

Thursday Afternoon, October 23, 2008

Surface Science

Room: 208 - Session SS2-ThA

Novel Reactive Surfaces

Moderator: S. Chiang, University of California Davis

2:00pm SS2-ThA1 The Photochemistry of Acetaldehyde on TiO₂(110), *R.T. Zehr, M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced decomposition of acetaldehyde adsorbed on the oxidized rutile TiO₂(110) surface was studied with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). Saturation coverage of acetaldehyde adsorbed on a reduced TiO₂(110) surface with 15 % oxygen vacancies exhibited a molecular desorption peak at 235 K along with a higher temperature shoulder at > 260 K that accounts for 1/3rd of the monolayer. Butene desorbing at 530 K was observed as a minor decomposition channel accounting for 1-2% of the adsorbed acetaldehyde. Saturation coverage of acetaldehyde adsorbed on oxidized TiO₂ (110) desorbs molecularly at 240 K with a minor decomposition channel (7%) forming adsorbed acetate. Surface bound acetate decomposes to form gas phase ketene in a broad desorption peak centered at 700 K. Acetaldehyde adsorbed on oxidized TiO₂ (110) undergoes a facile thermal reaction ($E_a = 8$ kJ/mol) to form a photoactive acetaldehyde-oxygen complex. Acetaldehyde adsorbed on reduced TiO₂ (110) was photo-inactive. UV excitation of substrate charge carriers initiated photofragmentation of the acetaldehyde-oxygen complex resulting in the ejection of methyl radical into gas phase and conversion of the surface bound fragment to formate. The identity of methyl radical was confirmed using isotopically labeled acetaldehyde. The presence of surface bound formate was confirmed by desorption of formate thermal decomposition product, CO, at 550 K. Ejection of reactive organic radical species in TiO₂ photooxidation of organics can potentially lead to alternate reaction pathways occurring away from the catalyst surface.

2:20pm SS2-ThA2 Cesium Promotion in Styrene Epoxidation on Silver Catalysts, *L. Zhou, R.J. Madix*, Harvard University

The promotion roles of cesium in styrene epoxidation on silver catalysts have been studied by means of temperature-program reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The TPRS data have shown that the addition of 0.1 ML cesium can inhibit the secondary oxidation of styrene on Ag(111), and more significantly, switch the partial oxidation pathway from the production of phenylacetaldehyde and phenylketene to the production of styrene oxide on Ag(110). The XPS studies have revealed the formation of selective oxametallacycle intermediate and the reduced transformation of this intermediate to a combustion intermediate in the reaction on 0.1 ML cesium-covered silver surface, comparing with the reaction on the clean silver surface. No significant change of the C 1s and O 1s binding energies for certain intermediates was observed, suggesting that cesium does not play obvious electronic effect on the bonding of the intermediates. The STM studies have disclosed an interesting (1x2) reconstruction of the Ag(110) surface induced by cesium and a (3x5) surface oxide structure on the cesium-reconstructed Ag(110) surface. This (3x5)-ordered surface oxide is superimposed on the highly corrugated Ag(111) micro-facets. Our studies provide the insight into the microscopic origins of the structural effects of cesium in styrene epoxidation on silver catalysts.

2:40pm SS2-ThA3 Selectivity and Enantioselectivity on Metal Surfaces, *A.J. Gellman*, Carnegie Mellon University **INVITED**

One of the key contributions of surface science to the discipline of catalysis has been the understanding of selectivity in catalytic surface chemistry. The key feature of surface science methodologies that leads to this contribution is the ability to isolate and study elementary chemical reaction steps occurring on single crystal surfaces. These are two independently important attribute of the surface science method. The ability to isolate and then study the kinetics of elementary steps, decouples their kinetics from those of the overall mechanism of which they are part. The use of single crystal surfaces provides homogeneous environments in which the kinetics are not masked by the influence of surface structure. The impact of these aspects of surface chemistry will be illustrated by three examples: study of transition states to elementary catalytic reaction steps, the study of conformational effects in the desorption of large molecules from surfaces and the observations of enantioselectivity in reactions of chiral molecules with chiral surfaces.

3:20pm SS2-ThA5 Tuning the Reactivity and Selectivity of Chiral Kink Sites on Surfaces through Alloying, *A.D. Jewell*, Tufts University, *J.W. Han*, Georgia Tech, *D.O. Bellisario*, *A.E. Baber*, *H.L. Tierney*, Tufts University, *D.S. Sholl*, Georgia Tech, *E.C.H. Sykes*, Tufts University

While chiral Cu surfaces have been shown to be enantioselective for certain dehalogenation reactions,^{1,2} we seek to develop a surface with a much more general enantiospecific reactivity. To this end, Cu surfaces have been alloyed with a range of more reactive atoms. Simulations of the segregation of different metals to the step edges of Cu(322) has shown that Pd and Ag are promising candidates for segregation to the chiral kink sites of a Cu surface. Depositing reactive atoms selectively at the kink sites will allow us to increase the reactivity while preserving the chiral nature of the kink and thus tune the surface's enantiospecificity. Low-temperature scanning tunneling microscopy has been used to follow the preferred adsorption site of Pd and Ag atoms deposited at step edges on a Cu{111} surface at a variety of temperatures. The Cu{111} is an ideal test bed for this study as it contains large terraces, step edges and equal numbers of R and S kink sites. Alloyed kink sites composed of both Cu and Ag or Pd atoms will have both structural and chemical asymmetry and thus one can expect their enantioselectivity to be enhanced.

