

# Wednesday Morning, October 31, 2012

## Surface Science

Room: 21 - Session SS-WeM

### Chemisorption on Metallic Surfaces

Moderator: C.H. Sykes, Tufts University

8:00am **SS-WeM1 An Atomic-scale Study of the Adsorption, Assembly and Reactivity of Methanol with Model Cu, O/Cu and Pd/Cu Alloy Surfaces with STM, TPD and XPS**, *T. Lawton, M. Boucher, A. Baber, G. Kyriakou, C.H. Sykes*, Tufts University

Hydrogen is green fuel capable of producing electricity. Methanol is a promising hydrogen storage molecule with a high hydrogen-to-carbon ratio (4:1). My research examines methanol oxidation and decomposition on model catalysts via variable temperature scanning tunneling microscopy (VT-STM) and temperature-programmed reaction (TPR).

Methanol desorption on Cu(111) was studied from 130 K (multilayer desorption) to 165 K (monolayer desorption) with STM. Analysis of STM images reveals several structures that are governed by hydrogen-bonding interactions. From the STM images, hexamers are the most thermodynamically stable structure on Cu(111). Hydroxyl-proton localization on the hexamers leads to two enantiomers.

The Cu surface was chemically modified in two ways to alter methanol reactivity. First, the effect of oxygen at various temperatures on Cu(111) was studied with STM. STM and XPS of a Cu(111) surface pre-adsorbed with oxygen after exposure to methanol show methoxy forms at the interface of the oxide-like domains and bare Cu.

The second avenue was a Cu-based bimetallic alloy containing small amounts of Pd. The TPD studies on model Pd/Cu catalysts interestingly reveal partial decomposition of methanol to formaldehyde and hydrogen. STM images acquired reveal that at temperatures above MeOH desorption, molecules only occupy sites near Pd atoms, suggesting these are the active sites.

8:20am **SS-WeM2 Imaging the Role of Ligand Groups in Surface Coordination Chemistry/Networks: Cyano- vs. Isocyano Groups**, *L. Bartels, M. Luo, S. Bobek, K.D. Cohen, C. Wang, R. Hooley*, University of California Riverside

We use STM to investigate the adsorption, self assembly and metal-coordination of isocyano- and cyano-based aromatic species on Cu (111). Despite their structural similarity, cyano and isocyano groups are chemically quite different. We investigate the effect of this distinction on the structures on the metal coordination structures they form and on the resultant geometric and electronic state of the metal coordination center. In particular we find very different structures for dicyano- and diisocyano-anthracene molecules. While the former generates a network consisting of trigonally coordinated metal centers, the latter generates molecular rows, i.e. more linear arrangement. Cyano- and Isocyano-naphthalene also generate different distributions of coordination compounds on Cu(111). The combination of these studies highlights the impact of the chemical structure of the ligand on the coordination center. Organic ligands are a common tool for affecting activity in homogeneous catalysis. Our study is aimed at exploring the capabilities of lateral coordination in controlling the activity of a surface.

8:40am **SS-WeM3 Chemisorption, Ordering, and Structural Transitions in the Terephthalic Acid Monolayer and Bilayer on Cu(100)**, *S.L. Tait*, Indiana University - Bloomington

The use of small organic molecules to control structure as well as electronic and chemical functionality of a surface is a critical field of surface chemistry. Interest in problems related to bonding, charge transfer and self-assembly of organic species at metal surfaces has grown, in correlation with stronger needs for inexpensive and highly functional organic technologies in energy conversion, sensors, electronics, and other applications. We have studied a prototypical system, terephthalic acid on Cu(100), using a set of complementary analysis tools to develop a complete picture of the chemisorption and structural transitions in this dynamic system, which is of key importance for structural control and organic-to-metal interface design. Scanning tunneling microscopy has been used to achieve molecular resolution structural characterization of the first layer structural transitions and of the second layer structures. High-resolution electron energy loss spectroscopy reveals orientation of the molecule in each layer and lends insight into the bonding interaction with the surface. X-ray standing wave spectroscopy and density functional theory calculations show a strong chemical bond to the surface and indicate that the apparent attractive

interaction between molecules is likely due to a substrate mediated interaction, sufficient to overcome any electrostatic repulsion between the negatively charged carboxylate groups on the molecules. This system has also laid the ground work for related advances in using terephthalic acid layers and related molecules for coordination bonded structures, some of which show high levels of chemical selectivity, and for ionically bonded structures. These results provide general insight in the development of self-assembled organic thin films at surfaces, especially with regard to the nature of the metal/organic interface and growth transitions to obtain a second layer that bridges substrate commensurability and a more bulk-like structure, key issues in organic thin film design.

