

# Tuesday Afternoon, October 16, 2007

## Surface Science

Room: 608 - Session SS1-TuA

## Bimetallics and Alloys

**Moderator:** I. Chorkendorff, Technical University of Denmark

1:40pm **SS1-TuA1 Atomic-Scale Assembly of a Heterogeneous Catalytic Site**, *P. Han*, Texas A&M University, *I. Lyubinetsky*, Pacific Northwest National Laboratory, *D.W. Goodman*, Texas A&M University

The distance between surface Pd atoms is known to control the catalytic formation of vinyl acetate from ethylene and acetic acid by AuPd catalysts. In this study, we use the thermodynamic properties and the surface lattice spacing of a AuPd(100) alloy single crystal model catalyst to control and optimize the number of Pd monomer-pair sites with a specific Pd-Pd distance. Scanning tunneling microscopy reveals that sample annealing has a direct effect on the surface Pd arrangements: short-range order preferentially forms Pd-pairs located at local  $c(2 \times 2)$  sites, sites known to be active for vinyl acetate synthesis. This methodology should be useful in the optimization of bimetallic industrial catalysts.

2:00pm **SS1-TuA2 Mechanistic Studies of the Steam Reforming of Methanol on PdZn Alloy Catalysts**, *E. Jerero*, *J.M. Vohs*, University of Pennsylvania

Methanol and other alcohols are potential bio-renewable sources of hydrogen. The use of alcohols, however, as a H<sub>2</sub> source or storage medium requires stable reforming catalysts that have high activity and selectivity at low temperatures. One such catalyst that has received much attention for steam reforming of CH<sub>3</sub>OH (SRM) [CH<sub>3</sub>OH + H<sub>2</sub>O → CO<sub>2</sub> + 3H<sub>2</sub>] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity (>95%) for the production of CO<sub>2</sub> and H<sub>2</sub> from methanol, in spite of the fact that bulk Pd exhibits nearly 100 % selectivity for the dehydrogenation of CH<sub>3</sub>OH to CO and H<sub>2</sub> under typical SRM conditions. While it has been demonstrated that formation of a PdZn alloy is required to obtain high selectivity, the mechanism by which Zn alters the reactivity of the Pd is not understood. In this talk we will present results of a study of model PdZn catalysts consisting of submonolayer amounts of Zn supported on Pd(111) that provide insight into the synergistic interactions between Zn and Pd and how they alter the reactivity of the Pd surface. Temperature programmed desorption (TPD) data for the reaction of methanol, formaldehyde and carbon monoxide on Pd(111) as a function of Zn coverage as well as results of a high resolution electron energy loss spectroscopy (HREELS) study of the bonding configurations of these molecules on Zn/Pd(111) surfaces will be presented. The TPD data show that the formation of the PdZn alloy significantly decreases the activity of the Pd surface for the dehydrogenation of CH<sub>3</sub>OH and CH<sub>2</sub>O. This change in reactivity is found to be due in part to a change in the bonding configuration of adsorbed formaldehyde intermediates. The experimental results also provide evidence for a strong electronic interaction between the Pd and Zn which affects the adsorption energies of CO and methanol.

2:20pm **SS1-TuA3 Revisiting the CO oxidation on a Au/Ni(111) Surface Alloy**, *J. Knudsen*, *L.R. Merte*, *R.T. Vang*, University of Aarhus, Denmark, *A. Resta*, *J. Schnadt*, *J.N. Andersen*, Lund University, Sweden, *F. Besenbacher*, University of Aarhus, Denmark

In the early 1990s our group showed that deposition of gold onto nickel single-crystal surfaces results in the formation of a stable alloy in the crystal's topmost layer, a surprising discovery considering that the two metals are immiscible in the bulk. This surface alloy was later shown to display interesting catalytic properties; for example, the presence of small amounts of gold in nickel catalysts hinders graphite formation during steam reforming of hydrocarbons.<sup>1</sup> Other studies explored the use of gold to inhibit CO dissociation on Ni(111) and the stability of the surface alloy under high-pressure conditions.<sup>2</sup> Most recently, Lahr and Ceyer reported that the Au/Ni(111) surface alloy catalyzes oxidation of CO to CO<sub>2</sub> at temperatures as low as 70K.<sup>3</sup> They conclude that gold atoms substituted into the top layer of the Ni(111) surface stabilize chemisorption of a reactive, non-dissociated O<sub>2</sub> species in a similar manner as has been reported for gold nanoclusters. We have used scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to study the adsorption, coadsorption and reaction of CO and O<sub>2</sub> on the Au/Ni(111) surface alloy and the clean Ni(111) surface with the goal of clarifying the mechanism or mechanisms behind this interesting

phenomenon. In agreement with the work of Lahr and Ceyer we find that molecular oxygen is required to produce CO<sub>2</sub> on the surface but our results seem to indicate a different reaction mechanism than the one proposed in their article.

<sup>1</sup> Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Norskov, J. K.; Stensgaard, L., Design of a surface alloy catalyst for steam reforming. *Science* 1998, 279, (5358), 1913-1915.

