

# Wednesday Morning, October 30, 2013

## Surface Science

Room: 201 A - Session SS+NS-WeM

## Nanostructures: Reactivity & Catalysis

Moderator: I. Lyubinetzky, Pacific Northwest National Laboratory

8:00am **SS+NS-WeM1 Structure Sensitivity of Glycerol Oxidation Catalyzed by Pt/SiO<sub>2</sub> under Mild Conditions**, Y. Li, F. Zaera, University of California, Riverside

The surface structures of catalysts have in some instances a large impact on their catalytic properties. On the other hand, historically, mild reactions are not considered to be surface structure sensitive. In this work we report on our observation that both the size and the shape of Pt nanoparticles strongly affect the selectivity of glycerol oxidation, a reaction that can proceed at room temperature and under atmospheric pressures. In a series of experiment using Pt/SiO catalysts with average particle sizes varying from 3.9 to 6.2nm, it was determined that selectivity toward primary carbon oxidation increases as the proportion of larger particles increases. Aside from this size effect, supported tetrahedral Pt and cuboctahedral Pt also exhibit different selectivity and kinetic behavior from the regular Pt catalysts. (See Fig. 1&2) We propose that these selectivity differences are due to the different adsorption state of the surface species. Dihydroxyacetone (the product of dehydrogenation on secondary carbon) is thermodynamically more stable than glyceraldehyde (the product of dehydrogenation on primary carbon) but with larger steric hindrance effect in the dehydrogenation process. While on the edge and corner parts of the Pt surface, the steric hindrance could be largely reduced comparing to smooth Pt surface, therefore dihydroxyacetone is more favored on smaller particles. (See Fig. 3) Further characterization of the catalysts and their detailed kinetic behavior is currently under way.

8:20am **SS+NS-WeM2 Heats of Adsorption and Surface Reaction for CO and O<sub>2</sub> on Pd Nanoparticles by Single Crystal Adsorption Microcalorimetry**, S. Schauer mann, M. Peter, J.M. Flores-Camacho, J.-H. Fischer-Wolfarth, S. Adamovski, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Establishing the correlation between the energetics of adsorbate-surface interaction and the structural properties of a catalyst is an important fundamental issue and an essential prerequisite for understanding the realistic catalytic processes. We apply a newly developed microcalorimetry set up to determine the adsorption heats of carbon monoxide and oxygen on Pd nanoparticles supported on a well-define Fe<sub>3</sub>O<sub>4</sub>/Pt(111) film. We systematically vary the Pd cluster size in the range of ~ 100 to 5000 Pd atoms to address the energetics of CO and O interaction with the nanoparticles of different dimensions. Particularly, two major structural factors were identified that determine the CO and oxygen binding energy on Pd: the local configuration of the adsorption site, and the particle size. We show that the change of the binding site from a three-fold hollow site at Pd(111) to the edges of Pd nanoparticles results in a strong increase of the oxygen binding energy, while this effect is absent for CO adsorption, pointing to the adsorbate-specific nature of this factor. In contrast, the decreasing particle size was shown to result in strongly decreasing binding energies for both adsorbates. In case of oxygen, these both counteracting trends were found to give rise to a non-monotonous dependence of the oxygen adsorption energy on the particle size [1,2].

[1] J.-H. Fischer-Wolfarth, J.A. Farmer, J.M. Flores-Camacho, A. Genest, I.V. Yudanov, N. Rösch, C.T. Campbell, S. Schauer mann, H.-J. Freund, Phys. Rev. B, 81, 2010, 241416(R)

[2] M. Peter, J. M. Flores Camacho, S. Adamovski, L.K. Ono, K.-H. Dostert, C.P. O'Brien, B. Roldan Cuenya, S. Schauer mann, H.-J. Freund, Angew. Chem. Int. Edit. DOI: 10.1002/anie.201209476

8:40am **SS+NS-WeM3 Size-dependent Correlations between Supported Cluster Electronic Properties and Catalytic/Electrocatalytic Activity**, S.L. Anderson, University of Utah **INVITED**

