated temperatures. We have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance. Furthermore, we use other in situ imaging techniques such as transmission electron microscopy, surface X-ray diffraction, and optical microscopy, all combined with mass spectrometry.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. Results for reactions such as NO oxidation and hydrodesulfurization will be discussed.

9:00am **SS+HC+PS-FrM3 Operando NAP-XPS and NAP-STM Investigation of CO Oxidation on CoO Nanoislands on Noble Metal Surfaces, Jonathan Rodriguez-Fernández, Z. Sun, E. Rattigan**, Aarhus University, Denmark; *C. Martín, E. Carrasco*, IMDEA Nanoscience, Spain; *E. Pellegrin, C. Escudero*, ALBA Synchrotron Light Source, Spain; *D. Ecija*, IMDEA Nanoscience, Spain; *J.V. Lauritsen*, Aarhus University, Denmark

Nanostructured cobalt oxides (CoOx) have proven to be interesting low temperature oxidation catalysts, for example for preferential oxidation (PROX) of carbon monoxide (CO). CoOx has been identified as one of the most active materials for CO oxidation showing activity down to temperatures as low as  $-80^{\circ}\text{C}$ . However, the pure oxide catalyst seems to be strongly poisoned by water. Some studies indicate that combining CoOx with gold synergistically improves the catalytic performance and poisoning resistance<sup>2-3</sup>, but an understanding of this metal-oxide effect is lacking. To obtain an atomic scale understanding of the improved catalytic performance of combined Au-CoOx catalysts we have designed a model system where cobalt oxide nanoparticles are synthesized on an Au single crystal surface by physical vapor deposition in an oxygen environment<sup>4-5</sup>.

Here, we significantly advance the mechanistic understanding of cobalt oxide nanocatalysts for CO oxidation by studying the surface chemistry of the model catalyst under *operando* conditions. We use powerful near ambient pressure techniques such as scanning tunneling microscopy (NAP-STM) and synchrotron X-ray photoelectron spectroscopy (NAP-XPS) to study CoO<sub>x</sub> nanoislands on Au(111) at mbar pressure in a CO/O<sub>2</sub> gas mixture. From STM results, we find that the structure of the ~20nm wide monolayer cobalt oxide nanoislands is static during exposure to a mixture of CO and O<sub>2</sub> gases at a pressure of 1.5 mbar. Under these conditions at room temperature, the nanoislands seem to exhibit activity towards CO oxidation, and we can detect CO, CO<sub>2</sub> surface species by NAP-STM

experiments and by analysis of the corresponding O1s and C1s core level NAP-XPS spectra. In addition, we study the morphological evolution by NAP-STM and the reactivity of the CoO nanoislands from RT to 300°C under *operando* conditions. At around 200°C, CO<sub>2</sub> is found in gas phase and decreasing at the surface. Furthermore, to observe the influence of the substrate, we repeated the CoO nanoislands on Pt(111), obtaining similar reactivity results.

References:

1. Xie, X., et al., Nature 458 (2009): 746-749.
2. Cunningham, D. A. H., et al., Catal. Lett. 25 (1994): 257-264.
3. Liu, Y., et al., J. Catal. 309 (2014): 408-418.
4. Fester, J., et al., Nature Communications 8 (2017): 14169.
5. Walton, Alex S., et al., ACS Nano 9.3 (2015): 2445-2453.

9:20am **SS+HC+PS-FrM4 Reaction of 2-Propanol on SnO<sub>2</sub>(110) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy, J.T. Diulus, R. Addou, Gregory Herman**, Oregon State University