<sup>2</sup> Vestergaard, E. K.; Vang, R. T.; Knudsen, J.; Pedersen, T. M.; An, T.; Laegsgaard, E.; Stensgaard, I.; Hammer, B.; Besenbacher, F., Adsorbate-induced alloy phase separation: A direct view by high-pressure scanning tunneling microscopy. *Physical Review Letters* 2005, 95, (12), 126101.

<sup>3</sup> Lahr, D. L.; Ceyer, S. T., Catalyzed CO oxidation at 70 K on an extended Au/Ni surface alloy. *Journal Of The American Chemical Society* 2006, 128, (6), 1800-1801.

2:40pm **SS1-TuA4 General Trends in the Electronic and Chemical Properties of Monolayer Bimetallic Surfaces**, *J.G. Chen*, University of Delaware

**INVITED**

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. The modification effect is especially important at the admetal coverages in the submonolayer and monolayer regime. However, it is difficult to know a priori how the chemical properties of a particular bimetallic surface will be modified relative to the parent metals. We have investigated the electronic and chemical properties of model bimetallic surface structures, in particular subsurface and surface monolayers, using a combination of experimental and theoretical modeling to gain further insights into these factors. In the current presentation we will first utilize the adsorption and desorption of hydrogen to demonstrate the correlation between the hydrogen binding energy and the center of the surface d-band in various bimetallic surfaces. We will also provide a general equation that allows one to predict how the electronic properties, especially the d-band center, will be affected in bimetallic systems. We will then use several probe reactions, including hydrogenation of alkenes and reforming of oxygenates, to show the correlation between the chemical activities and the surface d-band center of bimetallic surfaces. Finally, we will discuss the relative stability of surface and subsurface bimetallic structures in vacuum, and in the presence of adsorbed hydrogen and oxygen.

4:00pm **SS1-TuA8 Real-time STM Observations of the Oxidation of a Ti/Pt(111)-(2x2) Surface Alloy using O<sub>2</sub> and NO<sub>2</sub>**, *S. Hsieh*, National Sun Yat-Sen University, Taiwan, *G. Liu*, *B.E. Koel*, Lehigh University

We have used scanning tunneling microscopy (STM), low energy diffraction (LEED), and Auger electron spectroscopy (AES) to study the nascent oxidation of an ordered Ti/Pt(111)-(2x2) surface alloy exposed to oxygen (O<sub>2</sub>) or nitrogen dioxide (NO<sub>2</sub>) under ultrahigh vacuum conditions. The Ti/Pt(111)-(2x2) surface alloy was formed by depositing an ultrathin Ti film on Pt(111) and annealing to 1050 K. This produces an alloy film in which the surface layer is pure Pt and the second layer contains Ti atoms in a (2x2) structure that causes the pattern observed by STM and LEED. Real-time imaging of the surface at 300 K was carried out by continuously scanning with the STM while either O<sub>2</sub> or NO<sub>2</sub> was introduced into the chamber. O<sub>2</sub> exposures did not cause any gross structural changes, however oxygen was detected on the surface afterwards using AES. Annealing this surface to 950 K resulted in the formation of an ordered TiO<sub>x</sub> overlayer as characterized by both LEED and STM. In contrast, NO<sub>2</sub> exposures caused definite changes in the surface morphology at 300 K, and the RMS roughness increased from 3.5 to 7.1 Å after a 93-L NO<sub>2</sub> exposure. No ordered structures were produced by this exposure, but annealing the surface to 950 K formed an ordered pattern in LEED and corresponding clear, well-resolved structures in STM images. Disruption or reconstruction of the Ti/Pt(111)-(2x2) surface alloy because of Ti oxidation is an activated process. The energetic barrier to TiO<sub>x</sub> formation can not be surmounted at room temperature at low oxygen coverages and annealing the surface was necessary to initiate this reaction. However, the higher oxygen coverages obtained using the more reactive oxidant NO<sub>2</sub> lowered the chemical potential in the system sufficiently to overcome the activation barrier to extract Ti from the alloy and form a disordered TiO<sub>x</sub> film at room temperature. These results illustrate the importance of the surface oxygen coverage in nucleating the room temperature oxidation of the Ti/Pt(111)-(2x2) surface alloy.

4:20pm **SS1-TuA9 CO Tolerance of Pt Islets on Ru(1000) and their Implications for PtRu Nanocatalysts: Insights from First Principles Calculations**, *T. Rahman*, *S. Stolbov*, *M. Alcantara-Ortigoza*, University of Central Florida

Proton exchange fuel cells are promising tools for hydrogen economy. However, CO traces which are inevitably present, block active sites of the Pt anode and hence poison its reactivity. Recently, Ru nanoparticles with submonolayer Pt coverage are found<sup>1</sup> to be much more tolerant to CO than

commercial catalysts. To understand the rationale for this tolerance, we have performed density functional theory based calculations of the energetics of adsorption and diffusion of CO on Pt islets on Ru(0001). We find that the total energy of the system gradually decreases as the CO molecule moves from the center of the islets to its edge and further onto substrate. Diffusion barriers for CO are found to be low: 0.06 eV to move from the center of the island to its edge, 0.27 eV to "jump" from the Pt island edge to a neighboring substrate site, and 0.3 eV to move further along the Ru surface. Assuming the pre-factor of CO diffusion to be 1012 sec<sup>-1</sup>, the diffusion rate at the operating temperature 350K is estimated to be around 107 sec<sup>-1</sup>. These results suggest that this catalyst is CO tolerant because of the propensity of CO to move from active Pt island site to the Ru substrate. We trace this effect to the features of the local densities of electronic states around the Fermi-level.