9:00am **SS-WeM4 Attachment and Nanoscale Patterning of Alkyne Groups on Gold via Non-thermal Pathways**, *Q. Li*, Oak Ridge National Laboratory, *C.B. Han*, North Carolina State University, *M. Fuentes-Cabrera, H. Terrones, B.G. Sumpter, W.C. Lu*, Oak Ridge National Laboratory, *J. Bernholc*, North Carolina State University, *Z. Gai, A.P. Baddorf, P. Maksymovych, M.H. Pan*, Oak Ridge National Laboratory

Self-assembled monolayers are the basis for molecular nanodevices, flexible surface functionalization and dip-pen nanolithography. Yet self-assembled monolayers are typically created by a rather inefficient process involving thermally driven tethering reactions of precursor molecules to a metal surface, followed by a slow and defect-prone molecular reorganization. Here we demonstrate a non-thermal control over the self-assembly of phenylacetylene on gold that produces previously unachievable well-ordered three-dimensional monolayers, where the molecules are attached directly through the alkyne group. While thermal excitation can only desorb the parent molecule due to prohibitively high activation barriers for attachment, localized injection of hot electrons or holes not only overcomes this problem, but also enables an unprecedented control over subsequent ordering of attached molecules on the surface, including a nanoscale control over the size and shape of the self-assembly, defect structures and the reversible process between flatly and upright molecular configuration from single molecular level to mesoscopic scale. This work thus demonstrates the feasibility of non-thermal reaction pathways that may lead to unique and controllable self-assembly in supported molecular layers.

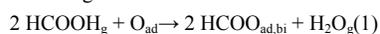
9:20am **SS-WeM5 Molecular Structure of a Mixed NH<sub>3</sub>-O<sub>2</sub> Overlayer on Pt(111)**, *Z. Liang*, University of Illinois at Chicago, *H. Kim, Y. Kim*, RIKEN, Japan, *M. Trenary*, University of Illinois at Chicago

The interaction of NH<sub>3</sub> with chemisorbed molecular O<sub>2</sub> on a Pt(111) surface has been studied at the single-molecule level with low temperature scanning tunneling microscopy. Chemisorbed O<sub>2</sub> molecules are found to form an ordered network at high coverages for adsorption temperatures below 50 K. Sites unoccupied by O<sub>2</sub> molecules on Pt(111) appear as holes in the network. Various hole-hole distances among nearest neighbors are observed reflecting variations in the arrangement of O<sub>2</sub> molecules. A hole-hole distance of 0.74 nm is found to be predominant on the surface and is assigned to be the most favorable one as it maintains the 3-fold symmetry of underlying platinum lattice. Ammonia molecules are observed to adsorb in the holes within the ordered network of O<sub>2</sub> molecules, which is also the a-top site with respect to the Pt(111) substrate. Further annealing of the ammonia-oxygen overlayer to 400 K results in the formation of a mixed p(2×2) overlayer of N, O and NH. This work provides new insights into the ammonia oxydehydrogenation reaction on platinum surface, which is an important catalytic reaction in the industrial production of nitric acid.

9:40am **SS-WeM6 Enthalpies of Formation of Formate Intermediates Adsorbed on Pt(111) by Microcalorimetry**, *T.L. Silbaugh, E.M. Karp, C.T. Campbell*, University of Washington

Knowing the heats of formation of adsorbed catalytic intermediates is an essential component in gaining the fundamental understanding of reaction mechanisms and the relationships between catalyst structure and activity necessary for rational design of heterogeneous catalysts. The current study utilizes the ultrahigh vacuum technique of single crystal adsorption calorimetry to determine the energetics of adsorbed formate species on Pt(111).

