

Tuesday Morning, November 10, 2009

Surface Science

Room: N - Session SS2-TuM

Reactions on Metals and Bimetallics

Moderator: S. Chiang, University of California, Davis

8:00am **SS2-TuM1 Surface Structure of the Pd-H System**, *K.F. McCarty*, Sandia National Laboratories, *B. Santos*, Universidad Autónoma de Madrid, Spain, *T. Herranz*, Instituto de Química-Física "Rocasolano", Spain, *J.I. Cerda*, *J.M. Puerta*, Instituto de Ciencias de Materiales de Madrid, Spain, *J. de la Figuera*, Instituto de Química-Física "Rocasolano", Spain

Palladium hydride, PdH, is the model transition-metal hydride. Surface-science studies of PdH are scarce for two reasons. First, hydrogen pressures in the 10's of torr range are needed to form PdH near room temperature. Second, the expansion of the lattice that occurs during hydride formation tends to destroy Pd single crystal. To overcome this latter problem, we use thin epitaxial films of Pd(111) on Ru(0001) and W(110) to examine the surface science of the Pd-H system. To achieve an effective higher hydrogen pressure, we expose the Pd films to atomic H. We use low-energy electron diffraction (LEED) to characterize the Pd surface after H exposure. By performing the LEED in a low-energy electron microscope (LEEM), we are able to collect diffraction data from the same, atomically flat regions before and after H exposure. Detailed analysis of the LEED IV curves shows that exposure to atomic H at about 200K expands the interlayer spacing of the top two Pd layers but does not affect deeper layers. We interpret these changes as the formation of a surface hydride. Exposure to atomic H while cooling from above room temperature also produces the surface hydride. The lack of diffusion deeper into the film suggests that an energy barrier inhibits diffusion past the second Pd layer. The synthesis of a bulk hydride was attempted by exposing a Pd film to 40 torr of hydrogen and then reducing the pressure after cooling. The resulting material presented sharp, 3-fold diffraction patterns with an IV response different than the surface hydride. We will discuss the structure of this material, which we tentatively assign to a bulk PdH.

8:20am **SS2-TuM2 Surface-catalyzed O₂ Adsorption on Quantum Thin Films**, *J. Kim*, *A. Khajetoorians*, The University of Texas, Austin, *W.G. Zhu*, *Z.Y. Zhang*, Oak Ridge National Laboratory, *C.K. Shih*, The University of Texas, Austin

Pure crystalline Pb is well known to be inert with respect to oxygen gas. By using scanning tunneling microscopy we demonstrate that the oxygen adsorption on Pb films is greatly increased by Cs adsorbates acting as catalysts. Our previous studies show that Cs atoms can be easily incorporated into the surface layer of thin Pb films through a substitutional process when they are evaporated at low temperature (100 – 120 K). In addition, this Cs-Pb surface alloying process works cooperatively with the quantum size effect, leading to formation of nano-islands. This study explores the effect of the surface alloying on the oxidation. With only a minute concentration of Cs (0.004 ML coverage), we found a great enhancement of surface oxidation rates. Theoretical DFT calculations have revealed that the oxygen adsorption energy is greatly enhanced at the Cs substitutional sites. Subsequent oxygen exposures lead to great enhancement of oxidation which can be identified as PbO. Furthermore, we have explored the effect of temperature on the formation of Cs-Pb alloy and its consequences for the oxidation of Pb.

8:40am **SS2-TuM3 Surface Reactions on Model Gold Catalysts**, *C.B. Mullins*, University of Texas at Austin **INVITED**

We have studied model gold catalysts consisting of gold clusters supported on planar titania supports and Au single crystalline samples employing standard UHV surface chemical probes in addition to molecular beam techniques. In this talk I will focus on our results relating to enhanced CO oxidation by adsorbed water and the oxidation of alcohols employing single crystalline bulk gold. Briefly, we have found that adsorbed water can greatly enhance CO oxidation on oxygen pre-covered bulk gold at low temperatures. Additionally, we have found that atomic oxygen pre-covered Au(111) can partially oxidize ethanol, 1- and 2-propanol, and 2-butanol to their respective ketone or aldehyde with high efficiency and selectivity.

9:20am **SS2-TuM5 Oxidative Removal of Carbodiimide (NCN) and Isocyanate (NCO) Species from Cu(001) Surfaces**, *E.Z. Ciftlikli*, *J. Lallo*, *E.Y.-M. Lee*, *S. Rangan*, *L. Tskipuri*, *R.A. Bartynski*, *B.J. Hinch*, Rutgers University

