

Wednesday Morning, November 2, 2011

Surface Science Division

Room: 109 - Session SS2-WeM

Chemisorption on Metal & Oxide Nanoparticles

Moderator: B. Roldan Cuenya, University of Central Florida

8:00am **SS2-WeM1 Temperature Program Desorption and X-ray Photoelectron Spectroscopy Study of Cu_x on CeO₂/YSZ (111)**, *J.C. Lofaro, Jr.*, Stony Brook University, *M.G. White*, Stony Brook University and Brookhaven National Laboratory

Energy research has increased in importance in the past decade due to our growing understanding of climate science and rising oil prices. Many catalysts center around expensive and rare transition metals, such as Pt and Pd, supported on oxide substrates. However, copper, a relatively cheap and abundant metal, supported on metal oxides has been used as a heterogeneous catalyst in industrial settings for various chemical processes.^{1,2} Recent works have shown that copper nanoparticles supported on metal oxides (ZnO, CeO₂, TiO₂) have higher activity for the water gas shift reaction (WGS) as well as other important chemical reactions when compared to their individual components.^{3,4} Understanding how these complex catalysts work on a fundamental level will allow for the design and implementation of more efficient and selective systems in the future. Here, using a homemade thermal evaporator, a model system of copper nanoparticles deposited on CeO₂ films (200 nm thick) grown on YSZ (111) single crystals is used. X-ray photoelectron spectroscopy (XPS) is used to characterize the oxidation state of supported copper nanoparticles and temperature programmed desorption (TPD) is used to probe their reactivity and thermal stability. Copper coverages ranging from 0.25ML to 1ML are investigated. Carbon monoxide and water are used as probe molecules since they are the reactants involved in the WGS. We have found that copper's stability is highly temperature dependent and have found evidence of its encapsulation by the support.

1. K. Klier, *Adv. Catal.*, 1982, 31, 243.

2. J. C. Bart and R. P. A. Sneedon, *Catal. Today*, 1987, 2, 124.

3. J. A. Rodriguez, P. Liu, J. Hrbek, J. Evans, M. Pérez, *Angew. Chem. Int. Ed.* 2007, 46, 1351.

4. X. Zhao, J. A. Rodriguez, J. Hrbek, M. Pérez, *Surface Science*, 2005, 600, 229.

8:20am **SS2-WeM2 X-ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy Characterization of the Active Edge Sites of MoS₂ Nanoclusters**, *A. Tuxen, S. Porsgaard, H. Goebel, F. Besenbacher, J.V. Lauritsen*, Aarhus University, Denmark

The atomic and electronic structure of MoS₂ nanoclusters is of considerable interest due to the catalytic application of MoS₂ in e.g. hydrotreating catalysis of crude oil and in photocatalysts and hydrogen evolution reactions. Previous atom-resolved STM results have shown in great detail that both the overall morphology and in particular the edge structure of MoS₂ nanoclusters, which are known to contain the most catalytically active sites for hydrotreating and H₂ dissociation, adopt a structure which is very dependent on the conditions under which the cluster are kept. Under sulfiding conditions, atom-resolved STM images show that the MoS₂ nanoclusters expose fully sulfide edges, whereas activation by H₂ or mixed H₂/H₂S exposures show that sulfur vacancies and S-H form on the cluster edges reflecting the MoS₂ catalyst in its active state. To dynamically follow such structural changes at the MoS₂ edges induced e.g. by hydrotreating reaction conditions we have here combined high-resolution x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) studies of single-layer MoS₂ nanoclusters with a well known structure. The XPS studies done on well-characterized samples reveal a set of edge specific core level shifts in the Mo3d photoemission peak that can be uniquely associated with the fully sulfide edges, edge with S vacancies or fully reduced edges. The XPS fingerprint thus allows us to dynamically follow changes between the catalytically active states of MoS₂ when exposed to sulfiding of sulfuroreductive conditions. Preliminary *in-situ* XPS results on the same MoS₂ samples obtained under a 10⁻² torr H₂ atmosphere on the Ambient Pressure X-ray Photoelectron Spectroscopy on beamline 11.0.2 of the Advanced Light Source Berkeley show a characteristic sequence of sulfur reduction steps on the catalytically interesting edges followed by decomposition of MoS₂ at higher temperatures. The present studies thus successfully shows that XPS in combination with STM can be successfully used as a tool to characterize the chemistry of highly dispersed active sites of well-defined nanoclusters, such as the active edges on MoS₂.

