

Wednesday Afternoon, October 31, 2012

Surface Science

Room: 21 - Session SS-WeA

Catalysis on Metals and Alloys

Moderator: G. Fisher, University of Michigan

2:00pm **SS-WeA1 A Novel MoS_x Structure with High Affinity to Adsorbate Binding**, *D.Z. Sun, W.H. Lu*, University of California Riverside, *D. Le*, University of Central Florida, *Q. Ma*, University of California Riverside, *M. Amanpour*, University of Central Florida, *S. Bobek, J. Mann*, University of California Riverside, *T. Raman*, University of Central Florida, *L. Bartels*, University of California Riverside

MoS₂ is a semiconducting material consisting of sulfur-molybdenum-sulfur tripledecker layers loosely bound by van der Waals interactions. Single layer MoS₂ can be exfoliated mechanically similar to graphene. This presentation shows an alternative avenue for the fabrication of MoS₂ monolayers at comparatively low temperature and mild conditions through sulfur loading of a copper substrate using thiophenol followed by the evaporation of Mo atoms and annealing. Here we also demonstrate that another MoS_x structure can be formed in this fashion, which has a far higher affinity to adsorbate interaction. Using anthraquinone and formic acid as test molecules, we titrate the various MoS_x and copper-based structures presented on our substrate in order to determine the relative strength of adsorbate interaction.

2:20pm **SS-WeA2 Atomic-Scale Determination of the Crystallographic Stacking at the Technologically-Important Cobalt-Copper Interface**, *E.A. Lewis, C.H. Sykes*, Tufts University

The deposition of Co on Cu has been studied extensively due to the use of layered Co/Cu systems in giantmagnetoresistance devices and the application of magnetic Co nanostructures in spintronics. Co deposited on Cu follows a Volmer-Weber type growth mechanism, forming bilayer-high, triangular islands. These islands grow in two orientations that are rotated 60° with respect to each other. The formation of triangular islands is dictated by the six-fold symmetry of the underlying Cu lattice, and triangular growth is preferred to hexagonal growth due to favored diffusion of Co from the (100) to the (111) facet of the islands during deposition. The consequence of this diffusion is that there must be a difference in the crystallographic packing between the two orientations of the islands. It is thought that one packing configuration of the Co islands is fcc, in which Co follows the stacking of the underlying Cu, but the second packing structure is still debated. Here we use low-temperature scanning tunneling microscopy to explore the stacking of these islands through adsorption of hydrogen on their surfaces.

Hydrogen adsorbs dissociatively on Co, and prefers to bind to fcc three-fold hollow sites, although it is calculated that there is only a 0.01 eV difference in the binding energy of hydrogen to fcc hollows vs. hcp hollows. We show that at 80 K, hydrogen is present on the Co surface in both adsorption sites, and that there is an electronic difference between the two states that is apparent in our STM images. Through high-resolution imaging of the hydrogen at the boundary between the two adsorption sites, we have been able to deduce the stacking of the underlying Co island lattice. We confirm that the majority orientation of the islands is indeed fcc stacking, and the minority of the islands follow Co's native hcp stacking. This has important ramifications in the development of Co/Cu/Co systems for GMR devices, as the interface between the two metals can significantly affect electron scattering.

2:40pm **SS-WeA3 Understanding the Growth and Surface Activity of Oxide-supported Bimetallic Clusters**, *R.P. Galhenage, H. Yan, A. Duke, K. Xie, D.A. Chen*, University of South Carolina **INVITED**

The nucleation, growth and surface composition of bimetallic clusters on titania have been investigated as model systems for understanding how surface chemistry can be controlled by bimetallic composition and interactions between the clusters and the oxide support. Specifically, we have focused on Au-based bimetallic systems (Au-Pt, Au-Ni, Au-Co) as well as Co-Pt systems. Scanning tunneling microscopy studies demonstrate that bimetallic clusters can be formed via sequential deposition when there is a difference in mobility between the two metals; the more mobile atoms (i.e. Au) can be nucleated at existing Ni, Pt and Co clusters. The surfaces of the Au-containing bimetallic clusters are almost pure Au at Au compositions greater than 50% due to the lower surface free energy of Au compared to other metals. In contrast, the Co-Pt clusters are rich in Pt despite the lower surface energy of Co. In the Au-containing bimetallic clusters, CO and methanol adsorbates induce diffusion of Pt and Ni to

surface, whereas this effect is not observed for CO on Au-Co. The activity of these model surfaces have been studied in a prototype recirculating loop microreactor.

