

Surface Science

Room: Picuris - Session SS1-TuM

Catalysis on Metal and Alloy Surfaces

Moderator: A.J. Gellman, Carnegie Mellon University

8:00am **SS1-TuM1 Sulfur-Induced Reconstruction of the Ag(100) Surface**, *S.M. Russell, M. Shen*, Iowa State University, *C.J. Jenks, D.-J. Liu*, Ames Laboratory, US-DOE, *P.A. Thiel*, Iowa State University & Ames Laboratory, US-DOE

Sulfur adsorption on Ag(100) is the object of this investigation because sulfur affects reshaping and decay of Ag nanostructures on this, and other, surfaces. We have studied sulfur on Ag(100) using STM. Consistent with prior LEED work [1-2], we find two structures that coexist at room temperature: a $p(2 \times 2)$ chemisorbed phase, and a $(\sqrt{17} \times \sqrt{17})R14^\circ$ reconstruction, the latter being the phase with higher sulfur coverage. As sulfur coverage increases, sulfur atoms replace Ag in the surface plane to form the $\sqrt{17}$, resulting in ejection of Ag and development of $\sqrt{17}$ islands on the terraces. DFT supports a model in which 5 Ag atoms are ejected per unit cell. In STM, the dominant local motif of the $\sqrt{17}$ reconstruction consists of rectangular groups of (primarily) four sulfur atoms, very similar to sulfur on Cu(100) in the $\sqrt{17}$ phase [3]. At room temperature, the $\sqrt{17}$ islands are dynamic, and can develop extensions of disordered material that link and island, transiently, to another $\sqrt{17}$ island or domain.

References

- [1] G. Rovida and F. Pratesi, *Surf. Sci.* **104**(2-3), 609 (1981).
- [2] M. P. Sotro and J. C. Boulliard, *Surf. Sci.* **162**(1-3), 285 (1985).
- [3] M. L. Colaianni and I. Chorkendorff, *Phys. Rev. B* **50**(12), 8798 (1994).

8:20am **SS1-TuM2 In-situ Spectroscopic Investigation of Adsorption and Reaction of Pyridine Molecules on Modified Pt Surfaces**, *R. Denecke, C. Wöckel, K. Fischer, S. Wickert*, Universität Leipzig, Germany, *R. Streber*, Universität Erlangen, Germany

Using high-resolution and time-dependent x-ray photoelectron spectroscopy (XPS) adsorption and reaction processes can be followed in-situ. From the data, adsorbed species as well as reaction intermediates and products can be determined and quantitatively analyzed. Time-dependent data allow for the determination of kinetic parameters.

We are applying this method to pyridine molecules adsorbed on flat and stepped Pt surfaces. Using a regularly stepped Pt(355) surface with (111) oriented terraces which are five atomic rows wide and (111) oriented monatomic steps, C 1s and N 1s core level data are recorded during adsorption at various temperatures. As additional parameter, the free Pt terrace width is varied by deposition of Ag atoms on the surface. At 300 K, they form rows along the step edges, thus effectively reducing the terrace width. Following the core level data while increasing the temperature with a fixed heating rate, temperature-programmed XPS data allow to follow the thermal reaction of the adsorbed species. The experiments have been performed at the synchrotron radiation facility BESSY II in Berlin.

Literature reports a temperature- and coverage-dependent reorientation of the pyridine molecules on Pt(111) [1]. While at 300 K an upright molecule is proposed, the situation changes for low temperatures from flat-lying at low to upright at higher coverages. In line with these reports, we observe distinct changes in the core level binding energies and intensities. While at 200 K only one strong N 1s feature is observed for all coverages, there is a change from two features to one for 300 K. Here, the remaining feature is observed at a higher binding energy. Temperature-dependent data show the change from the low to the high energy feature. This is accompanied by respective changes in the C 1s data, thus suggesting again temperature- and coverage-dependent changes.

The presence of steps and especially their decoration by Ag changes the situation quite drastically. This manifests itself in changed binding energies and reaction schemes. From a comprehensive analysis a scheme for adsorption and thermal reaction of pyridine on Platinum surfaces is derived.

- [1] S. Haq, D.A. King, *J. Phys. Chem.* **100** (1996) 16957.