Adsorbed isocyanate (NCO) species on Cu(001) undergoes oxidation, in the presence of O_(a), at temperatures as low as 373K. N_(a) remains and CO_{2(g)} evolves. On the other hand, a NCO/Cu(001) surface, in the absence of any other coadsorbates, is stable up to ~523K. Above this temperature, a bimolecular decarboxylation reaction is induced, which produces CO_{2(g)} and a surface bound carbodiimide (NCN) species alone. RAIRS measurements confirm a surface parallel species with an "sp" hybridized carbon atom. The introduction of oxygen at room temperature on NCN/Cu(001) leads to the reappearance of NCO species on the surface. The apparent yield of reformed NCO is not simply in proportion to the initial NCO dose levels. The chemistry of the NCO species is affected by the likely coadsorbates; N_(a), O_(a), and NCN_(a). The ν₃(NCO) bands observed in RAIR spectra of these partially oxidized surfaces, apart from being complex in shape, display a significant blue shift with respect to the ν₃(NCO) modes observed when similar quantities of NCO are adsorbed on coadsorbate-free surfaces. In addition, the annealing of these surfaces to 473K indicates only a partial further oxidation of NCO. Even at excessive O₂ doses, NCO is not fully oxidized by 473K. A further annealing to ~623K is required for complete NCO removal. We will discuss the possible factors that limit NCO oxidation in these surfaces.

9:40am **SS2-TuM6 Kinetics of HCN Decomposition and CNH₂ Formation on Pt(111)**, *X. Hu*, *M. Trenary*, *R.J. Meyer*, University of Illinois at Chicago

The kinetics of HCN (hydrogen cyanide) decomposition to H and CN and the subsequent hydrogenation of CN to the CNH₂ species on the Pt(111) surface were studied with time-resolved reflection absorption infrared spectroscopy (RAIRS). The use of RAIRS for kinetic studies can uniquely provide important information on the mechanisms of surface reactions, particularly when these reactions occur below the temperature at which products desorb from the surface. In addition, from the analysis of kinetic data, activation energies for elementary surface reactions on well-defined systems can be determined and thereby provide important experimental benchmarks for comparison with the results of state-of-the-art theoretical calculations. Hydrogen cyanide adsorbs on Pt(111) at a temperature of 85 K to give an intense CH stretch vibration at 3300 cm⁻¹. The time dependent decrease of this peak was monitored at temperatures between 120 and 135 K, the temperature range where the C-H bond of HCN breaks. The decrease in CH stretch peak intensity appears to follow first order kinetics and is attributed to both C-H bond breaking and HCN desorption. The CNH₂ species is characterized by RAIRS peaks at 3370 cm⁻¹ (N-H stretch), 1566 cm⁻¹ (NH₂ scissors), and 1324 cm⁻¹ (C-N stretch). The increase in coverage of the CNH₂ species was monitored by following the time dependence of the 1566 cm⁻¹ peak, the most intense mode of CNH₂, in the temperature range of 210 to 230 K. The CNH₂ formation rate is found to follow second order kinetics. The spectra show the appearance of an intermediate species with a peak at 3347 cm⁻¹, the intensity of which initially increases with time, reaches a maximum, and then decreases as CNH₂ is formed. This peak is identified as the N-H stretch of an HNC surface intermediate. Through kinetic modeling of the time dependence of the coverages of the HCN, HNC, and CNH₂ species, rate constants were derived at each temperature and activation energies were obtained from Arrhenius plots. The experimental results were then compared with the results of density functional theory (DFT) calculations on the stability and structures of the intermediates. Activation barriers for each step of the reaction were also obtained from the DFT calculations. The calculations confirm that CNH₂ is the energetically favored product of the reaction and that CNH₂ has the structure implied by the RAIR spectra. The calculations also predict that HNC is a stable surface intermediate. However, the structures of both adsorbed HCN and HNC as implied from the RAIRS data disagrees with the optimized structures obtained from the DFT calculations.

10:40am **SS2-TuM9 Surface Segregation on Composition Spread Alloy Films**, *A.J. Gellman*, *J.B. Miller*, *D. Priyadarshini*, Carnegie Mellon University

Surface segregation has been studied in Pd_xCu_{1-x} alloys used for hydrogen purification membranes. Surface segregation influences the performance of these alloys for hydrogen purification and furthermore, segregation at the surfaces of these materials is a sensitive function of the concentration of contaminants such as sulfur. Segregation is not just restricted to the topmost atomic layer of the alloy. The concentration of one component in the top few layers of the surface may differ from that of the bulk. Because surface

segregation is a continuous function of bulk composition, x , a complete understanding of segregation in a binary alloy requires the development of high throughput methods that allow concurrent measurements of surface segregation at all possible values of bulk composition.

Surface segregation has been studied in a $\text{Pd}_{70}\text{Cu}_{30}$ alloy using both x-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). The results show that the topmost atomic layer is rich in Cu. On the other hand, the near-surface region consisting of the immediate subsurface layers is rich in Pd. Furthermore, the adsorption of sulfur on the surface causes the complete elimination of Cu from the topmost layer.

A high throughput method for study of surface segregation has been developed that is based on the deposition of thin Composition Spread Alloy Films (CASFs) that contain all possible bulk compositions of the $\text{Pd}_x\text{Cu}_{1-x}$ alloy. Spatially resolved surface analysis of the surface of the $\text{Pd}_x\text{Cu}_{1-x}$ CASF has been achieved using XPS. The results show that the near-surface region of the alloy is Pd rich over a wide range of bulk Pd concentrations.