4:00pm **SS-WeA7 Synchrotrons, Catalysts and UOP: from Imaging to In Situ Spectroscopy**, *S.R. Bare*, UOP LLC, a Honeywell Company **INVITED**

The characterization methods available at today's synchrotron light sources are ideally suited to unravel the complexity of a practical working catalyst. This will be illustrated using examples from our work using a combination of synchrotron techniques including: (i) X-ray micro- and nano-tomography, (ii) X-Ray microprobe fluorescence and X-ray microprobe absorption fine structure (XAFS), and (iv) in situ XAFS combined combined with density functional theory (DFT) and DFT/MD calculations. Indeed, the use of in situ XAFS is now an integral catalyst characterization technique at UOP. The method provides detailed element-specific atomic-level structural and chemical information of the active catalyst. Often this information cannot be obtained by any other method. We have developed and implemented the appropriate equipment to allow these in situ studies to be performed. This equipment ranges from a plug flow reactor that operates at high pressure, to equipment that allows rapid collection of XAFS data from multiple samples simultaneously. These reactors are coupled to an automated gas manifold combined with on-line product analysis. Examples of our recent work will be presented. Each example will highlight a different aspect of the use of in situ XAFS in an industrial research environment. These examples will include in situ sulfidation of experimental hydroprocessing catalysts, and operando XAFS of rhenium-based catalysts. The talk will end with a look to the future.

4:40pm **SS-WeA9 Glycolaldehyde as a Probe Molecule for Biomass-derivatives**, *W. Yu, M. Barteau, J. Chen*, University of Delaware

Controlling the activity and selectivity of converting biomass-derivatives to syngas (H₂ and CO) is critical for the utilization of biomass feedstocks as renewable sources for chemicals and fuels. One key chemistry in the conversion is the selective bond scission of the C-OH and C=O functionalities, which are present in many biomass-derivatives. Because of the high molecular weight and low vapor pressure, it is relatively difficult to perform fundamental surface science studies of C6 sugars, such as glucose and fructose, using ultrahigh vacuum (UHV) techniques. Glycolaldehyde (HOCH₂CH=O) is the smallest molecule that contains both the C-OH and C=O functional groups, as well as the same C/O ratio as C6 sugars, and thus is selected as a probe molecule in the current study to determine how the presence of the C=O bond affects the reaction mechanism. Using a combination of density functional theory calculations and experimental measurements, our results indicate that the reaction pathway of glycolaldehyde to produce syngas can be enhanced by supporting monolayer Ni on a Pt substrate, which shows higher activity than either of the parent metals. Based on the comparison of the activity and reaction intermediates of ethylene glycol and glycolaldehyde, the presence of the C=O functionality enhances the activity on the Pt(111) surface. On the other hand, for surfaces with high activity toward the O-H bond scission, such as NiPt(111), the presence of C=O does not significantly affect the activity or reaction pathway of C2 oxygenates. Furthermore, the Pt substrate can be replaced by tungsten monocarbide (WC) to achieve similar activity and selectivity, indicating the possibility of using Ni/WC to replace Ni/Pt as active and selective catalysts with higher stability and lower cost.

5:00pm **SS-WeA10 Modifying Selectivity of Hydrocarbon Conversion Reactions by Alloying Sn and Pt: Benzene Formation from Acetylene**, *X. Yang*, Princeton University, *J. Gao, S. Podkolzin*, Stevens Institute of Technology, *B. Koel*, Princeton University

Bimetallic catalysts involving Sn and Pt have important applications in hydrocarbon conversion catalysis. We have performed experiments probing chemisorption and reaction kinetics on well-defined, ordered Pt-Sn surfaces in order to aid developments needed for improving catalyst selectivity and overall performance. One specific example from investigations of benzene formation from acetylene on Pt-Sn alloys with HREELS, TPD, and DFT calculations will be discussed. On Pt(111), $\mu_3\text{-}\eta^2$ -acetylene chemisorbed in a three-fold site is the most stable configuration, as indicated by DFT calculations, and has a C-C stretching frequency (ν_{CC}) of 1310 cm⁻¹. This configuration becomes less thermodynamically favorable in the presence of Sn compared to the bridge-bonded $\mu_2\text{-}\eta^2$ configuration ($\nu_{CC} = 1495$ cm⁻¹). The ν_{CC} peaks at ~1600 cm⁻¹ are assigned to π -bonded acetylene, which dominate the spectra collected at 90 K. Absence of three-fold Pt sites on the Pt₃Sn alloy inhibits the transformation of acetylene to CCH₂, and the ν_{CC} peak at 1412 cm⁻¹ assigned to CCH₂ appears only in the spectra of the Pt₃Sn alloy. DFT calculations show that the destabilizing effect of Sn alloying is

more significant for CCH₂ and CCH + H than for acetylene. This change in relative stability increases the barrier for acetylene decomposition and makes associative reactions more likely. Results from DFT calculations indicate that benzene formation on the Pt-Sn alloys proceeds through the formation of an upright cyclic C₆H₄ intermediate, which is predicted to produce benzene by reacting with an additional surface acetylene. This closely integrated experimental-computational study has enabled us for the first time to characterize the adsorption modes of acetylene on Pt-Sn alloys. In addition, we developed a molecular level reaction mechanism for benzene formation by consolidating HREELS and TPD experimental results with DFT calculations. The presence of Sn changes the preferential adsorption sites for hydrocarbons, decreases the stability of adsorbed species to varying degrees, and favors associative reactions, thus, enabling benzene production by cyclotrimerization of acetylene.

