

# Tuesday Afternoon, October 21, 2008

## Surface Science

Room: 208 - Session SS1+NC-TuA

## Reactions on Gold and BiMetallics

Moderator: D.A. Chen, University of South Carolina

### 1:40pm SS1+NC-TuA1 Surface-Mediated Partial Oxidation of Alcohols on Gold, X. Liu, C.M. Friend, Harvard University

Fundamental investigations of the chemical properties of oxygen on Au(111) will be described. These studies serve as a model for gold-based catalysis which efficiently promotes oxidation reactions of CO, alcohols, and olefins. Gold is also important in materials science more broadly because it is used for interconnects and as a substrate for self-assembled monolayers and for biological samples. Our studies of alcohol oxidation on gold single-crystal surfaces under ultra-high vacuum conditions have revealed mechanistic information for partial oxidation of alcohols that can be applied to explain the mechanism of heterogeneous catalytic processes. Furthermore, such basic knowledge is important for understanding and controlling factors that determine reaction selectivity. We have used a combination of reactivity, spectroscopic and imaging measurements in our work. These studies provide evidence that mechanistic information, established in single-crystal surface science studies, can serve as a valuable guide for understanding and designing catalytic reaction processes.

### 2:00pm SS1+NC-TuA2 Selective Oxidation Chemistry on Gold, J.L. Gong\*, R.A. Ojifinni, N.S. Froemming, T. Yan, G. Henkelman, C.B. Mullins, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions. We demonstrate that adsorbed O atoms ( $O_{ad}$ ) facilitate  $NH_{3,ad}$  decomposition even though ammonia does not dissociate on the clean Au(111) surface. The selectivity of the catalytic oxidation of ammonia to  $N_2$  or to NO on Au(111) is tunable by the amount of atomic oxygen pre-covering the surface. Both  $N_2$  and NO are formed via simple recombination reactions ( $N_{ad} + N_{ad}$  and  $N_{ad} + O_{ad}$ ). At low oxygen coverages ( $\theta_O < 0.5$  ML), adsorbed ammonia is stripped to  $NH_{3,ad}$  which decomposes to form gaseous  $N_2$ . We also present experimental and density functional theory (DFT) calculation results of formation and decomposition of the carbonate anion ( $CO_3 = CO_2 + O_a$ ) on atomic oxygen pre-covered Au(111). A reaction probability on the order of  $10^{-4}$  and an apparent activation energy of -0.15 eV are estimated for this reaction. The small values of reaction probability are likely part of the reason why an earlier study on Au(111) reported undetectable surface carbonate formation. Additionally, we have investigated partial oxidation of propanol on atomic oxygen covered Au(111). At reaction temperatures below 300 K, 1-propanol is oxidized to propaldehyde with 100% selectivity while acetone is the only products of 2-propanol partial oxidation. A small amount of  $CO_2$  is formed at higher surface temperatures (i.e., above 300 K).

### 2:20pm SS1+NC-TuA3 Model Catalysts for Steam Reforming and Water-Gas Shift Reactions, J. Hrbek, Brookhaven National Laboratory

INVITED

The molecular hydrogen used in many large scale processes in chemical industry and for operating fuel cells is produced by these catalytic reactions. Steam reforming can provide sustainable source of hydrogen when using ethanol as feedstock; water-gas shift is used to purify hydrogen by removing CO, a catalytic poison. I will describe the preparation and characterization of model catalysts, and discuss their surface interactions with reactants under vacuum and their catalytic reactivity under higher pressures. As we have shown recently (Science 318(2007)1757; Angew. Chem. Int. Ed. 46(2007)1329)) both the model catalysts (Au or Cu on  $CeO_2(111)$ ) and the inverse model catalysts ( $CeO_x$  or  $TiO_x$  nanoparticles supported on Au(111) or Cu(111)) have significant intrinsic activity for water-gas shift at elevated pressures. Neither Au(111) nor  $CeO_2(111)$  have any activity in the WGS reaction. Our photoemission data indicate that  $CeO_x$  nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the  $CeO_2$  nanoparticles are inactive. Water dissociates on O vacancies of the oxide nanoparticle (the rate limiting step in the WGS reaction), CO adsorbs on Au site located near the oxide-metal perimeter, and subsequent reaction steps take place at the metal-oxide interface. Our ability to identify reaction intermediates under

vacuum conditions and to link them with the structural characterization at the atomic level is critical for development of reaction models: specifically in the WGS process the oxide support is not a simple spectator and plays an essential role. I will also discuss experimental results obtained with the model catalysts for steam reforming of ethanol. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

