

Monday Afternoon, November 9, 2009

Surface Science

Room: N - Session SS2-MoA

Formation & Reactivity of Nanoclusters

Moderator: G.B. Fisher, University of Michigan

2:00pm **SS2-MoA1 Nanoplasmonic Sensing of Metal Hydride Formation and Catalytic Reactions on Metallic Nanoparticles**, *E.M. Larsson, C.M. Langhammer, B.H. Kasemo, I.L. Zoric*, Chalmers University, Sweden

A novel, nanoplasmonics-based optical sensing platform for real time studies of nanoparticle processes is described. Examples are presented for (i) surface catalytic reaction kinetics on nanoparticles and (ii) formation of a new phase in metal hydride forming nanoparticles. The remarkably sensitive and very versatile sensing platform consists of plasmonic sensing particles (Au nanodisks, $D=76\text{nm}$ and $h=40\text{nm}$, prepared on a transparent substrate), covered by a 10nm dielectric film onto which the nanoparticles to be studied are deposited (in the present case Pd or Pt, with a size range from 2 nm-10nm). The key to the sensing is utilization of localized surface plasmon resonances (LSPR). The LSPR of the sensing nanoparticle sensitively measures changes of the surface coverage (sensitivity $<0.05\text{ML}$) or the formation of the new phase in the studied nanoparticles via shifts in the LSPR extinction spectra. The versatility of this method is illustrated with the following examples:

a) Hydrogen absorption/desorption (hydride formation) studies of Pd nanoparticles in the size range 2-10nm. The main result from these studies includes the size dependent thermodynamics (p-C-T diagram) and kinetics of the H/Pd nanoparticle (1-5 nm) system. The kinetics exhibit a power and power-exponential size dependence of the time scales for the hydrogen uptake and release processes. The uptake is in agreement with Monte Carlo simulations of diffusion controlled hydriding kinetics, while the release (desorption) is explained by the effect of surface tension on the activation energy for hydrogen desorption from the nanoparticle.

b) Kinetic studies of CO and H₂ oxidation on Pt nanoparticles with particular emphasis on kinetic phase transition phenomena in these reactions. The latter occur as one varies reactant concentrations but keeps the total amount of reactants constant and are recognized by a sudden transition from oxygen covered nanoparticle surfaces at low CO (H₂) concentration, to high CO or H coverage for low O₂ concentrations,

c) NO₂ storage and conversion to N₂ on Pt/BaO. In this case NO₂ storage and conversion kinetics is followed via changes in the LSPR resonance of the Au sensing particles, coated with a thin layer of BaO onto which Pt nanoparticles were deposited. Exposure of the sensor to the gas mixture of NO₂+O₂ leads to a conversion of BaO to Ba(NO₃)₂ (NO_x storage) leading to a change of refractive index of the material surrounding the sensing nanoparticle. This leads to a LSPR peak shift that is monitored. Exposure to H₂ converts the stored NO₂ to N₂. Reversible changes were monitored for such NO₂ oxidation/reduction cycles.

2:20pm **SS2-MoA2 On the Role of Pd Ensembles in Selective H₂O₂ Formation on PdAu Alloys**, *H. Ham, G. Hwang*, University of Texas at Austin

Bimetallic Pd-Au alloys have been found to significantly increase catalytic efficiency, compared to the monometallic Pd and Au counterparts, in various reactions including direct synthesis of H₂O₂ from H₂ and O₂ and production of vinyl acetate monomers. Recent evidence suggests that the reactivity of bimetallic catalysts would be governed by creation of unique mixed-metal surface sites [the so called ensemble effect] and/or electronic structure change by metal-metal interactions [ligand effect], while mechanisms underlying the alloying effect still remain unclear. Very recently, the role played by Pd monomers in the direct H₂O₂ synthesis has also been studied using density functional theory calculations, yet detailed reaction mechanisms associated with Pd atomic arrangements are still lacking. In this talk, we will present some recent theoretical results we have on the role of Pd ensembles in determining the selectivity of direct H₂O₂ synthesis. Using periodic density functional theory calculations, we find that the H₂O₂ formation selectivity can be governed by the spatial arrangements of Pd and Au surface atoms, particularly the availability of Pd monomers surrounded by less active Au atoms. Our calculations suggest that the large activity difference between Pd and Au atoms is a key factor for selective H₂O₂ formation, by suppressing O-O bond scission. This work hints the importance of knowing how to properly tailor Au reactivity for achieving wanted reactions, while the relative activities of Au and Pd surface atoms can be a function of subsurface layer composition as well as catalyst size and shape.

