

Wednesday Morning, October 21, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

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

In-situ Studies Using X-ray Absorption Spectroscopy and Vibrational Spectroscopy for Catalytic and Energy Materials

Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:00am **IS+AS+SA+SS-WeM1 In Situ X-ray Absorption Spectroscopy Technique for Metal/Water Interface Characterization, Chenghao Wu***, University of California, Berkeley and Lawrence Berkeley National Laboratory, *J.-H. Guo, M.B. Salmeron*, Lawrence Berkeley National Laboratory

Most of the electrochemistry processes occur within the thin layer of electrolyte at the electrolyte/electrode interfaces, commonly denoted as the electrical double layer (EDL). Although some classic continuum theories about EDL have been established and widely accepted over the past century, very little experimental information is available regarding the molecular-level details at such solid/liquid interfaces. We have developed in-situ liquid cells to study such solid/liquid interfaces by means of soft x-ray absorption spectroscopy [1]. Because the fluorescence x-ray photon has much larger mean free path in condensed matters than the secondary electrons, by comparing the total fluorescence yield (TFY) and total electron yield (TEY) spectra, we can extract useful information about the compositional, structural or chemical difference between the bulk and the interfacial electrolyte. Under different bias, by modulating the incident x-ray, the TEY signal current becomes alternating and can be separated from the dominant faradaic current so that we can obtain surface-sensitive TEY signal under electrochemical conditions.

With this *in-situ* and *operando* XAS technique, we investigated the gold/water interface [1] and platinum/sulfuric acid solution interface. It was found that at gold/water interface, the interfacial water layer has significantly different hydrogen-bonding network structure compared to the bulk water. Under different bias, the polar water molecules respond to the external electrical field and reorient at the gold electrode surface, which significantly changes the amount of distorted or broken hydrogen bonds. First-principle simulations were able to corroborate the experimental results and qualitatively reproduce the change in the x-ray absorption spectra at different bias. In the platinum/sulfuric acid system, the charged solute species, such as SO_4^{2-} ions, hydronium ions, introduce extra complexity at the surface under different bias. Using the same *in-situ* technique, we were also able to identify some intermediate surface species in the potential window of OER reaction.

[1]. J.J. Velasco-Velez, C.H. Wu, T.A. Pascal, L.F. Wan, J.-H. Guo, D. Prendergast, and M. B. Salmeron, *Science*, **346**, 831-834 (2014).

8:20am **IS+AS+SA+SS-WeM2 Tip Enhanced Raman Spectroscopy (TERS) of Graphene Nano-Ribbons and Graphene on Au Surfaces: Imaging and Vibrational Spectroscopy of Surface Reaction Products, Delroy Baugh, S. Liu, T. Kumagai, M. Wolf**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces. TERS could therefore provide unique and heretofore unprecedented insight on adsorbate reactions at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well defined surface sites as well as monitor vibrational spectra to provide bond specific information about the reaction. However, in order to clarify the vibrational structure in TERS, the details of the enhancement mechanism and the issues regarding the plasmonic background that is almost always observed in TER spectra as well the "blinking" that occurs in the SERS part of TERS must be resolved. Towards this end here we will report studies of Graphene and Graphene Nanoribbons (GNR's) on Au surfaces as a model systems because their electronic and vibrational structure are clearly defined. Specifically, Near and Far-field Raman spectra will be reported for

these systems and the above issues will be addressed experimentally and a simple theoretical model will be presented for the TERS observations.

8:40am **IS+AS+SA+SS-WeM3 Isomerization of One Molecule Observed through Tip-Enhanced Raman Spectroscopy: Azobenzene Thiol on Au(111), Joonhee Lee, N. Tallarida, L. Rios, V.A. Apkarian**, University of California, Irvine

The reversible *cis-trans* isomerization of a single azobenzene thiol (ABT) molecule is captured in tip-enhanced Raman trajectories in which the anti-correlated flip-flop between discrete, on and off-states of the two structural isomers is seen. The strongly blue-shifted spectra are recorded from a molecule that appears at the junction plasmon of a scanning tunneling microscope (STM), consisting of an atomically flat Au(111) surface and a silver tip. The variation in frequencies of switching events identifies heterogeneously photocatalyzed chemistry. The chemisorbed ensemble of ABT molecules lie flat on Au(111) surface with azobenzene headgroup strongly coupled to the surface. Nevertheless, we establish through STM imaging that the ABT molecules undergo both current driven and photoinduced *cis-trans* isomerization. Rather than decoupling from the surface, we suggest that strong coupling of the reaction coordinate to a vibrational energy sink is required for *cis-trans* isomerization of azobenzenes on metal surfaces.