8:40am **SS2-WeM3 Charge-Mediated Chemisorption on Supported Clusters**, *M. Sterrer*, Fritz-Haber-Institute of the Max-Planck-Society, Germany **INVITED**

Among the many factors that influence catalytic activity of supported metal clusters, the effects of size and charge state of the clusters are most frequently discussed, e.g., in CO oxidation over supported gold. In this contribution, I will present results of our recent experimental efforts to characterize metal clusters supported on single-crystalline model oxide surfaces, using Au on MgO thin films as example. Using a combination of various surface science techniques including low-temperature scanning tunneling microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, and electron paramagnetic resonance, the properties of supported Au atoms and clusters were addressed in detail. Starting with the unusual CO chemisorption behavior of single Au atoms on the perfect MgO(001) surface, I will move on and show how the charge state of Au particles on the MgO surface, which in most cases is inferred from distinct CO chemisorption features, may be influenced by modification of the oxide surface, e.g. by their interaction with defects or hydroxyl groups, or by the MgO film thickness.

9:20am **SS2-WeM5 The Structure and Chemical Activity of Two-dimensional Gold Islands on Single-layer Graphene/Ru(0001)**, *L. Liu*, Texas A&M University, *Y. Xu*, Oak Ridge National Laboratory, *Z. Zhou*, Texas A&M University, *Q. Guo*, Chinese Academy of Sciences, China, *Z. Yan*, *Y. Yao*, Texas A&M University, *L. Semidey-Flecha*, Oak Ridge National Laboratory, *D.W. Goodman*, Texas A&M University

Single-layer graphene supported on transition metals provides a unique substrate for synthesizing metal nanostructures due to the high crystallographic quality, thermal stability, and chemical inertness of the graphene. Contrary to its formation of three-dimensional (3-D) nanoclusters on graphene supported on a SiO₂ substrate, Au forms two-dimensional (2-D) islands on graphene moiré/Ru(0001). These Au islands maintain their 2-D structures up to 1 monolayer (ML) equivalent of Au dosage and are stable at room temperature. Our scanning tunneling microscopy study further shows that the 2-D Au islands are most likely two layers high, and conform to the graphene moiré in the lateral direction. Spin- and angle-resolved photoemission studies indicate even though these Au islands are largely electronically isolated, a weak through-graphene coupling exists between the Au islands and the Ru(0001) substrate. The structure for these 2-D Au islands and the corresponding electronic band structures are proposed based on DFT calculations.

Parallel studies using polarization modulation infrared reflection absorption spectroscopic (PM-IRAS) and high resolution electron energy loss spectroscopic (HREELS) indicate that CO adsorbs on these 2-D gold islands at 85 K with a characteristic CO stretching feature at 2095 cm⁻¹ for a saturation coverage. Preliminary data obtained by dosing molecular oxygen onto this CO pre-covered surface suggest that the 2-D gold islands catalyze the oxidation of CO. These electron-rich, weakly coupled 2-D Au islands provide a unique platform to study the intrinsic catalytic activity of low-dimensional Au nanostructures.

