

# Thursday Morning, November 12, 2009

## In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference Room: C4 - Session IS+SS-ThM

### In-Situ Spectroscopy - Interfacial Science & Catalysis Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-ThM1 Reduction of Cationic Sn in SnO<sub>x</sub>/PtSn Alloy Surfaces**, *G. Liu*, Lehigh University, *H. Bluhm*, Lawrence Berkeley National Laboratory, *B. Koel*, Lehigh University

Understanding mechanisms of catalyst selectivity requires improved knowledge of oxidation and reduction reactions that occur at the metal/metal oxide interface. We describe studies that probe the thermal stability and reducibility of cationic Sn at SnO<sub>x</sub>/PtSn alloy interfaces for several different and well-defined surface phases of SnO<sub>x</sub> that can be formed depending on the temperature. Our investigations covered a wide range of conditions, from vacuum to the chemical changes during exposures to H<sub>2</sub> at pressures up to 5 Torr by using in-situ high pressure photoelectron spectroscopy (HP-PES). We find enormous differences in the reducibility of cationic Sn species showing that local surface structure and composition plays an key role in governing these reactions. These studies help to define the overall chemical reactivity of SnO<sub>x</sub> species at these interfaces, and in particular, clarify the role of reduced and cationic Sn sites in selective hydrogenation of crotonaldehyde.

8:20am **IS+SS-ThM2 In-situ Study of the Oxidation of Pt(110)**, *M. Grass*, *D. Butcher*, *F. Aksoy*, *H. Bluhm*, *G.A. Somorjai*, *Z. Hussein*, Lawrence Berkeley National Laboratory, *B.S. Mun*, Hanyang University, Korea, *Z. Liu*, Lawrence Berkeley National Laboratory

The formation of oxides on transition metal surfaces has been actively studied because of its importance in understanding heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxides on Pt(110) has received much attention. Oxidation reactions over Pt are both industrially significant and fundamentally intriguing. In particular, there has recently been much debate over the surface structure and reaction mechanism of CO oxidation at high O<sub>2</sub>/CO ratios on Pt(110).

In this study, we used both ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and high pressure scanning tunneling microscopy (HP-STM) to investigate oxidation of Pt(110) as a function of O<sub>2</sub> pressure, temperature and gas composition (CO, O<sub>2</sub>). AP-XPS results demonstrate that two different surface oxygen species form on Pt(110) surface above 500 mTorr O<sub>2</sub>: chemisorbed oxygen and an island structured species that extends at least two Pt layers deep. HP-STM images under the same conditions confirm the formation of these oxide islands. We present here the pressure and temperature dependence of both oxygen species as well as kinetic measurements of the reaction CO<sub>ad</sub> + O<sub>ad</sub> → CO<sub>2</sub> for each of the adsorbed oxygen species.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Light Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

8:40am **IS+SS-ThM3 Composition and Chemistry of the Liquid/Vapor Interface by In-Situ X-ray Photoelectron Spectroscopy**, *J.C. Hemminger*, University of California, Irvine **INVITED**

We use synchrotron based x-ray photoelectron spectroscopy (XPS) experiments to study the composition and chemistry at the liquid/vapor interface of aqueous solutions. These experiments are motivated by an interest in the fundamental behavior of aqueous interfaces as well as applications to aqueous aerosols in the atmosphere. We take advantage of the variable energy characteristic of synchrotron radiation to carry out XPS experiments as a function of experimental probing depth, thereby generating a depth profile of the liquid/vapor interface. Recent experiments in which we have studied the composition of aqueous salt solutions in the presence of organic surfactants will be described. In addition, studies of acid/base equilibria at the liquid/vapor interface will be described. Our depth profile experiments show that the acid/base equilibrium at the solution surface is modified by the differences in bulk solubility of the acid and base involved in the equilibrium. Two different experimental approaches have been used: an ambient pressure end station at the Advanced light source is equipped with a differentially pumped electron

energy analyzer allowing studies with the sample chamber at pressures of a few torr. This system has been used to study saturated aqueous solutions of alkali halide salts. A liquid/jet endstation at the BESSY synchrotron has allowed us to study the surface segregation of molecular ions such as nitrate in aqueous solutions as a function of solution concentrations.

9:20am **IS+SS-ThM5 Oxidation Studies of Gold by in Situ High-Pressure X-ray Photoelectron Spectroscopy**, *F. Borondics*, *P. Jiang*, Lawrence Berkeley National Laboratory, *S. Porsgaard*, Lawrence Berkeley National Laboratory & iNANO University of Aarhus, Denmark, *M. Köber*, *A. Caballero*, *H. Bluhm*, *M. Salmeron*, Lawrence Berkeley National Laboratory

The high catalytic activity of nanometer size gold particles in various chemical reactions has been intensively investigated in the recent years. However the origin of the exceptional catalytic properties of Au is still strongly debated in many cases ranging from the mobilization of gold under catalytic conditions through the oxidation state of the active Au species during the reaction.