We prepare model catalysts or catalyst-decorated electrodes by depositing size-selected Pd<sub>n</sub> and Pt<sub>n</sub> clusters on planar supports, including TiO<sub>2</sub>(110), alumina/Ta(110), alumina/Rh(0001) as well as glassy carbon and ITO/glass electrodes. The samples are prepared in UHV and characterized *in situ* by a combination of X-ray and UV photoelectron spectroscopy (XPS, UPS), and low energy He<sup>+</sup> ion scattering (ISS). The activity of the model catalysts for gas-surface reactions such as CO oxidation is studied using mass spectrometric methods, such as temperature-programmed

reaction/desorption (TPR, TPD). Electrochemistry is done in an attached UHV antechamber fitted with a three electrode cell that can be sealed against the sample surface, allowing electrochemistry to be done both without, and with prior exposure to laboratory air. Electrocatalytic activity is drastically altered by air exposure. Results will be presented for CO oxidation over various M<sub>n</sub>/oxide catalysts, and for electrochemical reactions observed under conditions appropriate for oxygen reduction or ethanol oxidation. One interesting result seen in many of these systems is a size-dependent anti-correlation between activity as oxidation catalysts, and shifts in the catalytic metal core level binding energies. Potential reasons for this correlation, and related studies of valence level shifts with UPS, will be discussed.

9:20am **SS+NS-WeM5 Characteristics of Sulfur-Vacancy Clusters in Single Layer MoS<sub>2</sub>: Insights from *ab initio* Calculations**, D. Le, T.B. Rawal, T.S. Rahman, University of Central Florida

Single-layer MoS<sub>2</sub> is proving itself to be a versatile material for a wide variety of electronic, optical and chemical applications. Sulfur depletion, without destabilization of the single-layer, is considered a prudent way for making the basal plane of the layer catalytically active. We will present results of our density-functional-theory based examination of vacancy structures on one side of a MoS<sub>2</sub> layer which point to their structural stability and chemical reactivity. We will show that the formation energy per sulfur vacancy is lowest (energetically favorable) when the vacancies form a row, and that the longer the row, the lower the formation energy. In addition, we will show that the lowest energetic barrier for spoiling these row structures by exchanging a vacancy with a nearby sulfur atom is 0.79 eV, and that this barrier increases as the row elongates. Furthermore, the presence of vacancy clusters will be shown to make the system thermodynamically facile for alcohol synthesis from syngas. (Work supported in part by DOE grant DE-FG02-07ER15842.)

9:40am **SS+NS-WeM6 A New Effect of Nanoconfinement on Chemical Equilibrium: Theory and Experimental Evidence**, L. Rubinch, M. Polak, Ben-Gurion University of the Negev, Israel

Recently<sup>1</sup> we predicted that when a reaction involving a small number of molecules occurs in a nanometric-scale domain entirely segregated from the surrounding media, the nanoconfinement can shift the position of equilibrium toward products via reactant-product reduced mixing. In this talk, we demonstrate how most-recently reported single molecule fluorescence measurements of partial hybridization of ssDNA confined within nanofabricated chambers provide the first experimental confirmation of this entropic nanoconfinement effect. Thus, focusing separately on each occupancy-specific equilibrium constant, quantitatively reveals extra stabilization of the product upon decreasing the chamber occupancy or size.<sup>2</sup> Namely, the DNA hybridization under nanoconfined conditions is significantly favored over the identical reaction occurring in bulk media with the same reactant concentrations. This effect, now directly verified for DNA, can be relevant to actual biological processes, as well as to reactions occurring on nanoparticle surfaces, and within molecular capsules, nanotubes, or other functional nanospaces.