9:40am **SS2-WeM6 Spatially Resolved Measurements of Catalytic Activity on Variable-Composition Pd-Cu and Pd-Cu-Au Thin Films using a Microfluidic Reactor Array**, *P. Kondratyuk*, *G. Gumuslu*, Carnegie Mellon University, *B.D. Morreale*, National Energy Technology Laboratory, *J.B. Miller*, *A.J. Gellman*, Carnegie Mellon University

A new experimental approach to mapping the relationship between composition and catalytic activity in metal alloy catalysts is presented. We apply this methodology to study H₂-D₂ exchange reaction on Pd-Cu and Pd-Cu-Au alloys. The activity measurements were performed on thin alloy films deposited in such a way that the elemental composition varied continuously across the film. We refer to these films as composition spread alloy films (CSAFs). CSAFs were prepared by co-deposition of Pd, Cu and Au onto a molybdenum substrate under UHV conditions. The top-layer and near-surface composition of the CSAFs were determined by low-energy ion scattering (LEIS) and X-ray photoemission spectroscopy (XPS) respectively. The activity of the alloy films in the H₂-D₂ exchange reaction was analyzed at atmospheric pressure using a 100-channel glass microfluidic device. During the spatially-resolved activity measurements, the microfluidic device delivers reactant gases to a 10x10 array of measurement points on the CSAF surface covering an area of 1 cm², each measurement point corresponding to a different catalyst composition. After coming in contact with the catalyst, the gases are withdrawn for mass-spectrometric analysis through a separate set of channels. The activity-composition relationship can then be established by correlating the XPS (or

LEIS) data with the product concentration in each channel of the microfluidic device.

10:40am SS2-WeM9 Surface Structure Dependence by Monofaceted CeO₂ Nanoparticles: Catalytic Oxidation Reactions, M. Li, Z. Wu, F.C. Calaza, D.R. Mullins, S.H. Overbury, Oak Ridge National Laboratory

Reducibility of pure and doped CeO₂ is of interest in emission control catalysts because of the ability of the CeO₂ to store and supply oxygen during oxidation catalysis. But, it is not known how the structure or crystallographic termination of the CeO₂ affects the catalytic reaction rates and selectivity. Using CeO₂ nanoparticles with controlled shapes including cubes, octahedra and rods that are terminated on (100), (111) and (110) surfaces respectively, we have investigated this structure dependence. Temperature programmed desorption, temperature programmed reaction, flow reactor rates, and in situ DRIFTS were used to probe adsorption states, desorption, reaction, oxidation rates and product selectivity for CO and ethanol oxidation. Results show pronounced differences between the three different morphologies. All morphologies show evidence of surface ethoxide species at room T, but during subsequent TPD, the DRIFTS exhibits variation in surface species between the different surfaces with evidence for formation of adsorbed acetaldehyde and acetate. Temperature induced changes in the C-H stretching regions, different also for each polymorph, suggest competing dehydrogenation and dehydration of surface species. Desorption temperatures and product distributions also vary. The ratio of H₂/H₂O, and the H₂ peak desorption temperature is highest for the octahedra, consistent with its highest vacancy formation energy and therefore least available oxygen. This ratio is lowest for high surface area multi-faceted nanoparticles, and its variability has important implications for tailoring and understanding CeO₂ catalysts or supports for production of H₂ in ethanol fuel cells. Product profiles during TPR of ethanol in O₂ were also dependent upon the surface structure. Octahedra show the highest selectivity to acetaldehyde and an onset of H₂ evolution above 400 °C while the cubes and rods showed lower temperatures for the onset of H₂, indicating that the hydrogen is evolved by two different pathways on different shaped ceria. Similarly, in a steady state flow reactor, the ratio of selective oxidation product (acetaldehyde) to the total oxidation product (CO₂) followed the order (111) > (100) > (110). Such results provide a basis for fundamental understanding of how surface coordination, bonding, decomposition and reaction are affected by the atomic structure of an oxide surface, especially important for reducible oxides.