8:40am **SS1-TuM3 Mechanisms of Catalytic Processes on Au: Imaging, Spectroscopy and Reactivity**, *C. Friend, Xu, Liu, Baker, Haurich, R.J. Madix*, Harvard University **INVITED**

The need for energy-efficient catalytic processes and the long fascination with Au as a material has spurred intense activity in the investigation of gold-based catalysis. There is on-going discussion of the origin of the activity of gold for oxidation reactions, including changes in the oxidation

state and electronic properties of Au nanoparticles. We have demonstrated that atomic oxygen bound to Au is highly active for a range of oxidative transformations on metallic Au. Well-prepared gold crystal surfaces are inactive for O₂ dissociation, so that ozone was used as an oxidant in order to probe the bonding and reactivity of O on Au. Oxidation of Au(111) leads to the release of Au nanoparticles on which O is adsorbed. A combination of scanning tunneling microscopy (STM), high resolution electron energy loss spectroscopy experiments complemented by density functional theory calculations show that the local bonding and degree of longer range order of the O-Au islands depends on the temperature of oxidation and the overall O coverage. Reactivity studies show that low coverages of O bound in sites of local three-fold coordination are most active for selective reactions. Investigations of the molecular-scale mechanism for oxidative coupling reactions promoted by atomic oxygen on Au will be presented. Oxidative coupling of oxygenates—alcohols and aldehydes—will be the focus of the talk. The coupling reactions yield organic esters, which are important products industrially because of their widespread use as precursors for fragrances, flavorings, and fabrics. We construct a general mechanism for this class of reactions that provides insight into the optimum conditions of selectivity for even complex mixtures of alcohols. These fundamental studies will also be related to parallel studies using nanoporous Au as a catalyst at atmospheric pressure to illustrate the value of fundamental studies of catalytic processes. In this case, the reactions of Au under ultrahigh vacuum conditions provide an understanding of reactions at higher pressure because of the low intrinsic reactivity of Au itself, the weak bonding of water to Au, and the low steady state concentration of reactants on the surface even at high pressure because of the low rate of O₂ dissociation on Au. This is an unprecedented success in bridging the pressure gap between fundamental studies and working catalytic conditions.

9:20am **SS1-TuM5 An Atomic-scale View of Metal Alloy Surface Chemistry**, *E.C.H. Sykes*, Tufts University

Palladium and its alloys play a central role in a wide variety of industrially important applications such as hydrogen reactions, separations, storage devices, and fuel cell components. The exact mechanisms by which many of these processes operate have yet to be discovered. Low-temperature scanning tunneling microscopy (STM) has been used to investigate the atomic-scale structure of Pd/Au and Pd/Cu bimetallics created by depositing Pd on both Au(111) and Cu(111) at a variety of surface temperatures. We demonstrate that *individual isolated* Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. The same mechanism does not operate for Pd in Au(111) surfaces, however, because the spillover is thermodynamically unfavorable. These results demonstrate the powerful influence an inert substrate has on the catalytic activity of individual Pd atoms supported in its surface. In addition, differential conductance spectroscopy has enabled the electronic structure of these active sites to be measured and quantitatively compared to that of the host metal.

9:40am **SS1-TuM6 Prediction of Surface Ensembles in Au-based Bimetallic Alloys using Combined DFT and Monte Carlo Simulations**, *J.A. Stephens, H.C. Ham, G.S. 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 have developed a scheme to predict the equilibrium arrangement of atoms in surface alloys at finite temperatures. It 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 have used it successfully to predict monomer and dimer concentrations in Au-Pd and Au-Pt fcc (111) surface alloys. The scheme will be presented in detail, as well as what we have learned about the effects of temperature and composition on ensemble formation in both fcc (111) and (100) surface alloys, including the size and shape distributions of larger ensembles. We will also discuss how the atomic arrangements affect the reactivity of gold-based alloy surfaces, particularly towards oxidation of hydrogen and carbon monoxide.

10:40am **SS1-TuM9 Structure and Segregation at Clean and Oxidized Pd₃Fe(111) Alloy Surfaces**, *X. Yang, B. Koel*, Lehigh University

Pd/Fe alloy catalysts have attracted attention in PEM fuel cell research because they have been found to be comparable to Pt electrocatalysts in oxygen reduction reaction (ORR) kinetics at the cathode. Higher electrocatalytic activity is also found when these bimetallic nanoparticles act as a support of Pt or Pd monolayers. The mechanism of enhancing ORR kinetics with this alloy is not well understood. We report here on the structure and segregation at a clean and oxidized Pd₃Fe(111) alloy using LEED, LEIS, XPS, and STM. Pd starts to segregate at the surface at 600 K and reaches a coverage of 0.9 monolayers at 1100 K. STM reveals a complex structure with 0.17 monolayers of Pd adatoms on top of the outermost alloy layer, which is different from other well-studied binary alloy systems. The experimental observation of this unusual Pd structure is supported by DFT calculations. Adsorption of oxygen reverses the segregation trend and causes Fe atoms to accumulate on the surface. Fe at the surface is oxidized by oxygen and initially protects Pd oxidation. Oxygen adsorption at different temperatures caused the formation of nanoclusters at lower temperatures (300-500 K) and several well-organized surface structures at higher temperatures. Such studies of structure, segregation and oxidation of these model Pd/Fe alloy catalysts may help explain the origin of enhanced ORR kinetics using these alloys.