9:00am **IS+AS+SA+SS-WeM4 In Situ Characterization and Reaction Studies of $\text{MnO}_x/\text{Co}_3\text{O}_4$ Catalyst for CO and CO_2 Conversion, Walter Ralston, G. Melaet**, University of California, Berkeley, *S. Alayoglu*, Lawrence Berkeley National Laboratory (LBNL), *G.A. Somorjai*, University of California, Berkeley

As the energy and fuel demands of our growing world continue to increase, non-fossil fuel carbon sources are increasingly attractive – especially if these carbon sources can be easily converted to transportable fuels and higher-value chemicals. Much attention has been focused on carbon dioxide, as capture and storage technology has emerged to mitigate emissions and CO_2 can be used to produce methanol.

Recently, we reported a catalyst for the low-pressure conversion of CO_2 to methanol¹. Manganese oxide nanoparticles supported in mesoporous Co_3O_4 produced methanol in high yields and at significantly lower pressure conditions than typical Cu/ZnO catalysts used industrially. The advantage of this catalyst is in its lower pressure requirement, its high yield of methanol, and its evidence of carbon-carbon bond formation (10% ethylene production).

Catalytic testing of the material has shown the catalyst to be more than the sum of its parts; when each component is tested separately (MnO_x nanoparticles supported in SiO_2 ; mesoporous Co_3O_4 alone) CH_4 and CO are the major products. Preparation and testing of an inverse catalyst – CoO_x nanoparticles on a mesoporous MnO_2 support – proves the importance of the hybrid architecture in determining the selectivity of the catalyst, as the inverse catalyst is dominated by the selectivity of the support (>80% selective to CO).

Towards understanding this catalyst, in-situ X-ray Absorption Spectroscopy (XAS) utilizing both soft and hard x-ray energies has allowed for a detailed characterization of the catalyst under oxidation, reduction, and reaction conditions. In addition to CO_2 , in-situ characterization under CO hydrogenation conditions was used to understand the Fischer-Tropsch activity of the catalyst for making longer chain hydrocarbons. The results of these in-situ studies are correlated with catalytic reaction data to help understand the nature of the active site/interface and guide future catalyst design.

References

(1) C. S. Li, G. Melaet, W. T. Ralston, *et al.* High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis. *Nature Communications*, 6:6538, 2015.

9:20am **IS+AS+SA+SS-WeM5 In Situ and Operando Raman Methodology to Understand the States of Oxide Catalysts and Alkane Oxidative Dehydrogenation and Ammoxidation Reactions, Miguel A. Bañares**, Instituto de Catálisis y Petroleoquímica, Madrid **INVITED**

Operando methodology combines in situ spectroscopy during reaction with simultaneous performance measurement in a cell that behaves like a catalytic reactor. Operando methodology connects changes in the performance and in the structure in a simultaneous manner; this is fundamental to assess the structure-performance relationships at a molecular level.

Molecularly dispersed vanadia on oxide carriers is a key component in many catalytic formulations in environmental and selective oxidation and

* ASSD Student Award Finalist

ammoxidation catalysis. The actual state of vanadia catalysts in specific environments depends on its surface density, the nature of the support and the presence of additives. We will summarize our experience on the state of supported vanadia paying particular attention to how the environment and reaction conditions finally shape the structure of vanadia catalysts. *Operando* Raman spectroscopy is an invaluable approach to fully understand the actual state of the catalyst, its transformations during reaction and how these correlate with changes in catalytic performance.

A single technique, may not deliver the complete vista, thus collaboration with complementary talents and techniques is critical. We show the outcome of collaborations with theoretical chemistry approaches to bring the rationale behind structure-activity relationships inferred through *operando* Raman methodology. We also show the interaction with engineering approaches.

11:00am **IS+AS+SA+SS-WeM10 *Operando* Studies of Dynamic Restructuring of Working Catalysts by Correlated Imaging and Spectroscopy Probes, Anatoly Frenkel, Yeshiva University INVITED**

Understanding mechanisms of reactivity is often hindered by complexity of nanoscale supported metal catalysts. In the size range of 1-5nm, they feature a variety of structural motifs, sizes, shapes, compositions, degrees of crystalline order as well as multiple temporal scales. Hence, new experimental methodologies are called for, ones that are capable to capture not only the details of kinetic, dynamic and catalytic properties of metal clusters, but also their statistical distributions over ensemble of such clusters in a particular working catalyst, i.e., in reaction conditions. I will present our recent results obtained at the National Synchrotron Light Source, Advanced Light Source and Center for Functional Nanomaterials, where we combined x-ray absorption spectroscopy, high resolution transmission electron microscopy and micro-IR spectroscopy studies of a complex catalytic system *in operando*, using the same portable micro-reactor. This method will be illustrated on the example of supported Pt and Pd catalysts undergoing dynamic restructuring during ethylene hydrogenation reaction. Our results demonstrate a complexity of structures exhibited in this system and their dynamic, responsive transformations throughout changing reaction conditions. The new method is both general and generalizable to quantitative *operando* studies of complex material systems of broad interest to areas as diverse as catalysis science, applied physics and materials science, using a wide variety of x-ray and electron based experimental probes.