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11:00am SS2-WeM10 Tuning the Adsorption Properties of an Oxide Material Via Doping: Au Clusters onto Cr-doped MgO(001) Films, F. Stavale, N. Nilius, H.-J. Freund, Fritz-Haber-Institute of the Max-Planck-Society, Germany

The doping of metal oxides has been explored in several investigations with the aim to prepare better materials for catalysis, optics and electronic applications. Doping of wide-gap oxide materials can be realized by the controlled introduction of various types of lattice defects, including point defects such as oxygen vacancies, line defects (e.g. grain boundaries and dislocations) and impurity atoms. In this study, we have exploited photon-scanning tunneling microscopy used in imaging as well as in cathode-luminescence mode to investigate Au clusters supported on thin, single crystalline MgO(001) and Cr-doped MgO(001) films grown on Mo(001). First of all, we have prepared Cr-doped MgO films on a Mo(001) support as a model system for a transition-metal doped wide-gap insulator with interesting applications in catalysis. To elucidate the role of the Cr in the MgO matrix, the morphological and optical properties of the system were analyzed as a function of the Cr load, using the STM. The Cr was incorporated into the film either by Cr-Mg co-deposition in oxygen or post-evaporation followed by an annealing step. From the distinct light emission properties of the doped oxide, a detailed picture has been developed on the Cr³⁺ position inside the MgO lattice and the associated modifications in the electronic structure. The role of the Cr dopants on the adsorption behaviour of the oxide film was investigated by depositing small amounts of Au. While on pristine MgO films, Au nucleates into 3D particles, mainly 2D aggregates form on the doped oxide support. We assign this change in the Au growth mode to charge transfer processes from the Cr centres into the Au clusters and will discuss possible consequences on the chemical activity of the doped metal-oxide system.

11:20am SS2-WeM11 Hydrogen Adatom Manipulation on the Rutile TiO₂(110) Surface using LT-STM, P. Sutter, D. Acharya, N. Camillone III, Brookhaven National Laboratory

Characterization and control of the structure of TiO₂ surfaces at the single-atom level are vital to the development of a fundamental understanding of the chemistry and physics of this technologically important oxide. In this

work we investigate the use of a low-temperature scanning tunneling microscope (LT-STM) tip to manipulate individual hydrogen adatoms on the rutile TiO₂(110) surface at 77 K. We show that applied voltage pulses are effective for transferring hydrogen atoms from the surface to the STM tip with single-atom control. This tip-induced 'desorption' is useful for unambiguously distinguishing between surface hydroxyls (OH_{br}) and bridging oxygen (O_{br}) vacancies—two common surface defects whose appearance in STM images is quite similar. In addition we show that individual atoms can be redeposited on the surface precisely at selected O_{br} sites, allowing for the controlled preparation of arbitrary hydrogen adatom assemblies. Such control is a prerequisite for the investigation of the structural dependence of surface photo- and thermal reactivity at the single-molecule level.

11:40am SS2-WeM12 Reaction of Water with Terminal Hydroxyls on TiO₂(110) Surface, I. Lyubinetzky, Y.G. Du, Pacific Northwest National Laboratory, N.A. Deskins, Worcester Polytechnic Institute, Z. Zhang, Baylor University, Z. Dohnalek, M. Dupuis, Pacific Northwest National Laboratory

We report a combined experimental and theoretical investigation of the reaction of molecular water with terminal hydroxyls (OH_t's) on reduced TiO₂(110)-(1x1) surface at 300 K. We show that OH_t's have a significant effect on the water reactivity and extract molecular-level details about the underlying reaction mechanisms. By tracking the same surface area with high-resolution scanning tunneling microscopy before and after water exposure, we demonstrate that there are two distinctive reaction pathways involving multiple proton transfers [1]. For water interaction with OH_t on an adjacent Ti row, the proton can be transferred through bridging oxygen to OH_t, which leads to the formation of a new water molecule and apparent across-row motion of OH_t due to O scrambling. This process further manifests the existence of the equilibrium between molecular and dissociated states of water on TiO₂(110) [2]. If H₂O interacts with OH_t along the same Ti row, fast multi-step OH_t motion along the Ti row is observed. Our density functional theory results show that this process is caused by the fast diffusion of (OH_t + H₂O) pairs, whereby the underlying mechanism involves proton transfer and H₂O hopping over OH_t.

[1] Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnálek, M. Dupuis, and I. Lyubinetzky, *Phys. Chem. Chem. Phys.* 12 (2010) 6337.

[2] Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnálek, M. Dupuis, and I. Lyubinetzky, *Phys. Rev. Lett.* 102 (2009) 096102.

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