2:40pm **SS2-MoA3 Well-defined, Highly Uniform Metallic Nano-Structures as Selective Heterogeneous Catalysts and Platforms for Chemical Characterization**, *S. Linic, Christopher*, University of Michigan

INVITED

I will present our recent work where we explored potential utilization of highly uniform metallic nano-structured materials as selective heterogeneous catalysts. The advantage of these materials compared to conventional catalytic materials is that their structure can be controlled with almost atomic precision, and that it is possible to synthesize highly homogeneous structures. We demonstrated some of these advantages recently when we showed that well-defined, tailored Ag nano-structures are much more selective in heterogeneous epoxidation of ethylene to form ethylene oxide (EO) ($\text{ethylene} + \frac{1}{2} \text{O}_2 \rightarrow \text{EO}$) than conventional industrial catalysts.

We showed using quantum chemical Density Functional Theory (DFT) calculations, where we studied critical elementary chemical steps that govern the selectivity to EO in the process, that the Ag(100) surface should be inherently more selective than the Ag(111) surface. We note that catalytic particles, synthesized using conventional synthesis procedure and currently used in commercial ethylene epoxidation process, are dominated by the (111) surface. To synthesize Ag nano-structures which are dominated with the Ag(100) faces, we employed a synthesis procedure which uses organic stabilizer molecules to direct the growth of the nano-structure in a particular direction and to control the surface facets that terminate the nano-structure. This synthetic strategy allowed us to synthesize well-defined and highly uniform Ag nano-wires and nano-cubes which are dominated by the (100) facet. Subsequent experiments showed that Ag nano-wires and nano-cube catalysts can achieve selectivity to EO, which is, at differential conversion, by ~ 40 % higher than for conventional Ag catalysts.

We have also recently started exploring these metallic nano-structures as possible platforms for chemical characterization. The features of these nano-structures that are particularly appealing are: (i) the nanostructures are well defined on atomic level, and their surface to volume ratio is fairly high, which makes these structures inherently better suited for the studies of surface chemical processes compared to traditional single crystal model systems, which are while very well defined, characterized by low surface to volume ratio, (ii) we can synthesize the nanostructures with high degree of uniformity in size and shape, which rules out possible effects due to diversity in size and shape, i.e. these, (iii) the nanostructures are effective scatterers of electromagnetic radiation which make them suitable as platforms for a number of chemical characterization techniques including surface enhanced Raman (SERS) or IR spectroscopies. We will demonstrate the utility of the nano-structures for chemical characterization by a way of an example, where we monitored in-situ ethylene epoxidation.

3:40pm **SS2-MoA6 2009 AVS Peter Mark Memorial Award Lecture - Towards the Understanding of Catalytic and Vibrational Properties of Metal Nanostructures**, *B.R. Cuenya**, University of Central Florida

INVITED

Metallic nanostructures are of great interest in many scientific fields due to their novel size-dependent physical and chemical properties. The origin of the enhanced catalytic reactivity and selectivity displayed by small metal nanoparticles is yet to be explained. However, it is generally agreed that the design of the next generation of nanocatalysts requires detailed knowledge of the correlation between their reactivity and their physical properties such as morphology, electronic structure, chemical composition, and interactions with their support. Intriguing effects including phonon confinement and phonon localization at interfaces have also been observed in low dimensional systems. Such modifications of the vibrational density of states of nanoscale materials are of scientific and technological relevance, because they profoundly affect their thermodynamic properties. In addition, their understanding could help further our insight in the field of catalysis, since phonons might play a decisive role in certain chemical processes. To systematically study these effects, homogeneous and size-selected nanostructures are needed. Diblock-copolymers can aid the synthesis of such well-defined nanoscale systems.

The first part of my talk will illustrate the formation, stability, as well as the electronic and catalytic properties of size- and shape-selected Au, AuFe, Pt, and Pt-M (M = Au, Fe, Ru and Pd) nanoparticles synthesized by micelle encapsulation. CO oxidation and alcohol decomposition and oxidation have been used as model reactions. Emphasis will be given to the role of the nanoparticle support and the oxidation state of the active catalytic species in their reactivity.