¹ Rampulla, D. M.; Gellman, A. J., *Surf. Sci.* 2006, 600, 2823-2829.

² Rampulla, D. M.; Francis, A. J.; Knight, K. S.; Gellman, A. J., *J. Phys. Chem. B* 2006, 110, 10411-10420.

4:00pm SS2-ThA7 STM Investigation of the Conversion of Ethylene to Carbon Clusters and Graphite on Pt(111), *A.B. De La Ree*, University of California, Irvine, *V. Johánek*, University of Virginia, *J.C. Hemminger*, University of California, Irvine

New insight has been obtained on the conversion of ethylene to carbon clusters by thermal dehydrogenation on Pt(111). Previous experiments have shown that thermal dehydrogenation following saturation exposure of ethylene to Pt(111) results in the formation of well defined carbon clusters. This occurs through a process of aggregation during the dehydrogenation process in the temperature range from 400K to 700K. Previous experiments have shown that heating an ethylene covered Pt(111) surface to temperatures above 800K leads to the formation of large sheets of monolayer graphite (graphene). The aggregation to form carbon clusters leaves open Pt areas available for additional adsorption. It had not been previously determined whether the adsorption and dehydrogenation of additional ethylene would lead to the growth of the initial clusters or to the nucleation of more clusters of the same size. We have utilized UHV-Variable temperature scanning tunneling microscopy (VT-STM) to address this question. In our experiments, a saturation coverage of ethylene is adsorbed on the Pt(111) surface at room temperature forming a layer of the well known ethyldyne dehydrogenation intermediate. The surface was then heated to 700K leading to further dehydrogenation and formation of carbon clusters that are easily observed by VT-STM. Our STM images show that these carbon clusters are 15±2 Å in diameter and containing an average number of 34±9 carbon atoms per cluster. The surface was then exposed to additional ethylene at room temperature and again heated to 700K. This process was repeated in a number of cycles until the dehydrogenation activity of the Pt(111) surface was completely suppressed. Repeated dosing of ethylene onto the surface followed by annealing led to an increase in the number of carbon clusters without an increase in the size of previously produced clusters. The Pt(111) dehydrogenation activity was completely suppressed after 4 such cycles. The only growth in cluster size that was observed was due to agglomeration of clusters once the surface was covered with a high density of clusters. Continued cycles, such as were utilized in these experiments, leads to the formation of a graphite adlayer on the platinum (presumably via agglomeration of the clusters at high cluster density). This was observed at temperatures well below the onset of long range graphene formation in single ethylene dose experiments.

4:20pm SS2-ThA8 Catalytic Activity and Morphology of Pt Clusters on the Graphite Surface, *T. Kondo*, *K. Watahiki*, *J.P. Oh*, *K. Izumi*, *Y. Iwasaki*, *D. Sekiba*, *H. Kudo*, *J. Nakamura*, University of Tsukuba, Japan

Catalytic activity and surface morphology of Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by hydrogen-deuterium exchange reaction, scanning tunneling microscopy (STM), temperature programmed desorption (TPD) of CO and in-situ measurement of helium atom scattering (HAS). Based on the STM observation, Pt particles deposited on HOPG with sub-monolayer coverage at room temperature are found to form mostly monolayer clusters on a graphite surface with the reduction in the nearest-neighbor atomic distance of the platinum atoms by as much as 13 % compared to that of the single crystal platinum. Turn over frequency of the hydrogen-deuterium exchange reaction at 24 Torr and 340 K is found to be one order magnitude higher for

the monolayer Pt cluster than three-dimensional Pt cluster at 340 K, indicating the smaller adsorption energy of hydrogen on the Pt monolayer cluster. Based on the TPD experiment of CO from Pt/HOPG, the similar catalytic property is found for the monolayer Pt cluster: lower binding energy of CO with Pt compare to the case on the single crystal platinum. These specific catalytic activities are however found to be lost by the slight annealing of Pt/HOPG above 350 K. The change in the catalytic activity is attributed to the change in the morphology of the Pt cluster from monolayer to three-dimensional phase based on the HAS and STM measurements. The higher specific catalytic activity for the Pt monolayer cluster will be discussed in terms of the interface interaction between Pt atoms and the graphite surface.