Tin dioxide (SnO<sub>2</sub>) has a wide range of applications, including gas sensors, transparent conductors, and oxidation catalysts. The surface chemistries for each of these applications can be strongly influenced by the surface structure and cation oxidation states. The oxidation of volatile organic compounds (VOC) has recently been demonstrated using SnO<sub>2</sub>, where 2-propanol was used as the probe molecule. More recently it was observed that the surface Sn<sup>2+</sup>/Sn<sup>4+</sup> ratio strongly influenced the activity of carbon monoxide oxidation. In this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to characterize the surface chemistry of 2-propanol on well-defined SnO<sub>2</sub>(110) surfaces. We have prepared stoichiometric and reduced surfaces which were characterized with both AP-XPS and low energy electron diffraction. AP-XPS was performed on these surfaces for 2-propanol pressures up to 1 mbar, various 2-propanol/O<sub>2</sub> ratios, and a range of temperatures. These studies allowed us to evaluate the chemical states of 2-propanol on the SnO<sub>2</sub>(110) surface under a wide range of experimental conditions. The effect of surface preparation, 2-propanol/O<sub>2</sub> ratios, and sample temperature was evaluated using AP-XPS and mass spectrometry. Using valence-band spectra, we have found that the surface was reduced from Sn<sup>4+</sup> to Sn<sup>2+</sup> when the sample was heated in 2-propanol and that the main reaction product in the gas phase was acetone. This suggests that the reaction occurs through a mechanism where bridging oxygens are hydroxylated upon adsorption of 2-propanol. These bridging hydroxyl groups can react and result in water desorption. This process leads to the reduction of the SnO<sub>2</sub>(110) surface. We have found that the low temperature AP-XPS spectra (300-400 K) was nearly identical for 2-propanol and 2-propanol/O<sub>2</sub> mixtures. After running the reactions at higher temperatures we found that the surface remained oxidized. Several oxidation products were also observed in the gas phase. Based on the experimental results we find that the surface was inactive for the oxidation of 2-propanol for temperatures below 500 K. With 2-propanol/O<sub>2</sub> mixtures the reactivity increased substantially at lower temperatures. Furthermore, we propose that in 2-propanol/O<sub>2</sub> mixtures the reaction occurs through a Mars-van Krevelen mechanism.

9:40am **SS+HC+PS-FrM5 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages, Daniel Killelea, M.E. Turano**, Loyola University Chicago; *R.G. Farber, K.D. Gibson, S.J. Sibener*, The University of Chicago; *W. Walkosz*, Lake Forest College; *R.A. Rosenberg*, Argonne National Laboratory

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O<sub>sub</sub>); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O<sub>sub</sub> into the selvedge alters the surface structure and chemistry. The oxygen - Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or

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subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O<sub>2</sub>. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of O<sub>sub</sub> and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O<sub>sub</sub> is present. This enhanced reactivity is located at the interface between the less reactive RhO<sub>2</sub>oxide and O-covered metallic Rh. These results reveal the conditions under which O<sub>sub</sub> is formed and stable, and show that O<sub>sub</sub> also leads to enhanced reactivity of oxidized metal surfaces.

10:00am **SS+HC+PS-FrM6 Molecular Processes on Icy Surfaces in the Interstellar Medium and the Outer Solar System**, *Edith Fayolle, R. Hodyss, P. Johnson*, Jet Propulsion Laboratory, California Institute of Technology; *K. Oberg*, Harvard University; *J-H. Fillion, M. Bertin*, Sorbonne Université

## INVITED

Molecular ices have been observed in various planetary and astrophysical environments: from patches in permanently shadowed regions on Mercury and the Moon, to the ice crust of outer Solar System bodies, and onto dust grains in prestellar cores, protostellar envelopes, and protoplanetary disks. Interstellar and planetary ices are mostly composed of H<sub>2</sub>O, and more volatile molecules, e.g. N<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NH<sub>3</sub>, held together as a solid through van Der Waals forces and dipole-dipole interactions, such as hydrogen bonding. They are found as mixtures or pure layers and display crystalline or amorphous structures.

Understanding ice formation, sublimation, and composition is crucial to interpret both gas phase and solid state observations, constrain the physical conditions encountered in space, and test for the likely chemical inheritance from star-forming environments to planetary systems. Vacuum and cryogenic techniques are used to reproduce astrophysical conditions and grow ice analogues. Analytical techniques, including IR-UV spectroscopy, mass spectrometry, and microgravimetry, are employed to measure fundamental parameters such as desorption, diffusion energies, and reactions products & rates in the solid phase.

In this talk, I will show several examples of astrochemical experiments relevant to icy environments. The fundamental parameters derived from these experiments are further used as inputs for astrochemical models simulating the formation and evolution of ices on various bodies. In some cases, these experiments can directly explain recent observations, for e.g., the unexpected variety of molecules detected in lunar cold traps by the Lunar Crater Observation and Sensing Satellite mission or the location of snowlines in protostellar and protoplanetary environments probed by radio-interferometers like the Atacama Large Millimeter Array.