1. Polak, M.; Rubinch, L. Nano Lett. 2008, 8 (10), 3543–3547.

2. Rubinch, L.; Polak, M. Nano Lett. 2013, DOI: 10.1021/nl4008198.

10:40am **SS+NS-WeM9 Encapsulation of Noble-Metal Clusters on ZnO(10-10) and Its Impact on Catalytic Reactivity**, Z. Zhang, F. Liu, Louisiana State University, L. Liu, Texas A&M University, E.W. Plummer, P.T. Sprunger, R.L. Kurtz, Louisiana State University

Supported metal clusters on ZnO are important catalysts for industrial synthesis of methanol from syn-gas. The active site of this reaction has long been debated. We have employed model single crystal catalysts and surface characterization tools to elucidate key aspects of the cluster structure and reactivity. Specifically, we have probed the CO oxidation reaction at high pressure (tens of Torr). In the case of Cu/ZnO(10-10), both LEIS and EELS show an encapsulation of the cluster with an ultrathin layer of ZnO which is thermally driven (up to 725 K) and promoted with oxygen exposure. Other spectroscopies, including XPS and UPS, suggest a self-limiting ZnO film thickness of 1 – 2 ML. UPS measurements on the bare (un-annealed) Cu/ZnO clusters show that CO adsorbs molecularly at 85K while it dissociates on an encapsulated cluster at the same temperature, indicating that the ZnO coating is crucial to reactivity. Similarly CO<sub>2</sub> reacts strongly with the encapsulated Cu clusters indicating that the ultra-thin ZnO is participating in the adsorption process. High-pressure studies at 50 Torr at RT show that there is a greatly enhanced reactivity for CO oxidation for the encapsulated clusters compared to either the bare ZnO substrate or the un-encapsulated clusters. Similar results have been seen in the case of Au

clusters on ZnO(10-10) and corresponding encapsulation, however differences in reactivity and structure exist. These results offer a new understanding of the “support” role of ZnO on this heterogeneous catalyst system, and may lead to new means to drive the mechanism of methanol synthesis and help to develop new designs of this important industrial catalyst.

11:00am **SS+NS-WeM10 ALD ZnO 3D Hierarchical Nanostructures for Enhanced Photocatalytic Dye Degradation Kinetics**, *J. Zhao, A. Bagal, Q. Yang, X. Zhang, C.-H. Chang, M.D. Losego, G.N. Parsons*, North Carolina State University

ZnO has been used as photocatalyst to degrade organic compounds, such as phenol, phenol derivatives, naphthalene, anthracene, and dye molecules. In order to overcome the limitation of ZnO nanosurfaces, immobilized photocatalyst with high S/V ratio nanostructure is needed. Previously, ZnO-nanowire-decorated pore-array films, polymer fiber mats and ZnO nanoplates have been fabricated and reported with enhanced photocatalytic properties. However, diffusion of dye molecules into nanostructures was found to limit the photocatalytic performance. Since the structures of these photocatalysts were not made periodic or uniform in size, the effects of nanostructure dimension could not be investigated. Periodic 3D nanostructures with tunable sizes are therefore needed.

A series of ZnO hierarchical 3D nanostructures were fabricated for photocatalytic applications. Nano-pillars were patterned on photoresist (PFi88A7) using interference lithography, and were coated with a conformal ZnO seed layer (~40nm) using atomic layer deposition (ALD). ZnO nanowires were grown onto the nano-pillars via hydrothermal synthesis. With varied growth time, we decorated the ALD ZnO coated nano-pillars with ZnO nanowires of different lengths (60~150nm). Scanning electron microscopy confirmed the 3D hierarchical nanostructures. Photodegradation kinetics of methyl orange was measured to characterize the photocatalytic property of the ZnO nanostructures. Apparent first order rate constant ( $k_{app}$ ) of dye degradation was improved by 35% with ALD ZnO coated nano-pillars, compared with ZnO flat film catalyst. By decorating the nano-pillars with ZnO nanowires of 120 nm length,  $k_{app}$  was further increased by 88% to 1.75 h<sup>-1</sup>. We compared the photocatalytic property of our nanostructures with varied sizes. We will show how the nanostructures controlled the diffusion rate of dye molecules and affected the overall photocatalytic performance.