From previous literature, it is known that formic acid dosed on Pt(111) precovered with oxygen adatoms (O<sub>ad</sub>) at 190K reacts completely to form adsorbed bidentate formate (HCOO<sub>ad,bi</sub>) and gas phase water (H<sub>2</sub>O<sub>g</sub>) according to the reaction:



where HCOO<sub>ad,bi</sub> bonds in a bridging configuration. The heat of Reaction (1) extrapolated to zero coverage was found to be -110 kJ/mol. A simple

thermodynamic cycle that uses this and other known adsorption energies provides a heat of formation of  $\text{HCOO}_{\text{ad,bi}}$  of -418 kJ/mol.

Prior studies have shown that submonolayer coverages of formic acid on O-precovered Pt(111) at 130K first produce monodentate formate ( $\text{HCOO}_{\text{ad,mon}}$ ) and adsorbed hydroxyl ( $\text{OH}_{\text{ad}}$ ) via the reaction:



where  $\text{HCOO}_{\text{ad,mon}}$  forms a single Pt—O bond to the surface. The heat of Reaction (2) extrapolated to zero coverage was found to be -93 kJ/mol, which provides a heat of formation of  $\text{HCOO}_{\text{ad,mon}}$  of -354 kJ/mol. At this same temperature, this monodentate formate converts to bidentate bonding, but at a rate that is slow relative to the 100 ms heat measurement time, so this slower reaction does not complicate thermodynamic measurement of the formation of this monodentate species. Together with our earlier measurements of the heats of formation of  $-\text{OCH}_3_{\text{ad}}$  and  $-\text{OH}_{\text{ad}}$ , these allow us to estimate reaction energies for conversion pathways between formate and methoxy intermediates in Pt catalysis.

#### 10:40am SS-WeM9 Adsorption Energy of Oxygen on Pt(111): Errors in Calorimetry Values and Consequences for the Enthalpy of Related Hydroxyl Species, C.T. Campbell, E.M. Karp, University of Washington

Beautiful calorimetric measurements of the adsorption enthalpy of  $\text{O}_2_{\text{g}}$  to make 2 Oad on Pt(111) were performed by Fiorin et al.<sup>1</sup> However, we show here that they used a calibration that relied upon a value for the optical reflectivity of Pt(111) that was incorrectly reported in the literature. This error in reflectivity led to a 40% error in the adsorption energies they originally reported. We use here our more accurate reflectivity of 76% to recalibrate their oxygen adsorption enthalpy data and show that it gives nearly identical results to the heats of adsorption below 0.15 ML determined from activation energies for desorption of oxygen from Pt(111) measured with temperature programmed desorption (TPD) by two separate groups (Campbell et al.2 and Parker et al.3). Differences arise above 0.15 ML, but we attribute these to the very low sticking probability of  $\text{O}_2_{\text{g}}$  on Pt(111) (< 0.05) above 0.15ML, which we argue lead to large errors in the adsorption energies measured by calorimetry. Given this, we propose that the most reliable values for the adsorption enthalpy of oxygen on Pt(111) up to  $\frac{1}{4}$  ML are those derived from those TPD experiments, rather than the more recent calorimetry data, except below 0.15 ML where they agree after this calibration correction. The best values are well described by  $(217-151\theta)$  kJ/mol below  $\frac{1}{4}$  ML, where  $\theta$  is the Oad coverage in ML (i.e., Oad per Pt surface atom). We further use these corrected adsorption enthalpy data to revise the energetics of hydroxyl species on Pt(111) that we previously measured<sup>4</sup>. This gives revised values for the standard enthalpies of formation of the coadsorbed (DO-D2O)ad complex and of ODad on Pt(111) of  $-511 \pm 7$  and  $-210 \pm 7$  kJ/mol, respectively, and a revised O-Pt bond enthalpy in adsorbed hydroxyl of  $248 \pm 7$  kJ/mol. These three corrected enthalpies are all 16 kJ/mol smaller in absolute value than originally reported.