* Peter Mark Memorial Award Winner

In addition to changes in reactivity, nanostructuring materials also affects their vibrational properties. The second part of my talk will discuss the size- and composition-dependent vibrational dynamics of ^{57}Fe , $^{57}\text{FePt}$, and $^{57}\text{FeAu}$ clusters as well as of nanostructured metal multilayers prepared by molecular beam epitaxy in UHV. The phonon density of states of those systems will be extracted from nuclear resonant inelastic X-ray scattering measurements. An enhancement of the density of low- and high-energy phonon modes as well as non-Debye-like behavior was observed on ^{57}Fe clusters. The latter effects were found to depend on the chemical nature of the surface shell on the nanoclusters. Thickness-dependent phonon confinement and interface localization effects were detected on nanoscale $^{57}\text{Fe}/\text{M}$ multilayers ($\text{M} = \text{Cu}, \text{Pd}$ or Ag). All these effects show the unique physical properties of metal nanoparticles, and their promise in technological applications.

Website: <http://www.physics.ucf.edu/~roldan>

4:20pm **SS2-MoA8 Growth, Composition and Surface Chemistry of Ni-Au Clusters on $\text{TiO}_2(110)$** , *D.A. Chen, S.A. Tenney, J.S. Ratliff, C.C. Roberts*, University of South Carolina

Scanning tunneling microscopy (STM) studies show that bimetallic Ni-Au clusters supported on $\text{TiO}_2(110)$ are formed by deposition Au on top of Ni clusters. Due to the higher mobility of Au compared to Ni atoms on $\text{TiO}_2(110)$, deposited Au is nucleated at existing Ni clusters. Low energy ion scattering experiments demonstrate that the surface of the bimetallic clusters is predominantly Au for compositions above 50% Au, but 10-15% Ni also exists at the surface. The presence of Ni at the surface is in contrast to the expected Ni core-Au shell structure based on bulk thermodynamics; the large bulk miscibility gap for the two metals and the lower surface free energy of Au compared to Ni predicts that only Au should be at the cluster surface. Furthermore, adsorption of CO onto the Ni-Au clusters appears to induce the diffusion of Ni to the cluster surface. After annealing the Ni-Au clusters to 800 K and above, the clusters become encapsulated by stoichiometric titania. Although Ni and Au clusters annealed to 1000 K are roughly the same size, the addition of Ni to the Au clusters suppresses cluster sintering.

4:40pm **SS2-MoA9 Deposition of RuSn Nanoparticles onto a $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$ Surface from a Gas Phase Organometallic Precursor**, *A. Uhl*, University of Illinois at Chicago, *E. Trufan, R.D. Adams*, University of South Carolina, *R.J. Meyer, M. Trenary*, University of Illinois at Chicago
Scanning tunneling microscopy (STM) was used to characterize RuSn nanoparticles deposited from a gas phase organometallic precursor ($\text{Ru}_3(\text{CO})_9(\mu\text{-SnPh}_2)_3$) onto an Al_2O_3 film grown on a $\text{Ni}_3\text{Al}(111)$ substrate. This novel method allows for the specific preparation of small metal clusters that range between single atoms and larger, bulk-like particles. It also assists in bridging the gap between previous studies based on metal evaporation and industrial catalysis, where the use of precursor compounds for the active species is common. The STM images of the $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$ substrate prior to the exposure of the precursor show two distinct areas, with the first one exhibiting the dot structure of the alumina film, as reported in the literature. The second area does not exhibit any regular structure. After exposing the sample to the precursor at room temperature, the precursor was found to adsorb preferentially onto the second area, but also on the first area in significant amounts. In a subsequent series of images acquired for increasingly higher annealing temperatures, the discrepancy between the two areas in the interaction with the adsorbates is strongly increased. While the surface with the dot structure becomes almost fully depleted of the adsorbates, except for a few small (up to 3 nm in diameter) and roundish protrusions, the other area is covered by larger polygonal protrusions. Similarly shaped depressions in the surface are observed along with the protrusions. A control experiment in which the bare $\text{Ni}_3\text{Al}(111)$ surface was exposed to the precursor indicates that the second area of the $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$ surface consists of patches of bare metal. A striking difference between the protrusions on the oxide and the metal is that the size of the latter increases dramatically with increasing annealing temperature, while the former do not grow at all. Nevertheless, both features are observed even up to 925 K, from which it is concluded that the annealing removes the ligands from the metal centers of the precursor molecules, after which the metal nanoparticles can form. These results show that by using an organometallic precursor, small uniform metal nanoparticles with high thermal stability can be successfully deposited onto an oxide thin film. This paves the way for subsequent studies of the surface chemistry associated with model oxide-supported metal catalysts consisting of metal nanoparticles of a uniform size.

