

## Surface Science

### Room 203 - Session SS3-ThM

#### Reactivity of Bimetallic Surfaces

**Moderator:** R.A. Bartyński, Rutgers University

**8:20am SS3-ThM1 Temperature Effects on the Nucleation and Growth of Ag Films on 5-fold Surfaces of Icosahedral Al-Pd-Mn Quasicrystal, B. Unal,** Iowa State University; *T.A. Lograsso, A.R. Ross,* The Ames Laboratory; *C.J. Jenks, J.W. Evans, P.A. Thiel,* Iowa State University and the Ames Laboratory

Growth of thin films on surfaces of complex intermetallics, such as quasicrystals, can provide new insights into nucleation, growth, and the thermodynamic factors that control film structures. We have used scanning tunneling microscope to study the growth and nucleation of the first few monolayers of Ag on the fivefold surface of an icosahedral Al-Pd-Mn quasicrystal surface at different temperatures. While Ag films grow layer by layer at 127K and 200K, the growth mode switches at about room temperature. Between 300 and 365 K, the Ag segregates in islands that are 4 and 5 monolayers high, on the terraces. When the temperature reaches 420K, islands grow at the step edges rather than on the terraces. This behavior will be discussed in terms of the existence of different types of diffusion barriers on the quasicrystal surface.

**8:40am SS3-ThM2 Pd-Au Model Catalysts: From Planar Surfaces to Nanoclusters, K. Luo, C.-W. Yi, T. Wei, D.W. Goodman,** Texas A&M University

Pd-Au bimetallic model catalysts were synthesized as planar surfaces and as well-dispersed alloy clusters on Mo(110) and SiO<sub>2</sub> ultra-thin films, respectively, under ultrahigh vacuum (UHV) conditions. The surface composition, geometric and electronic structures, and CO adsorption properties have been characterized using ion scattering spectroscopy (ISS), X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS), and temperature programmed desorption (TPD). Stable Pd-Au alloy surfaces, where the surface is significantly enriched in Au relative to the bulk, are obtained upon sequential deposition of Pd and Au followed by an anneal. Characteristic isolated Pd sites are identified on the Pd-Au planar and supported Pd-Au clusters. Ethylene adsorption and dehydrogenation show a clear structure-activity correlation with respect to these Pd-Au model surfaces.

**9:00am SS3-ThM3 Site-Directed Chemistry at Pt-Sn Alloy Surfaces, B.E. Koel,** University of Southern California

**INVITED**

Achieving higher activity and selectivity of heterogeneous catalysts, electrocatalysts, and sensors requires advances in controlling structure and chemistry relevant to interfacial reactions at the nanoscale. One can now exploit an unprecedented ability to investigate such phenomena on alloy surfaces to obtain new information about how and why composition, structure, and defects alter chemical reactions that occur at specific sites. We have been probing this site-directed chemistry at alloy surfaces in a wide range of chemisorption and catalytic reactivity studies. The talk today will focus on how recent results for several Sn/Pt(111) and Sn/Pt(100) ordered surface alloys have helped to define the overall chemical reactivity of Pt-Sn bimetallic surfaces, clarified the role of a second metal in altering the chemistry of Pt alloys, and led to general principles for understanding the reactivity and selectivity of alloy catalysts. Specifically, I will discuss exploiting Pt-Sn alloys for selective hydrogenation of 1,3-butadiene based on studies of well-defined model catalysts, i.e., Pt(111) and the (2x2)-Sn/Pt(111) and (3x3)-Sn/Pt(111) surface alloys, that probe the influence of alloyed Sn on the reaction barrier to butadiene hydrogenation and the effect of surface Sn concentration on hydrogenation activity and selectivity. Fundamental concepts emerging from such studies enhance our understanding and ability to tailor local properties of alloy surfaces, which should facilitate the design of new catalysts and sensors.

**9:40am SS3-ThM5 Probing Complex Adsorption Structures: A Joint Experimental and Theoretical Study of Prenal Adsorbed on Pt(111) and Pt-Sn Surface Alloys, J. Haubrich<sup>1</sup>,** University of Bonn, Germany; *D. Loffreda, F. Delbecq, P. Sautet,* Ecole Normale Supérieure de Lyon, France; *A. Krupski, C. Becker, K. Wandelt,* University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes on transition metal surfaces