In this study we focus on the interaction of oxygen with Au that has been proposed to play an important role in the mechanism of oxidation reactions. Using in situ high-pressure X-ray photoelectron spectroscopy (HP-XPS) and in situ scanning electron microscopy we studied the different model systems, such as bulk gold, evaporated sub-monolayer and different size nanoparticle samples using single crystalline TiO<sub>2</sub> (110) as substrate.

Our results show that gold oxidation can be induced under certain conditions, such as high intensity X-rays or reactive ozone atmosphere. The existence of gold oxide has been mentioned in the literature, but our systematic studies provide a better understanding of the formation and stability of this compound, which is not only a chemical curiosity being the oxide of the noblest metal, but can be very important in designing more efficient catalysts. In addition, we would like to draw the attention of the community to a number of artifacts that can easily lead to misinterpretation of experimental data.

The implications of our results should be considered in the field of catalysis, nano- and surface science as well as in situ high-energy spectroscopies.

9:40am **IS+SS-ThM6 Anchoring of N3 Dye Molecule on TiO<sub>2</sub>(110) Surface and its Influence on Energy Level Alignments**, *P. Nachimuthu*, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *Z. Zhu*, *K.M. Beck*, *S. Thevuthasan*, *M.A. Henderson*, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the electronic coupling between the dye-sensitizer and TiO<sub>2</sub> determines the alignment of energy levels and the electron transfer dynamics. This electronic coupling is strongly modified by the way in which the dye molecules are adsorbed and anchored to TiO<sub>2</sub> surface, its relative orientations and geometrical structures. The present study is an attempt to understand how the dye molecules are bound to TiO<sub>2</sub> single crystal surface and their influence on the energy level alignments and electron transfer dynamics. Controlled adsorption of dye molecules (bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II) is known as N3) onto TiO<sub>2</sub> surface has been carried out to obtain desired anchoring and orientations by varying the concentration, hydrophobic substituents on dye and defect concentrations (in TiO<sub>2</sub>). ToF-SIMS and PEEM mapping techniques were used to understand the distribution of dye molecules on TiO<sub>2</sub> surface. The XPS and UPS measurements were carried out to determine the structural and electronic properties including the stoichiometry of dye molecules on TiO<sub>2</sub> surface, the relative energy levels and band offsets in the absence and presence of UV light. The XPS results show that the atomic ratios of S to Ru and N to S are ~1 and ~5, respectively, which correspond to a non-stoichiometric composition of N3 molecule on TiO<sub>2</sub> surface. The theoretical atomic ratios of S to Ru and N to S in N3 molecules are 2 and 3, respectively. This suggests that an isothiocyanide group from N3 molecule is lost from the surface of TiO<sub>2</sub>. The XPS from multilayers of N3 molecules on Si surface however show stoichiometric composition.

10:40am **IS+SS-ThM9 Scanning Transmission X-ray Microscopy of Inorganic and Organic Nanoparticles in the Environment**, *S.C.B. Myneni*, Princeton University **INVITED**

Inorganic and organic nanoparticles are common in the environment, and play an important role in the biogeochemical reactions occurring in the natural systems. However, their chemistry and behavior are poorly understood. Using STXM, researchers can examine the chemistry and mineralogy of these particles, and the functional group chemistry of associated organic molecules. While XANES spectral features are used routinely to identify the oxidation states of elements in minerals

successfully, fine variations in spectral features of minerals can be used in the identification of minerals and the crystallinity of precipitates/nanoparticles. The XANES spectra are also sensitive to different functional groups and their protonation (or deprotonation) and metal complexation; unique features in XANES spectra can also be used in mapping the distribution and relative concentrations of organic molecules and their complexes at a resolution better than 25 nm in environmental samples. In the last 4-5 years, we made significant progress in the understanding of the mineralogy and chemistry of important environmental nanoparticles and biominerals because of the development of STXM capabilities. A summary of applications of STXM in studying environmental nanoparticles, and highlights of some of these recent findings will be discussed.

11:20am **IS+SS-ThM11 In-situ Characterization of Arsenic on Model Iron Oxide Surfaces**, *S. Kaya, F. Mbuga*, SLAC National Accelerator Lab, *T. Kendelewicz*, Stanford University, *J. Newberg, H. Bluhm*, Lawrence Berkeley National Lab, *H. Ogasawara*, SLAC National Accelerator Lab, *G.E. Brown*, Stanford University, *A. Nilsson*, SLAC National Accelerator Lab

Natural contamination of groundwater by arsenic has become an important water quality problem in many parts of the world [1]. Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. Iron oxides play a significant role in controlling dissolved As concentration and limit the mobility and availability of As(III) and As(V). Arsenic adsorption mechanisms involve exchange of the As species for surface water and surface OH groups therefore in-situ characterizations of iron oxide surfaces in the presence of water are crucial.