### 3:00pm SS1+NC-TuA5 Role of the Oxide Substrate on $O_2$ Dissociative Adsorption on Au Nanostructures: First Principle Studies, S. Stolbov, T.S. Rahman, University of Central Florida

In this work we apply the density functional theory calculations to explore the mechanism of high reactivity of Au nanoparticles on oxide substrates. We test the idea that the substrate – nanoparticle interaction makes the  $O_2$  dissociative adsorption favorable on this system, in contrast to bulk Au, and then the O atoms, so adsorbed, are consumed by reactants for further oxidation. We exploit the observation that the 1.5-layer Au film on  $TiO_x$  displays an exceptionally high reactivity as compared to a monolayer Au film, as well as those with 2 or more layers.<sup>1</sup> We calculate the energetics of dissociative adsorption of  $O_2$  on the surfaces 1.5, 2, 2.5, 3, 4.5, and 5 Au(001) layer structures in two environments: 1) free standing layers, 2) on  $TiO_x$  fragments (modeling a substrate). For all missing row  $n+0.5$  Au structures under consideration, the total energy is found to decrease upon the  $O_2$  dissociative adsorption. However, analysis of entire pathway for this reaction suggests that the  $O_2$  dissociative adsorption is favorable only for 1.5Au/ $TiO_x$  structure. This result along with the experimental finding<sup>1</sup> point to the  $O_2$  dissociative adsorption as being the main mechanism for the observed reactivity of Au nanostructures. Calculated local densities of electronic states and local charges in the system will be presented for further insights into the nature of the effect.

<sup>1</sup>M. S. Chen, D. W. Goodman, Science 306, 234 (2004). Work supported in part by DOE under grant # DE-FG02-03ER15842.

### 4:00pm SS1+NC-TuA8 Hydrogen Splitting on Ru and Pt Nanoparticles, E. Fiordaliso, M. Johansson, S. Murphy, R. Nielsen, I. Chorkendorff, Technical University of Denmark

Here we investigate the hydrogen splitting rate as a function of particle size for Pt and Ru by measuring the rate of the H-D exchange reaction at 1 bar. The study is mainly motivated by fuel cell applications, where highly dispersed Pt is used as the anode catalyst in the Proton Exchange Membrane (PEM) fuel cell. It was found in an earlier study that at 1 bar, Ru gives a higher rate for the H-D exchange reaction than Pt.<sup>1</sup> The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.<sup>2</sup> Model catalysts in the form of spots with a diameter of 1 mm are prepared by electron-beam evaporation of metal onto a sputtered highly ordered pyrolytic graphite (HOPG) substrate. The amount of metal corresponds to an average thickness between 0.2 and 50 Å. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent  $D_2$  in  $H_2$  and the temperature was varied in the range 40 to 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM) before and after the high-pressure measurements. A simple model is used in order to extract the sticking probability for  $H_2$  from data for the H-D exchange rate. Once the sticking probability has been obtained, the dissociative adsorption/desorption rate for  $H_2$  can be calculated. The apparent desorption energy,  $E_{des}$ , for  $H_2$  at the H coverage corresponding to 1 bar pressure is then extracted from data for the desorption rate as a function of temperature. It is found that at 0.2 Å average metal thickness,  $E_{des}$  is approximately 0.2 eV for Ru and 0.27 eV for Pt, and that the metals form particles with a mean diameter less than 10 Å. As the metal loading is increased, the particle size increases whereas  $E_{des}$  decreases. Above approximately 15 Å, an almost continuous metal film is formed and  $E_{des}$  becomes constant, 0.02 eV for Ru and 0.21 eV for Pt. Hence, the desorption energy for  $H_2$  decreases with increasing particle size for both Pt and Ru, but the effect is more pronounced for Ru.

<sup>1</sup>M. Johansson, O. Lytken, I. Chorkendorff, J. Chem. Phys. 128 (2008) 034706.