4:40pm SS2-ThA9 Surface Structures and Alloy Formation for Ge Deposition on Pt, B.E. Koel, G. Liu, Lehigh University

We have investigated surface structures formed by Ge deposition on Pt(111) and (100) single-crystal substrates by using STM, LEED, ALISS, and XPD. This combination of techniques provides an atomic level description of the surface structures necessary to understand the "site-directed" chemistry of these surfaces and can be used to distinguish formation of adlayers and surface alloys. We find large apparent differences between the behavior of Ge on Pt(100) compared to Pt(111) substrates. An ordered $p(\sqrt{19} \times \sqrt{19})R23.4^\circ$ -Ge/Pt(111) surface alloy was formed on Pt(111) by annealing at 900 K. This structure substitutionally incorporates 4%-ML Ge atoms into the Pt surface layer located very close to substitutional Pt atomic positions, without any corrugation or "buckling". In contrast, and despite extensive bulk solubility of Ge in Pt, it was found that Ge remains on top of the Pt(100) surface as adatoms even after annealing to 1200 K. Furthermore, Pt adatoms produced by lifting of the Pt(100)-hex reconstruction in the vicinity of adsorbed Ge do not intermix with the Ge but rather segregate to form pure-Pt islands with Ge adsorbed on top. We interpret the $c(2 \times 2)$ Ge overlayer that is produced by 0.5 ML Ge deposition and annealing at 600 K as formation of a unique surface alloy or "layer compound". The Pt(100) substrate thus is covered by a surface alloy film with the structure of a body-centered tetragonal Pt_2Ge layer compound. TPD shows that both CO and NO adsorb more weakly on the Pt-Ge bimetallic surfaces than on the clean Pt surfaces.

5:00pm SS2-ThA10 Revisiting the Oxidation Kinetics of Plutonium Surfaces, H.G. García Flores, University of Nebraska-Lincoln and Los Alamos National Laboratory, **D.P. Moore, J.P. Baiardo, D.L. Pugmire,** Los Alamos National Laboratory

The oxidation of metal surfaces is an important application of kinetic modeling because it allows for the study of the influence of transport processes in a gas-solid reaction. Understanding the oxidation kinetics of plutonium is desired because this process can have an impact in the storage and handling of this radioactive element. The goal of this presentation is to investigate the early stages of the corrosion of plutonium in an attempt to elucidate the oxidation kinetics, in particular at the initial rapid stage of the oxidation. The data presented here will be evaluated with an inverse-logarithmic kinetic rate law, which has not previously been used to describe the oxidation kinetics of plutonium. The parabolic and parabolic models generally employed to describe oxide film growth of plutonium do not explain this rapid initial stage of oxide film growth of plutonium. To this aim, ellipsometry, x-ray photoelectron spectroscopy (XPS) & Auger electron spectroscopy (AES) data recently collected at Los Alamos and the ellipsometry data presented by Larson & Cash in the Journal of Physical Chemistry¹ will be used to perform a comparison of the kinetic models for oxygen corrosion of plutonium.

¹ D.T. Larson, D.L. Cash, J. Phys. Chem., 73 (1969) 2814.

5:20pm SS2-ThA11 Kinetics of Hydride Front in Zircaloy 2 and H Release from a Fractional Hydrided Surface, M. Diaz, Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council, Spain, **B. Remartinez, S. Perez,** Iberdrola, S. A., Spain, **J.L. Sacedon,** Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council

In these Zirconium based materials, when the H_2 dissociation at a surface is enough efficient, a continuous and compact hydride layer is formed, increasing in thickness with time. Using a UHV equipment and method, specifically developed to compare the resistance to hydriding of tubular nuclear fuel claddings,¹ the propagation kinetics of the Hydride/metal interface through the cladding thickness is obtained. It results in a hydride thickness vs time dependence $th = K t^a$, where a is close to 1/2 and a rate dependence on the thickness $dth/dt = C th^b$ where b is close to -1. They are near to the expected values from an H ideal diffusion through the Hydride layer, and differ from the linear kinetics ($a = 1$) and other fractional exponents obtained from thermo-gravimetric methods. At difference, in our method the sample is directly heated in an UHV environment, which allows a fast control of the local temperature where the hydriding reaction takes

place. At the same time, pure H_2 flows inside the tube, starting the hydriding from the inner tube surface. The method allows determining the formation enthalpy of $ZrH_{1.5}$ (Zircaloy2) $H = -117 \pm 8$ kJ/mol at 295.5 K, giving the second determination of this value in the literature.² Being the Hydride composition determinate by X ray diffraction methods, mass spectrometry allows to follow the H_2 desorption produced by the surface reaction $H_s + H_s = H_2$ ³ at the external surface of the tube, opposite to surface where the hydriding begins. A kinetic model and expression that explain the H_2 desorption curves is presented. In this model the H desorption rate, is proportional to a fractional surface Hydride coverage. This coverage increase in time by the excess of H precipitated from the H oversaturated metal. The Hydride/ metal interface acts as a very weak H source feeding the metal over saturation. The ratio between the of H flux precipitated at the external metal surface to that precipitated at the Hydride / metal interface is determinate to be $\leq 10^{-6}$.

¹ J. L. Sacedón, M. Diaz, J.S. Moya, B. Remartinez and J. Izquierdo, Journal of Nuclear Materials. 327 (2004) 11.

² P. Dantzer, W.L., T. B. Flanagan and J. D. Clewley, Metall. Transact. A. 24 (1993) 1471.

³ D. E. Shellefman, D. Shaltiel and I. T. Steinberger, J. Alloys and Compounds. 223 (1995) 81.

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