represent a challenge to both experimentalists and theoreticians. Although numerous studies have been dedicated to systems like acrolein or prenal on Pt(111) in recent years, the details of the molecule-surface bonding still remain under debate. Yet the selectivities of such processes depend crucially on the adsorption complexes. Their characterization is even more complicated when alloy surfaces are considered because alloying is often used to optimize the properties of the catalyst. We here present a joint experimental and theoretical study on molecule-surface bonding of prenal on Pt(111) and two Pt-Sn surface alloys based on the interpretation of HREEL spectra using ab initio density-functional theory (DFT). Additionally TPD and LEED studies of prenal adsorbed at 100K on these surfaces were performed. While on Pt(111) the desorption of prenal is detected at 160K (multilayer) and 199K, also fragmentation reactions are observed giving rise to desorption of H<sub>2</sub> and CO. On Pt<sub>2</sub>Sn and Pt<sub>3</sub>Sn/Pt(111) this fragmentation process is suppressed. The HREELS experiments were carried out between 100K and 500K on Pt(111) show highly complex spectra of the adsorbed prenal and its fragments, which can be detected above 300K. On both Pt-Sn surface alloys very similar HREEL spectra of prenal are recorded. Combining the HREEL spectra with the results of the vibrational analysis obtained from the DFT calculations, we are able to identify stable adsorption geometries, interpret the normal modes corresponding to the measured loss peaks and to point to likely reaction intermediates.

**10:00am SS3-ThM6 Catalytic CO Oxidation at 70 K on a Au/Ni Surface Alloy, D.L. Lahr,** MIT; *S.T. Ceyer,* MIT, US

A Au/Ni surface alloy catalyzes the oxidation of CO at low temperature by at least three distinct mechanisms. At the lowest temperature of 70 K, molecularly adsorbed O<sub>2</sub>, spectroscopically characterized by high resolution electron energy loss spectroscopy as peroxy or superoxy species bound at multiple sites with vibrational frequencies of 865 and 950 cm<sup>-1</sup>, are the reactants with CO. A third molecularly adsorbed O<sub>2</sub> species, characterized by an O-O stretch mode at 790 cm<sup>-1</sup>, does not react with CO. Between 105-125 K, CO<sub>2</sub> production coincides with O<sub>2</sub> dissociation, suggesting a "hot atom" mechanism in which an O atom, formed upon dissociation of adsorbed O<sub>2</sub>, reacts with CO before equilibrating with the surface. The CO that reacts is characterized by a C=O stretch mode at 2170 cm<sup>-1</sup>. Given the relatively high frequency, the reacting CO is likely bound to a Au atom. Above 125 K, CO bound to Au reacts with atomically adsorbed O atoms, characterized by a O-Au stretch mode at 660 cm<sup>-1</sup>. These results show that nanosize Au clusters bound to oxide supports are not a necessary condition for Au catalyzed, low temperature CO oxidation. In addition, the lower temperature at which the CO oxidation reaction occurs on the Au/Ni surface alloy as compared to the reaction temperature (~200 K) on the supported Au nanoclusters demonstrates that the activation energy is significantly lower on the Au/Ni surface alloy than on Au nanoclusters.

**10:20am SS3-ThM7 The Chemical Properties of Pd-Au Alloy Surfaces, T. Wei, J.H. Wang, C.-W. Yi, D.W. Goodman,** Texas A&M University

The chemisorptive behavior of CO on Pd-Au alloy films and silica-supported Pd-Au nano-clusters has been studied by infrared reflection adsorption spectroscopy (IRAS). The relative influence of geometric versus electronic effects has been addressed by comparing the alloy and single component surfaces. A unique CO vibrational feature at 2088 cm<sup>-1</sup>, corresponding to CO adsorbed on isolated Pd sites on Au, is clear evidence of an ensemble effect. On the other hand, the IRAS data for CO adsorbed on Pd-Au alloy surfaces show no evidence for an electronic effect of Au on Pd. The surface concentration of isolated Pd sites can be controlled by systematically altering the Pd-Au alloy composition, allowing detailed studies of isolated Pd sites as active sites for adsorption and reaction.

**10:40am SS3-ThM8 Unoccupied Electronic Structure and CO Adsorption in Ni/Cu(100) System, H. Yao, S. Rangan, A.G. Danese, R.A. Bartyński,** Rutgers University

Ultrathin (i.e. several monolayers thick) metal films in the nanometer thickness range exhibit quantum size effects in their electronic structure. These effects often lead to interesting magnetic, optical or chemical properties. The particular materials selected in our work here Ni/Cu(100) system are motivated by two main reasons: First, because its applications in spin valve structures; second, we would expect that the study of this system will help us to understand the anomalous downward dispersion of unoccupied states in Cu/Ni/Cu(100) systems. We performed a series of inverse photoemission (IPE) studies of the unoccupied electronic structure of the Ni/Cu(100) and CO/Ni/Cu(100) systems as a function of Ni thickness.