11:00am **SS2-TuM10 Catalytic Hydrogenation of Butadiene on Bimetallic Surfaces**, *M. Moors, C. Breinlich*, University of Bonn, Germany, *T. Kobiela*, Warsaw University of Technology, Poland, *C. Becker, K. Wandelt*, University of Bonn, Germany

Investigations of bimetallic systems with regard to their surface composition, morphology and adsorption properties for reactive gases are essential for the development of new catalysts with higher efficiency and durability. An interesting catalytic reaction is the partial hydrogenation of butadiene to 1-butene without complete hydrogenation to butane and the coking of the catalyst due to decomposition of the educt. In this work the hydrogenation of butadiene has been investigated on bimetallic Sn-Pd(111) and Au-Pd(111) surface alloys by means of Ultraviolet Photoelectron Spectroscopy (UPS) and Temperature Programmed Desorption (TPD). The bimetallic surfaces were prepared by depositing Sn or Au onto a clean Pd(111) surface followed by controlled annealing. Annealing at at least 4 ML thick Sn film to 750 K results in an ordered $\sqrt{2}\times\sqrt{2}$ Pd₃Sn surface alloy as evidenced by Low Energy Electron Diffraction (LEED). Further annealing to 850 K leads to the formation of the thermodynamically more stable $\sqrt{3}\times\sqrt{3}$ Pd₃Sn surface alloy. After annealing to 1000 K all Sn has diffused into the Pd(111) substrate. No ordered alloy phase has been found for the Au-Pd system. Annealing to temperatures gradually higher than 450 K leads to a continuous decrease of the Au surface concentration until at 1050 K Au has completely disappeared into the bulk. Under UHV conditions the Sn-Pd(111) alloy surfaces exhibit a lower hydrogenation rate of butadiene in comparison to the pure Pd(111) surface. The butene production strongly decreases with increasing Sn amount at the surface. This decreasing reactivity, however, is accompanied by an increasing selectivity and decreasing coking of the surface. Alloying Pd with Au on the other hand results in a significantly improved reactivity towards butene compared to pure Pd(111), while the selectivity is only slightly decreased. Furthermore, the coking of the Au-Pd(111) surface is even lower than observed on pure Pd(111), which makes this system a promising hydrogenation catalyst.

11:20am **SS2-TuM11 Buffer Layer Assisted Deposition of Pb-Au Bimetallic Nano-clusters: Characterization and Chemical Reactivity**, *M. Asscher*, Hebrew University of Jerusalem, Israel

Control over size and density of metallic nano-particles on oxide surfaces is important for studying model heterogeneous catalysts.

We have deposited metallic clusters on model SiO_2 / Si(100) support, assisted by amorphous solid water (ASW) as a buffer. One may control this way the average size and density of metallic clusters independently by changing the ASW layer thickness, metal dosage and then repeat the deposition process. Bimetallic Pd-Au clusters were prepared this way and characterized by IR spectroscopy, AFM, SEM and TEM measurements in order to determine their structural and crystalline nature.

Directly deposited pure Pd clusters, 5 ± 2 nm diameter, were found reactive in acetylene trimerization to benzene. The buffer assisted Pd-Au bimetallic clusters in comparison, are at least three times more reactive than the pure Pd, in spite of having smaller surface density of Pd atoms. Acetylene hydrogenation to ethylene was also studied. This product is two orders of magnitude more probable than benzene. Once again the bimetallic alloy was significantly more reactive than the pure Pd. Clean gold clusters were totally inactive. Preliminary results reveal the effect of pre-annealing to temperature below 300K, suggesting strong sensitivity to sintering. The possibility of size dependent reactivity will be discussed.

11:40am **SS2-TuM12 Theoretical Prediction of Ordering and Reactivity of Bimetallic Gold Alloy Surfaces**, *J. Stephens, H. Ham, G. Hwang*, University of Texas at Austin

Bimetallic materials have shown great promise for the development of superior catalysts. The recent surge of new interest in catalysis by gold has led researchers to investigate the effects of adding gold to other metals. While mechanisms underlying the alloying effect are still not understood in detail, recent evidence suggests that the enhanced reactivity of bimetallic catalysts can be attributed to a combination of metal-metal interactions (ligand effect) and unique mixed-metal surface sites (ensemble effect). The ability to accurately predict the arrangements of constituent atoms in a surface alloy is indispensable to unraveling the roles played by the ensemble and ligand effects in the performance of bimetallic model catalysts. We might expect that the arrangement of surface and near-surface atoms is a complex function of temperature, stoichiometric ratio, and surface facet, but thus far, only very limited theoretical effort has been undertaken to determine the atomic distribution of bimetallic alloys. We have developed a scheme to predict the equilibrium arrangement of atoms in surface alloys at finite temperatures. Our scheme is based on the Ising model, and is capable of reproducing DFT-predicted total energies to within no more than a few meV per surface atom. We will present our scheme in detail, as well as what we have learned about the effects of temperature, composition, surface facet, and particle identity on the arrangement of surface atoms for various gold-based binary alloys including gold-palladium and gold-platinum. We will also discuss how the atomic arrangements affect the reactivity of gold-based alloy surfaces particularly towards oxidation of hydrogen and carbon monoxide.

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