11:40am **IS+AS+SA+SS-WeM12 A Correlation of Raman and Single and Multiple Layer Graphene Conductivity as Detected with a Cryogenic Multiprobe AFM with On-line Raman, NSOM and Other SPM Modalities, Aaron Lewis, The Hebrew University of Jerusalem and Nanonics Imaging Ltd, Israel, O. Zinoviev, A. Komissar, E. Maayan, D. Lewis, Nanonics Imaging Ltd, Jerusalem, Israel**

It is a challenge to study 2D materials, such as Graphene, MoS₂, WSe₂, etc. at temperatures down to 10°K when one considers the wide variety of physical phenomena that have to be applied to get a full picture of the functionality of these materials. This involves questions of structure, nanometric photoconductivity, electrical properties, thermal properties, near-field optical in the apertured and scattering modes, Kelvin probe, and of course Raman. All of these phenomena are common not only to 2D materials but also to carbon nanotubes and related nanomaterials. This presentation will describe both the instrumental development of such a multiprobe cryogenic system that allows for state of the art on-line optical measurements and will also include a review of the probe developments that permit such multifunctional multiprobe operation with on-line full optical access. The system that will be described has a completely free optical axis from above and below that is not obscured by electrical or other probes that have been developed for this system for multiprobe operation. This permits on-line Raman and Tip Enhanced NanoRaman Scattering. With such a system we have investigated graphene and HfO₂ using multiprobe electrical, Kelvin probe, NSOM and on-line Raman. The results have yielded new insights into the chemical changes that are correlated to the electrical conductivity.

12:00pm **IS+AS+SA+SS-WeM13 Surface Structure and Chemistry of Rh(110)-1×2 Under Reaction Condition and During Catalysis explored with AP-XPS and HP-STM, Franklin (Feng) Tao, L. Nguyen, University of Kansas**

High pressure scanning tunneling microscopy (HP-STM), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and computational studies were used to study the surface chemistry and structure of Rh(110)-1×2 and Rh(110)-1×1 at atomic scale in CO at different pressure and different temperature, and during CO oxidation at different pressure and different temperature. In gas of CO at a low pressure of 8×10^{-8} Torr, a Rh(110)-1×2 covered with CO is formed at 25C by replacing the adsorbed oxygen atoms

adsorbed on Rh(110)-1×2 by CO molecules of gas phase. A pressure dependent structure of adsorbate layer of CO on Rh(110)-1×2 was revealed. In gas of CO at a high pressure of 0.08 Torr, the portion of CO molecules bound in atop configuration in the adsorbed layer increases along with the increase of pressure of CO gas though there is no restructuring of Rh(110)-1×2 at 25C in the pressure range of 8×10^{-8} to 0.8 Torr. This is supported by the calculated coverage-dependent binding energy of CO on this surface. At a relatively high temperature of 55C, Rh(110)-1×2 in 0.08 Torr CO is restructured to Rh(110)-1×1 (Figure 1b). This restructuring of surface restructuring is much lower than 153C for Rh(110)-1×2 in UHV. Theoretical simulation suggests that adsorbed CO molecules promote this restructuring compared to the restructuring in UHV since adsorption of CO on the intermediate structures of this restructuring in gas of CO lower the activation barrier of these intermediate structures. Rh(110)-1×2 is restructured to Rh(110)-1×1 during catalysis in the mixture of CO (0.08 Torr) and O₂ (0.02 Torr) even at 25C. Compared to the lack of restructuring in pure CO of 0.08 Torr at 25C, this restructuring during catalysis could result from a local heating of the catalyst surface by the exothermic reaction of CO oxidation. During CO oxidation, certain number of CO molecules are still remained on the catalyst surface. In the temperature range of 50-130C the active phase of catalysis is metallic Rh(110)-1×1. However, at 200C the active phase is surface rhodium oxide. These in-situ studies of surface structure and chemistry integrated with computational studies of Rh(110) in pure CO and in mixture of CO and O₂ clearly demonstrate the complexity of surface structure of a catalyst under reaction condition and during catalysis. The pressure-dependent structure of adsorbate layer, temperature-driven surface restructurings, generation of a new active surface phase of catalyst during catalysis, suggest the significance of in-situ studies of structure and chemistry of surface of a catalyst during catalysis.

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