<sup>1</sup> Morton S. Traum Award Finalist

# Thursday Morning, November 3, 2005

IPE spectra from Ni films exhibit very rich structures. A phase accumulation model (PAM) calculation suggests only one of the three main features is consistent with metallic quantum well (MQW) State in Ni film. CO adsorption strongly modifies the spectrum by dramatically suppressing one of the main features indicating that this feature is a Ni surface resonance. Furthermore, by comparing spectra from Ni/Cu(100) with results from Cu/Ni/Cu(100), we suggest the third feature is a state confined to the Ni/Cu interface, and the Cu/Ni interface state plays key roles in the anomalous dispersion of the unoccupied states in the Cu/Ni/Cu (100) system. The correlation between chemisorption properties of Ni films of different thickness and their electronic structures are studied with Temperature Programmed Desorption (TPD) and IPE. First principles calculations illustrating the evolution of the electronic structure of Ni/Cu structures as a function of both Ni and Cu film thickness will also be presented and compared to the experimental measurements.

11:00am **SS3-ThM9 Atomically and Time Resolved Pattern Formation in Strained Metal Films: S on Submonolayer Ag/Ru(0001), B. Diaconescu**, University of New Hampshire, US; *K. Pohl*, University of New Hampshire

Strained metallic interfaces can lead to highly ordered misfit dislocation networks that can be utilized as a bottom-up patterning method for the growth of cluster arrays of specific size and density. The great potential of this natural templating method is that the characteristic length scales are predicted to depend on the interfacial stress. 2D sulfur cluster growth on the misfit dislocation network of submonolayer Ag on Ru(0001) relaxes the 6nm x 4nm unit cell of the strained Ag film into a large-scale ordered triangular array of S filled vacancy islands, 5nm apart.<sup>1</sup> Variable Temperature STM and LEED studies reveal that 2D S cluster growth takes place in two regimes: (1) At low S coverage a dilute phase of S clusters, etched at the threading dislocation sites of the Ag film forms. S clusters have an average size of 1.5nm<sup>2</sup> corresponding to two S atoms per cluster, and a highly temperature dependent mobility. (2) At a S coverage above 0.018 ML the solid S cluster phase forms after all the available threading dislocation sites of the Ag film were etched. In this regime the highly ordered S cluster array shows a S coverage dependent cluster size and a p(2x2)S/Ru(0001) structure. In the growth process S partially relieves the strain in the Ag film as seen by the relaxation of the misfit dislocation network. For S coverage beyond 0.33 ML on the Ru(0001) terrace, the compressed S phase pushes Ag atoms into the second layer and the ordering of the S clusters is partially destroyed. It is found that exchange-induced inhomogeneous nucleation of S adatoms modifies the interfacial stress in the submonolayer Ag/Ru(0001) film and, that the size of the S-filled vacancy islands in the ordered self-assembled array can be controlled with S coverage. <sup>1</sup> K.Pohl et al. Nature 397, 238 (1999) \* Supported by NSF-CAREER-DMR-0134933 and ACS-PRF-37999-G5.

11:20am **SS3-ThM10 Experimentally and Theoretically Determined Core-Level Shifts for Ultrathin Pd, Ag and AgPd Films on Ru(0001), J. Onsgaard**, L. Bech, Aalborg University, Denmark; *W. Olovsson*, Uppsala University, Sweden; *I. Abrikosov*, Linköping University, Sweden

Ultrathin composed metal films deposited on a relatively inert substrate are complex systems that are subject to both thin-film and surface-alloying effects. The evolution during build-up of ultrathin films of Pd and/or Ag deposited on Ru(0001) was followed by means of synchrotron-based photoelectron measurements (PES) of the valence band and of the Pd and Ag 3d<sub>5/2</sub> core levels. Similarly, the evolution during stepwise annealing of ultrathin films of Ag and Pd deposited one-by-one on Ru(0001) was followed. LEED was applied to gain information on the atomic structure. The sample temperature was close to room temperature during data acquisition, whereas it typically was kept at ~550 K during metal exposures. Characteristic changes observed during film growth and annealing will be demonstrated. Further, experimentally obtained core level PES measurements will be compared with results of Density Functional Theory (DFT) calculations, which are based on the coherent potential approximation (CPA) and carried out within the complete screening picture, which includes both the initial and final state effects of PES.

11:40am **SS3-ThM11 The Photoemission Study of Oxygen Adsorbate on Pt@sub 3@Ni (100), (110), and (111) Surfaces, B.S. Mun**, Lawrence Berkeley National Laboratory, US; *M. Watanabe*, *M. Rossi*, *V. Stamenkovic*, *N.M. Markovic*, *P.N. Ross*, Lawrence Berkeley National Laboratory

The electronic structures of oxygen covered surfaces on Pt@sub 3@Ni (100), (110), and (111) alloys are studied with photoemission spectroscopy. The positions of local d-band center and the widths from valence band density of state (DOS) measurements are compared before and after the

oxygen adsorption at various temperatures. The correlations between the electronic structures of oxygen-adsorbed surfaces and the chemical properties are discussed. Modified electronic structures of Pt@sub 3@Ni surfaces are also compared to those of Pt single crystals surfaces. The density functional theory calculation is carried out for the comparison of the experimental results to the theory.

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