<sup>1</sup>S. R. Brankovic, J. X. Wang, and R. R. Adžić, *Electrochem. Solid State Lett.* 4, A217 (2001).

<sup>2</sup> Work supported in part by DOE-BES under grant DE-FG02-07ER15842.

4:40pm **SSI-TuA10 Effect of Quantum Well States on Adsorption of CO Molecules**, *W. Kim, S. Han, D. Lee, C. Hwang*, Korea Research Institute of Standards and Science, *C. Min*, Seoul National University, Republic of Korea, *H. Lee, H. Kim*, Pohang Accelerator Laboratory, Republic of Korea

Formation of quantum well states in the metallic thin film systems satisfying specific boundary conditions leads to the oscillation of the electron density of states at Fermi level as the thickness of the film increases.<sup>1</sup> We investigated the effect of the oscillation on adsorption of CO molecules in case of the Cu/Co/Cu(100) system. The quantum well states and resulting oscillation of density of states at Fermi level in wedge-shaped Cu/Co/Cu(100) system were confirmed by angle-resolved photoemission spectroscopy. After adsorption of CO molecules at the substrate temperature of 100 K, we observed the shift of binding energies of quantum well states, which could be understood in the scheme of phase accumulation model. C 1s core level photoemission spectra of the adsorbed molecules were measured as a function of temperature for each Cu thickness. The initial feature of the C 1s spectra show well-known three peak structure similar to that of CO molecules adsorbed on Cu(100). From the temperature dependence of the intensity of measured C 1s core level spectra, we could determine the desorption temperature of CO molecules for each Cu thickness, which showed clear dependence on the density of states of Fermi level with oscillating variation of 15 K. We also evaluated the relative ratio of the first satellite peak to main peak in C 1s core level spectra and found out that the ratio showed oscillatory behavior and strong correlation with the density of states at Fermi level. Our observations confirm the old theoretical explanation on the origin of three peak structure of C 1s core level spectra of CO molecules adsorbed on the Cu(100) surface.<sup>2</sup>

<sup>1</sup> Z. Q. Qiu and N. V. Smith, *J. Phys.: Condens. Matter* vol.14, R169.

<sup>2</sup> O. Gunnarsson, and K. Schönhammer, *Phys. Rev. Lett.* vol 41, 1608.

5:00pm **SSI-TuA11 Modifying the Adsorption of Molecules at Metal Surfaces by Quantum Confinement of Electrons**, *L. Tskipuri, R.A. Bartynski*, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. Quantum confinement of electrons forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we found that MQW states modify the strength of CO bonding to Cu MQW overlayers on the pseudomorphic fcc-Co/Cu(100) and fcc-Fe/Cu(100) systems.<sup>1</sup> In these systems, the CO-metal bond strength oscillates, in correlation with MQW states, as a function of Cu overlayer thickness. Here we extend these studies with IR studies of CO adsorbed on Cu MQWs and report on the adsorption properties of the pseudomorphic transition metal layers themselves. These systems have partially filled d-bands may be grown in a metastable structure. We have examined the unoccupied electronic structure and CO bonding strength on the n-ML fccNi/Cu(100) and n-ML fccCo/Cu(100) systems using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). In the case of Co, the as-grown films exhibit well-defined unoccupied MQW states, but they do not cross the Fermi level. This allows us to investigate adsorbate-MQW interactions that involve MQW states away from the Fermi level. Upon CO adsorption a well-defined structure centered about 3.8 eV above the Fermi level appears and is assigned to the unoccupied CO 2 $\pi$  orbital. CO adsorbs molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 375 K, which is about 30 K lower than what is observed for CO adsorbed on the hcp Co surfaces. When Co films are dosed at low temperatures (~ 100K), we find a second CO desorption peak around 230 K, once again similar to what is seen for hcp Co, but as a markedly lower temperature. These peak desorption temperatures change as a function of film thickness and are correlated with two different C-O stretch vibrational frequencies observed

in the IR spectra. We have observed similar desorption peak temperature shifts when CO desorption from the Ni/Cu(100) system as a function of thickness and as compared to single crystal Ni(100). The role of quantum confinement and surface strain in producing the observed effects will be discussed.

<sup>1</sup> A. G. Danese, F. G. Curti, and R. A. Bartynski, *Phys. Rev. B* 70, 165420 (2004).

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