10:40am **SS+HC+PS-FrM8 Bilayer Silicates as Models for Space-weather-mediated Water-cycling Processes at the Interface of Airless Bodies**, *B. Dhar, William E. Kaden*, University of Central Florida

Following recent observations indicating the presence of water and/or hydroxyl groups inhomogeneously distributed across the surface of the moon, many groups have worked to put forward feasible models necessary to rationalize both effects. From those models, there seems to be reasonable agreement that a solar-wind mediated, H<sup>+</sup> implantation-based mechanism is responsible for initial hydration/hydroxylation at the lunar surface. How and why the OH-group concentration varies with both latitude and longitude, however, remains debated in the literature. A recently reported kinetics model provided a plausible temperature-dependent recombinative desorption/dissociative readsorption pathway, which accurately predicts observed systematic trends in the concentration of OH groups as a function of latitude when also accounting for daily oscillations in photon and proton flux vs. latitude over long periods of time. Key to the postulated OH-group migration pathway is the presence of mineral surfaces with atypically low barriers to recombinative water desorption; something that varies with both surface composition/structure and OH group concentration. To account for the effects of the average lunar mineralogical surface composition, the author's simply modeled the moon as a homogenous distribution of simple binary oxides present at concentrations corresponding those associated with each of the corresponding metals.

In the work presented in this talk, we have used recently developed recipes allowing for the growth of extremely well-defined, atomically-planar, and crystalline silicate sheets to serve as tailor-designed analogues of mineralogically relevant structures containing deliberately varied surface sites expected to be present at the surface of the moon and elsewhere. More specifically, we have grown and fully characterized two bilayer films; one consisting of pure silica (SiO<sub>2</sub>) and the other present as a two-dimensional alumino-silicate (Al<sub>0.33</sub>Si<sub>0.67</sub>O<sub>2</sub>). Using temperature programmed desorption, we have then characterized differences in the OH-silicate interactions as a function of one deliberately varied surface-site's coordination, and then link our observations to help provide a more nuanced insight into how and why water may evolve and cycle into and out of the surface of airless bodies in the presence of the solar wind.

11:00am **SS+HC+PS-FrM9 Unraveling the Evolution of the Solid-Electrolyte Interphase Layer at Li-Metal Anodes**, *Venkateshkumar Prabhakaran, S. Roy, G.E. Johnson*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research; *M.H. Engelhard, V. Shutthanandan, A. Martinez, S. Thevuthasan*, Pacific Northwest National Laboratory; *K.T. Mueller, V. Murugesan*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research

Chemical transformations of electrolyte constituents (such as solvent and solvated electroactive ions) at the Li-metal electrode determine the evolution of the solid-electrolyte interphase (SEI). The ability to rationally design an SEI layer that will provide efficient charge transfer processes will improve the performance of Li-batteries. The main challenge is to unravel the complex set of interfacial reactions that occur during charge transfer processes and subsequently delineate the pathways of various decomposition reactions and phase formation. Herein, we report progress in understanding such complex interfaces using bottom-up assembly of solvated cations and bare anions of selected composition on Li-metal anodes. Soft landing of mass-selected ions, a versatile approach to surface modification, is ideally suited for building the interface with selected electroactive ions which will help unravel the complexity associated with the multitude of interfacial processes occurring during evolution of the SEI layer.<sup>1,2</sup> Ion soft landing combined with operando infrared reflection-absorption spectroscopy (IRRAS) and in-situ x-ray photoelectron spectroscopy (XPS) were used to characterize the decomposition of counter anions and solvent molecules on bare Li metal surfaces. Specifically, we soft-landed isolated electrolyte anions (e.g., bis(trifluoromethane)sulfonimide, TFSI<sup>-</sup>, polysulfides, S<sub>x</sub><sup>-</sup>) and solvated Li solvent cluster cations (e.g. Li-(dimethoxyethane)<sub>n</sub>) on bare Li metal surfaces without their corresponding counter ions, and monitored their spontaneous decomposition using IRRAS and XPS. Our in-situ multimodal measurements captured the spectroscopic signatures of reaction pathways of the electrolyte anions and solvent molecules on the reactive Li surface. We will discuss the evolution of the SEI layer based on multimodal spectroscopic analysis of electrochemical interfaces prepared using the ion soft landing approach. In particular, the chemical signatures of transient species that evolve during decomposition at well-defined interfaces will be discussed.

## References:

1. Johnson, G. E.; Hu, Q.; Laskin, J., Soft landing of complex molecules on surfaces. *Annual Review of Analytical Chemistry* **2011**, *4*, 83-104.
2. Prabhakaran, V.; Johnson, G. E.; Wang, B.; Laskin, J., *In situ* solid-state electrochemistry of mass-selected ions at well-defined electrode-electrolyte interfaces. *Proceedings of the National Academy of Sciences* **2016**, *113*, 13324-13329.

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