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5:20pm **SS-WeA11 Composition Spread Alloy Films for Study of Alloy Catalysis Across Composition Space**, *A.J. Gellman, B. Fleutot, P. Kondratyuk, J.B. Miller, G. Gumuslu*, Carnegie Mellon University

Composition spread alloy films (CSAFs) are alloy libraries that contain a continuous distribution of alloy compositions (A_xB_yC_{1-x-y}). Spatially resolved measurements of catalytic reactivity across CSAF libraries map catalytic reactivity as function of alloy composition. In many implementations CSAFs span continuous regions of ternary alloy composition space, but not the entire composition space. We describe the design and implementation of a method for deposition of a 1x1 cm² CSAF that contains all possible compositions of a ternary alloy (A_xB_yC_{1-x-y} with $x = 0 \rightarrow 1$ and $y = 0 \rightarrow 1-x$), all three binary alloys (A_xB_{1-x}, A_xC_{1-x}, and B_xC_{1-x} with $x = 0 \rightarrow 1$) and all three pure component species. These CSAFs can be characterized using a number of methods including energy dispersive spectroscopy, electron back scatter diffraction, x-ray photoemission spectroscopy, and low energy ion scattering spectroscopy. The bulk structure of Cu_xPd_{1-x} binary CSAFs matches that of the bulk phase diagram. XPS and LEISS show that the surface is enriched in Cu across the entire composition space. The catalytic reactivity of Cu_xPd_{1-x} binary CSAFs a Cu_xAu_yPd_{1-x-y} ternary CSAF have been mapped across composition space using a 100 channel microreactor array. The reactivity changes with bulk composition can be correlated to the electronic structure of the alloys. The suite of methods allows a comprehensive study and understanding of alloy catalysis across composition space.

5:40pm **SS-WeA12 Role of Dissociated Hydrogen in Stabilizing Catalytic Sites and Regulating Surface Reactions for Hydrogen Storage in Metal Hydrides**, *I. Chopra*, University of Texas at Dallas, *S. Chaudhuri*, Washington State University, *J.-F. Veyan, Y.J. Chabal*, University of Texas at Dallas

There has been an ongoing quest to find cheaper hydrogen activation routes based on aluminum. Recently it was shown that aluminum doped with very small amounts of Ti can activate molecular hydrogen at temperatures as low as 90K. The method is based on the ability to introduce a high flux of molecular hydrogen seeded with a guest molecule (CO) to probe the catalytic activity and H₂ dissociation. Once dissociated, hydrogen forms a complex with adsorbed CO (CO-H), characterized by a substantially and uniquely blue-shifted CO internal frequency.

We use this new method to determine that Titanium when present on the surface is catalytically more active (~30%) than subsurface Titanium. Dissociated hydrogen stabilizes Ti on the surface and as the surface becomes saturated with hydrogen it is possible for Ti atoms sitting in originally sub surface configurations to be pulled out of their original positions by the dissociated hydrogen into surface configurations. These "pulled" Ti atoms then contribute towards additional hydrogen activation when Ti is present in specific (nearest neighbor and next nearest neighbor) configurations.

Finally we show that this dissociated hydrogen protects the CO in the CO-H complex from additional reactions as is demonstrated by no isotopic exchange between CO16 and CO18. Dissociated hydrogen is present in the hollow sites around the Ti and protects the Ti-Al back-bond from further chemical activation. Similar experiments performed on surfaces with no hydrogen (Al/Ti, AlO/TiOx) show isotopic exchange reactions between CO16 (of the complex) and adsorbed CO18. The barrier for this isotopic exchange is the lowest for adsorbed CO on TiOx (desorption temperature ~140K) and highest for CO on Ti (desorption temperature ~>300K).

These results provide critical information about the role of dissociated hydrogen in stabilizing Ti catalytic sites and the CO-H complex. A complete understanding of such mechanisms will help enhance material performance for hydrogen activation using cheap catalyst materials.

References:

- [1] Chopra, I. S., Chaudhuri, S., Veyan, J.-F., and Chabal, Y. J., *Nature Materials*, 10, 884–889 (2011)

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