11:20am **SS+NS-WeM11 Phase/Catalytic Activity Correlations of TiO<sub>2</sub> ALD Functionalized Nanoporous Gold**, *M. Bagge-Hansen*, Lawrence Livermore National Laboratory, *A. Wichmann*, University Bremen, Germany, *J.R.I. Lee, T.M. Willey*, Lawrence Livermore National Laboratory, *A. Wittstock*, University Bremen, Germany, *J. Biener*, Lawrence Livermore National Laboratory, *M. Bäumer*, University Bremen, Germany, *M. Biener*, Lawrence Livermore National Laboratory

Nanoporous metals have many promising technological applications, such as catalysts, photo-catalysts, and electrodes in batteries, but their practical use is often limited by their tendency to coarsen at elevated temperatures. Here we demonstrate that atomic layer deposition (ALD) of nanometer-thick TiO<sub>2</sub> films can drastically improve the thermal stability and mechanical properties of nanoporous gold (np-Au) while further adding functionality—such as dramatically improved catalytic activity. Aerobic CO oxidation was used to test the effects of annealing on the catalytic activity of the TiO<sub>2</sub>/npAu hybrid materials, and the observed changes in catalytic activity will be discussed in terms of annealing induced morphology and phase changes. We characterized these annealing-induced changes of morphology and phase composition by cross-sectional scanning electron microscopy (xSEM), x-ray photoemission spectroscopy (XPS), and near-edge x-ray absorption fine structure (NEXAFS). The Ti L<sub>2,3</sub>-edge in NEXAFS is well known to exhibit exceptional sensitivity to Ti coordination and structure. Amorphous, anatase and rutile polymorphs of TiO<sub>2</sub> can be clearly distinguished and reveal a smooth and strong variation in the predominant TiO<sub>2</sub> phase as a function of annealing. Our results provide new insights into the thermal stability of functionalized electrodes for energy storage and harvesting applications.

This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344

11:40am **SS+NS-WeM12 Nanostructured Gold Model Catalysts on Oxygen-Free Substrates**, *L. Liu*, Texas A&M University, *F. Womack*, Louisiana State University, *Z. Zhou*, Texas A&M University, *M. Patterson*, Louisiana State University, *B. Habenicht, Y. Xu*, Oak Ridge National Laboratory, *P.T. Sprunger, R.L. Kurtz*, Louisiana State University

A new class of nanostructured gold model catalysts has been synthesized by depositing gold on single-layer graphene and boron nitride (BN) thin films formed on refractory metals. These thin films, which are oxygen-free and devoid of strong adsorption sites in themselves, develop moiré

superstructures due to lattice mismatch with the metal substrates, which present periodic, identical traps on the potential energy surface for possible cluster nucleation. STM studies have shown that gold atoms form two-dimensional (2-D) islands on graphene/Ru(0001) but small monodisperse clusters on BN/Rh(111). The electronic structures of these gold nanostructures have been characterized by electron energy loss spectroscopy (EELS) and angle resolved photoemission spectroscopy (ARPES), and the geometric structures have been studied by scanning tunneling microscopy (STM). CO and O<sub>2</sub> are used to probe the activity of these gold model catalysts. On 2-D gold islands, adsorbed CO molecules demonstrate a stretching frequency characteristic of anionic Au and can be titrated by O<sub>2</sub> molecules. On gold clusters on BN/Rh(111) substrates, both CO and O<sub>2</sub> chemisorption is demonstrated in temperature programmed desorption (TPD). Furthermore, density function theory (DFT) calculations have been used to elucidate the adsorption sites and adsorption configurations for CO and O<sub>2</sub> on the two different gold model catalysts. Our findings illustrate the critical importance of size to the reactivity of gold catalysts and the exciting possibility of corrugated thin films such as graphene and BN moirés functioning as templates to form model nanocatalysts.

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