5:00pm **SS2-MoA10 Formation, Thermal Stability and In-situ Gas Phase Catalytic Properties of Supported Au, Fe, and $\text{Au}_x\text{Fe}_{1-x}$ Nanoparticles**, *L.K. Ono, A. Naitabdi, B. Roldan Cuenya*, University of Central Florida

Metal-loaded diblock-copolymer micelles have been used to synthesize size-selected self-assembled Au, Fe, and Au-Fe nanoparticles (NPs). In-situ scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the formation and thermal stability of $\text{Au}_x\text{Fe}_{1-x}$ ($x = 1, 0.8, 0.5, 0.2, 0$) NPs supported on $\text{TiO}_2(110)$ [1]. Upon step-wise annealing from 300°C to 1060°C, a remarkable thermal stability of the Au-Fe NPs was observed, maintaining their original hexagonal spatial arrangement on the TiO_2 surface up to 900°C. A majority phase of a gold-iron alloy (solid solution) was achieved for our $\text{Au}_{0.5}\text{Fe}_{0.5}$ NPs in the temperature range of 700°C - 800°C, and for $\text{Au}_{0.2}\text{Fe}_{0.8}$ NPs at 800°C, while a phase mixture of bcc Fe and Au-Fe alloy was observed for the $\text{Au}_{0.8}\text{Fe}_{0.2}$ system at 800°C - 900°C. For all samples the segregation of Au atoms towards the NP surface was detected upon high temperature annealing (800°C) in vacuum. Nearly complete Au desorption was observed by XPS at 900°C for $\text{Au}_{0.2}\text{Fe}_{0.8}$ NPs, at 1000°C for $\text{Au}_{0.5}\text{Fe}_{0.5}$ NPs, and at 1060°C for $\text{Au}_{0.8}\text{Fe}_{0.2}$ NPs. The enhanced thermal stability of Au in the $\text{Au}_{0.8}\text{Fe}_{0.2}$ NPs is believed to be related to the formation of core(Fe)/shell(Au) structures. Furthermore, contrary to the case of pure Fe or Fe-rich NPs where nearly complete Fe desorption or Fe diffusion into TiO_2 was observed at 1000°C, an Fe signal was detected at this temperature for the Au-rich samples ($\text{Au}_{0.8}\text{Fe}_{0.2}$ and $\text{Au}_{0.5}\text{Fe}_{0.5}$).

The reactivity of our pure Au, pure Fe, bimetallic Au-Fe and a sample with a mixture of pure Au and pure Fe NPs will be compared via in-situ (UHV) temperature programmed desorption measurements. CO oxidation has been used as probe reaction.

[1] A. Naitabdi, L.K. Ono, F. Beharfarid, B. Roldan Cuenya, *J. Phys. Chem. C* 113 (2009) 1433.

5:20pm **SS2-MoA11 Secretive Lives of Multi-component Nanoparticles during Reactions**, *F. Tao**, *M. Grass, D. Butcher, J.R. Renzas, Y. Zhang, C. Tsung, S. Aloni, M. Salmeron, G.A. Somorjai*, Lawrence Berkeley National Lab

The bimetallic catalyst is one important category of heterogeneous catalysts for numerous industrial processes and energy conversion. Surface structure and chemistry of three bimetallic catalysts, Rh-Pd, Rh-Pt, and Pd-Pt nanoparticles during catalysis, oxidation, and reducing reactions have been systematically studied in-situ using XPS in a Torr pressure range and high resolution TEM. The $\text{Rh}_x\text{Pd}_{1-x}$ and $\text{Rh}_x\text{Pt}_{1-x}$ nanoparticles undergo reversible changes in both atomic fractions and chemical states corresponding to the switch of reaction environments between oxidizing and reducing conditions. Rh atoms in $\text{Rh}_x\text{Pd}_{1-x}$ and $\text{Rh}_x\text{Pt}_{1-x}$ segregate to surface layers and are largely oxidized in oxidizing conditions while in reducing atmospheres the Pd atoms in $\text{Rh}_x\text{Pd}_{1-x}$ and Pt atoms in $\text{Rh}_x\text{Pt}_{1-x}$ diffuse to the surface regions and Rh atoms are largely reduced. In contrast to $\text{Rh}_x\text{Pd}_{1-x}$ and $\text{Rh}_x\text{Pt}_{1-x}$, no significant segregation of Pd or Pt atoms was found in $\text{Pt}_x\text{Pd}_{1-x}$ nanoparticles; Pd atoms are alternatively oxidized and reduced under oxidizing and reducing conditions, whereas Pt atoms do not. The capability of restructuring nanoparticles through chemical reactions illustrates the flexibility of the structure of bimetallic nanoparticle catalysts and suggests a new method for the development of new catalysts.

Reference: F. Tao et al. 322, 932 (2008)

* TFD Young Researcher Award Winner

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