11:00am **SS1-TuM10 Role of Ensembles in Determining the Catalytic Activity of Au-Pd and Au-Pt Surface Alloys towards CO Oxidation and Oxygen Reduction Reaction: A First Principles Study**, *H.C. Ham, J.A. Stephens, G.S. Hwang*, University of Texas at Austin

Gold-based bimetallic alloys have been found to significantly increase catalytic efficiency, compared to their monometallic counterparts in various reactions including low temperature oxidation of CO, direct synthesis of H₂O₂ from H₂ and O₂, and production of vinyl acetate monomers. Recent experimental and theoretical studies have suggested that the reactivity of bimetallic catalysts can be governed by creation of unique mixed-metal surface sites (ensemble effect) and/or electronic structure change by metal-metal interactions (ligand effect), while mechanisms underlying the alloying effect still remain unclear. In this talk, we will present the recent results of our first principles calculations on the mechanisms of CO oxidation and oxygen reduction reaction (ORR) on AuPd and AuPt alloy surfaces. Using periodic density functional theory calculations, we find that the rate of CO oxidation can be a strong function of Pd/Pt ensembles, while the ensemble effect is likely to be more important in the AuPd case. In addition, we find that ORR tends to be promoted on PdAu alloys, compared to the pure Pd case. This work provides valuable hints on the importance of the interplay of the ensemble and ligand effects in determining the catalytic activity of Au-based bimetallic catalysts particularly toward CO oxidation and ORR.

11:20am **SS1-TuM11 Adsorption Studies on Unsupported PdZn Alloy Powders**, *B. Halevi*, University of New Mexico, *B. Kiefer*, New Mexico State University, *K. Artyushka, P. Atanassov, A. Datye*, University of New Mexico

Estimating the true catalytically active surface area for complex 3-D surfaces such as powders is both important for evaluating the true catalytic performance of the material and difficult. Since most industrially relevant catalysts are metallic particles supported on Carbon or Oxides evaluating their chemically relevant surface area is even more difficult. In an effort to better quantify the active surface area of supported catalysts we synthesized an unsupported phase pure and compositionally homogeneous PdZn powder and evaluated by DFT and experiments the thermo- and electro-chemical adsorption of H₂, O₂, and CO on the powder. These benchmark values can be used to evaluate the available surface area of supported catalysts as well.

11:40am **SS1-TuM12 Reactivity of Epitaxial Vanadium Oxide Layers**, *M. Li, E.J. Altman*, Yale University

Monolayers of vanadia supported on other oxides can be uniquely active and selective for a number of reactions including the selective catalytic reduction of NO and the partial oxidation of methanol to formaldehyde. A number of explanations have been offered in the literature to explain the unique properties of vanadia monolayers and the influence of the support, but these have been hampered by the inability to control both the chemical interaction of the vanadia with the substrate and the structure of the vanadia layer. We have addressed this issue by using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) to grow ordered vanadia monolayers and multilayers on rutile (110), anatase (001) and (101), WO₃(100) and LaCoO₃ (100). By control of the atomic oxygen flux, monolayers and multilayers with the same surface structure can be obtained. For the monolayers, oxygen adsorption oxidizes all of the vanadium to 5+ while for the multilayers the bulk stoichiometry is VO₂ but oxygen adsorption oxidizes the surface to V₂O₅. Comparing the reactivity of monolayers and multilayers of vanadia on rutile (110) and anatase (001) reveals the importance of direct chemical interactions with the support versus the

importance of maintaining non-bulk V₂O₅ structures. For both the rutile and anatase support, we find that as long as the films are epitaxial that the direct chemical interaction with the support is not required to observe oxidative dehydrogenation of 1-propanol to propionaldehyde in thermal desorption; vanadia on both supports desorbed 1-propionaldehyde in a peak at ~400 K independent of the thickness of the vanadia layer. Differences between anatase and rutile as well as monolayers and multilayers were observed however. In particular, the fraction of adsorbed alcohol that reacted on the vanadia monolayer was much higher than any other vanadia surface, a finding attributed to the propensity of the rutile (110) surface to form defects that are highly active for alcohol deprotonation, the first step in the reaction. Thus the titania supports can influence the reactivity by both stabilizing reactive, non-bulk structures, and by facilitating the first step in reactions of alcohols. The reactivity data will be compared with results for vanadia on LaCoO₃(100) which has the same surface unit cell as anatase (001), and thus in the monolayer regime the influence of chemical interactions on the reactivity of the vanadia are characterized with the structure held constant.

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