We have studied chemical nature of As on Fe<sub>3</sub>O<sub>4</sub>(111) and Fe<sub>3</sub>O<sub>4</sub>(111)/Fe(OH)<sub>x</sub> thin films in the presence of water (P<0.5 Torr) using Ambient Pressure Photoemission Spectroscopy (APPES) at Advanced Light Source (ALS) [2]. Hydroxylation of pristine Fe<sub>3</sub>O<sub>4</sub>(111) surface commences at low relative humidity (RH) values and is followed by adsorption of molecular water with increasing RH. In 0.5 Torr water H<sub>2</sub>O:OH ratio at room temperature is about one and all acidic sites are fully hydroxylated. As 3d spectra taken in presence of 0.5 Torr water suggests that oxidation state of arsenic depends on degree of hydroxylation of iron oxide surfaces studied. In addition to the hydroxylation process, increasing RH leads to oxidation of arsenic from As(III) to As (V). Fe<sup>2+</sup> surface sites plays an important role in the oxidation states of arsenic and the reasons of which will be discussed based on the changes in formal charges during hydration-dehydration processes.

[1] R. Nickson, et. al., *Nature*, 395 338 (1998).

[2] H. Bluhm et al., *MRS Bulletin*, 34 1022 (2007).

11:40am **IS+SS-ThM12 Kinetic Studies of the Dissociation of Molecular Oxygen on Pt(111)**, *H. Ogasawara, L.-Å. Näslund, D.J. Miller, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

Thermally programmed X-ray photoelectron spectroscopy was used to study the dissociation of molecular oxygen on Pt(111) under ultrahigh vacuum conditions. Sub-monolayer coverages of molecular oxygen were dosed onto a clean crystal of Pt(111) at 60 K, a temperature well below the dissociation onset of roughly 95 K. Kinetic analysis of the XPS data indicate that they are consistent with a barrier to O<sub>2</sub> dissociation that is less than 0.4 eV. This result is in striking contrast to the most recent theoretical studies with density functional theory, which all indicate barriers in excess of 0.5 eV (0.5 - 0.9 eV). On the basis of this low observed barrier, we speculate that the direct dissociation of molecular oxygen could be a viable alternative to the associative and peroxide pathways that are presently assumed to be operative in the oxygen reduction reaction.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Aksoy, F.: IS+SS-ThM2, 1  
Anniyev, T.: IS+SS-ThM12, 2

## — B —

Beck, K.M.: IS+SS-ThM6, 1  
Bluhm, H.: IS+SS-ThM1, 1; IS+SS-ThM11, 2;  
IS+SS-ThM2, 1; IS+SS-ThM5, 1

Borondics, F.: IS+SS-ThM5, **1**  
Brown, G.E.: IS+SS-ThM11, 2  
Butcher, D.: IS+SS-ThM2, 1

## — C —

Caballero, A.: IS+SS-ThM5, 1

## — G —

Grass, M.: IS+SS-ThM2, **1**

## — H —

Hemminger, J.C.: IS+SS-ThM3, **1**  
Henderson, M.A.: IS+SS-ThM6, 1  
Hussein, Z.: IS+SS-ThM2, 1

## — J —

Jiang, P.: IS+SS-ThM5, 1

## — K —

Kaya, S.: IS+SS-ThM11, **2**  
Kendelewicz, T.: IS+SS-ThM11, 2  
Köber, M.: IS+SS-ThM5, 1  
Koel, B.: IS+SS-ThM1, **1**

## — L —

Liu, G.: IS+SS-ThM1, 1  
Liu, Z.: IS+SS-ThM2, 1

## — M —

Mbuga, F.: IS+SS-ThM11, 2  
Miller, D.J.: IS+SS-ThM12, **2**  
Mun, B.S.: IS+SS-ThM2, 1  
Myneni, S.C.B.: IS+SS-ThM9, **1**

## — N —

Nachimuthu, P.: IS+SS-ThM6, **1**  
Näslund, L.-Å.: IS+SS-ThM12, 1

Newberg, J.: IS+SS-ThM11, 2

Nilsson, A.: IS+SS-ThM11, 2; IS+SS-ThM12, 2

## — O —

Ogasawara, H.: IS+SS-ThM11, 2; IS+SS-ThM12,  
2

## — P —

Porsgaard, S.: IS+SS-ThM5, 1

## — S —

Salmeron, M.: IS+SS-ThM5, 1  
Somorjai, G.A.: IS+SS-ThM2, 1

## — T —

Thevuthasan, S.: IS+SS-ThM6, 1

## — Y —

Yu, Z.Q.: IS+SS-ThM6, 1

## — Z —

Zhu, Z.: IS+SS-ThM6, 1