<sup>2</sup>M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum. 75 (2004) 2082.

\* Morton S. Traum Award Finalist

4:20pm **SSI+NC-TuA9 Novel Pathways to Hydrogen Dissociation and Diffusion on Pd Alloys**, *H.L. Tierney, A.E. Baber*, Tufts University, *J.R. Kitchen*, Carnegie Mellon, *E.C.H. Sykes*, Tufts University

Dissociation of molecular hydrogen on the surfaces of Pd-based alloys is a key step in a number of energy-related technologies, including CO<sub>2</sub> conversion and hydrogen separation. An understanding of the nature of H<sub>2</sub>-surface interactions, including molecular adsorption, dissociation and surface diffusion provides a basis for the development of next-generation energy technologies. In this low-temperature scanning tunneling microscopy study we have demonstrated that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. The atomic-scale composition of both Pd/Cu{111} and Pd/Au{111} near-surface alloys were elucidated and H uptake was quantified. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H<sub>2</sub> flux on a Pd/Au sample with identical atomic composition and geometry. Based on a simplistic model involving the adsorption energies of H on Pd{111}, Cu{111} and Au{111} it would appear that the barrier for H to migrate from Pd to Cu or Au is too high to occur at 400 K. DFT calculations provided insight into this unusual activity of Pd/Cu alloys for dissociation and uptake of H. The calculations revealed that the barrier for diffusion of H away from isolated Pd sites on Pd/Cu{111} alloys is lower than that of pure Pd{111}, but that this same diffusion barrier is insurmountable at 400 K on Pd/Au alloys. These results demonstrate the powerful influence an inert substrate has on the catalytic activity of Pd atoms supported in its surface.

4:40pm **SSI+NC-TuA10 Alloy Nanocluster Distinct Surface Segregation Phenomena Related to the Coordination Dependence of Bond-Energies: Introduction and Application of a New Theoretical Approach**, *L. Rubinovich, M. Polak*, Ben-Gurion University, Israel

This work introduces some novel aspects concerning alloy nanocluster equilibrium surface segregation phenomena and their modeling. The first involves the extraction of the Coordination dependence of Bond Energy Variations from DFT computed surface energies (the CBEV method). In particular, polynomial functions in terms of pair coordination numbers were fitted to DFT data reported recently for energies of pure Pt, Pd and Rh surfaces and small clusters. These functions yield elemental bond energy variations pertinent to any site at the cluster surface and subsurface layers. The second novel aspect, revealed when using the bond energy variations as input in statistical-mechanical computations based on the "free-energy concentration expansion method" (FCEM<sup>1</sup>), concerns the finding that preferential pair-bond strengthening can lead to quite unique surface segregation characteristics. In particular: (i) In spite of the general tendency of Pd to segregate at Pt-Pd alloy surfaces, in cuboctahedron clusters certain (111) surface sites are populated by Pt, namely, a segregation reversal is predicted; (ii) Distinct Pd segregation profiles with maximal concentration at the subsurface layer are obtained for the Pt-Pd cluster (100) face, compared to subsurface oscillation in the Rh-Pd cluster (100) face. Further computations for Rh-Pd revealed inter-cluster separation involving "magic number" Pd segregated structures exhibiting various types of order. At higher temperatures atomic exchange among surface sites as well as surface-core desegregation processes are reflected in distinct configurational heat capacity peaks of the Schottky type.<sup>2</sup> As a test case, CBEV/FCEM computations done for the Pt-Rh(111) two-layer (oscillatory) profile show better agreement with previously reported experimental data as compared to our earlier work based on the NRL-TB/FCEM approach.<sup>3</sup> Using the highly efficient CBEV/FCEM method enables to explore also compositional structures and properties of Rh-Pt-Pd ternary nano-clusters. Compared to current other approaches, this method is highly transparent, yielding better insight into the origin of surface segregation in bulk alloys and nanoclusters.

<sup>1</sup> M. Polak and L. Rubinovich, Surf. Sci. Rep. 38 (2000) 127.

<sup>2</sup> M. Polak and L. Rubinovich, Phys. Rev. B 71 (2005) 125426.

<sup>3</sup> M. Polak and L. Rubinovich, Phys. Rev. B 75 (2007) 045415.

5:00pm **SSI+NC-TuA11 Stability, Electronic, and Catalytic Properties of Supported Metal Clusters**, *B. Roldan Cuenya*, University of Central Florida

The next generation of nanocatalysts requires detailed knowledge of the correlation between their structure and reactivity. Size- and shape-selected Au, Pt and AuFe nanoclusters with well defined intercluster distances were synthesized by diblock copolymer encapsulation. Significant changes in the electronic local density of states (LDOS) of TiC-supported Au clusters, in particular, the onset of non-metallic behavior, were observed by scanning tunneling spectroscopy with decreasing cluster size. In addition, evidence for substrate-induced modifications in the LDOS of interfacial gold atoms was found.<sup>1</sup> Our temperature programmed desorption (TPD) measurements indicated a size-dependency in the catalytic activity of Au/TiC for CO oxidation.<sup>2</sup> Furthermore, interparticle interactions were found to affect the activity and life-time of our catalysts.<sup>3</sup> The stability of oxidized gold species

formed upon cluster exposure to atomic oxygen was investigated using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy and TPD.<sup>4</sup> Our work demonstrates the formation of surface and sub-surface Au<sub>2</sub>O<sub>3</sub> on Au nanoparticles. Interestingly, the stability of these species upon thermal treatment was found to depend on the reducibility of the oxide support. Finally, the formation, surface reconstruction and high-temperature mobility of size-selected bimetallic AuFe<sup>5</sup> and Pt nanoclusters deposited on TiO<sub>2</sub>(110) will be presented.

<sup>1</sup>A. Naitabdi, L. K. Ono, B. Roldan Cuenya, Appl. Phys. Lett. 89, 043101 (2006)

<sup>2</sup>L. K. Ono, D. Sudfeld, B. Roldan Cuenya, Surf. Sci. 600, 5041 (2006)

<sup>3</sup>L. K. Ono, B. Roldan Cuenya, Catal. Lett. 113, 86 (2007)

<sup>4</sup>L. K. Ono, B. Roldan Cuenya, J. Phys. Chem. C 112, 4676 (2008)

<sup>5</sup>A. Naitabdi, B. Roldan Cuenya, Appl. Phys. Lett. 91, 113110 (2007).

5:20pm **SSI+NC-TuA12 The Morphology and Reactivity of Metallic Nano Clusters Deposited on SiO<sub>2</sub> via Water Buffer Layer**, *E. Gross, M. Asscher*, The Hebrew University of Jerusalem, Israel

Nanometer size gold clusters supported on metal oxide surfaces were reported as having size dependent catalytic activity. This has motivated us to prepare clusters under clean, high vacuum conditions with control over the clusters size and density. Gold nano clusters were prepared by two different growth procedures. In the first, the clusters were prepared by direct deposition (DD) of gold atoms on SiO<sub>2</sub>/Si(100) substrates. The second growth mode is based on initial evaporation of gold atoms on top of amorphous solid water as a buffer layer at 100K which separates the small gold seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth and (cold) deposition of nano-clusters on the substrate in a Buffer Layer Assisted Growth (BLAG) mechanism. In order to increase the BLAG clusters density we have introduced a Multi-Cycle BLAG procedure (MC-BLAG). By repeating the BLAG procedure up to seven times consecutively, the cluster density can be increased by 5 fold without affecting the clusters size. BLAG clusters are more 3D in nature, have larger height to diameter ratio than DD clusters, yet their interaction with CO is very similar to DD clusters. This is reflected by the practically identical CO stretch observed on both clusters at 2106±2cm<sup>-1</sup>. UV-Visible absorption spectroscopy measurements have shown that differences in clusters morphology lead to variations in their surface plasmon resonance. The Multi-Cycle BLAG method also enables the growth of bi-metallic clusters. By modifying the preparation procedure either separated Au and Pd clusters or alloyed (Au-Pd) clusters can be prepared on the substrate. The catalytic reactivity of these bimetallic clusters is of great potential importance. We currently investigate the catalytic reactivity of bi-metallic clusters (such as gold and palladium or gold and copper) on dehydrogenation reactions. These reactions are of potential importance for various hydrogen energy applications, e.g. fuel cells.

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