- (1) Fiorin, V.; Borthwick, D.; King, D. A., *surf. sci.*, 2009, 603, 1360.
- (2) Campbell, C. T.; Ertl, G.; Kuipers, H.; Segner, J., *surf. sci.*, 1981, 107, 220.
- (3) Parker, D. H.; Bartram, M. E.; Koel, B. E., *surf. sci.*, 1989, 217, 489.
- (4) Lew, W.; Crowe, M. C.; Karp, E.; Lytken, O.; Farmer, J. A.; Arnadottir, L.; Schoenbaum, C.; Campbell, C. T., *J. Phys. Chem. C.*, 115, 11586.

Work supported by the National Science Foundation.

#### 11:00am SS-WeM10 Mechanism of Halogenated Solvent Pre-Treatment of Polymeric Substrates to Significantly Improve Noble Metal Thin Film Adhesion, B.H. Augustine, W.C. Hughes, A.K. Mo, James Madison University, H.M. Meyer, Oak Ridge National Laboratory, T.C. DeVore, James Madison University

Many emerging microfabrication technologies such as microfluidic devices rely on the deposition of metal features onto polymeric substrates. Au and Pt thin film metallization are particularly important for electrodes, IR reflectors, interconnects and catalytic surfaces in these devices. However, due to the inert nature of Au and Pt, adhesion to polymeric substrates is generally poor. We report on the use of halogenated organic solvents as a pre-treatment onto poly(methyl methacrylate) (PMMA) substrates to improve the adhesion of an array of 121 electron-beam or magnetron sputter deposited 1.5 mm diameter metal dots by up to a factor of five compared to deposition on cleaned PMMA substrates. We have observed improvement by both spin-casting and vapor phase pre-treatment of the PMMA surface. Nearly 90% of the Au dots remain after a standard tape pull-test for samples pre-treated with  $\text{CHCl}_3$  compared with only 17% remaining on the untreated samples. The adhesion of  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHBr}_3$  pre-treated samples are also significantly improved compared to remote  $\text{O}_2$  plasma pre-treatment (26% adhesion). Atomic force microscopy roughness data shows

that this is not due to surface roughening, and we have shown through X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) studies that the halogenated solvent molecules form a Lewis acid-base adduct with the polymer chains leaving a halogen-rich surface. A covalent bond is then formed between the Cr metal adhesion layer and the surface terminated Cl which results in the strong metal adhesion. Molecular modeling has been performed to understand the origin of the enhanced adhesion. DFT calculations are consistent with the presence of adduct formation having a interaction enthalpy of  $\sim 35$  kJ/mol. The mechanism of improved chemical metal bonding will be discussed.

#### 11:20am SS-WeM11 HREELS Investigation of Hydrocarbon Dehydrogenation on Oxide-Supported Platinum Nanoparticles, M.H.C. Van Spyk, K.A. Perrine, J.C. Hemminger, University of California Irvine

Factors such as support type and nanoparticle morphology are known to impact catalytic activity, but detailed studies are required to elucidate the effect of nanoparticle size on the mechanism of dehydrogenation over nanoparticles supported on oxides. In this work, high resolution electron energy loss spectroscopy (HREELS) was used to characterize the dehydrogenation of hydrocarbons on platinum nanoparticles supported on an  $\text{Al}_2\text{O}_3$  film grown by oxidation of a NiAl(110) single crystal. The alumina film is a good representation of the high surface area oxides used as catalyst supports in industry, and the flat surface enables investigation by electron inelastic scattering techniques. The platinum nanoparticles were deposited on a fresh alumina film at cryogenic temperatures, and platinum deposition was monitored by the reduction in elastic peak intensity in the HREEL spectra. Cyclohexane was used as a model hydrocarbon because the dehydrogenation on Pt(111) has been studied extensively and thus provides a good point of comparison for the nanoparticle studies. The HREELS spectra of cyclohexane on Pt(111) show a distinct low frequency peak at  $2600\text{ cm}^{-1}$  which can be monitored to determine the temperature at which dehydrogenation begins.<sup>1,2</sup> The HREELS annealing profile from an alumina film does not exhibit cyclohexane adsorption at 170 K, or upon successive annealing. In contrast, the HREEL spectra from platinum nanoparticles on alumina exhibit cyclohexane adsorption at 170 K with the  $\nu_{\text{C-H}}$  stretch energy loss peak observed at  $2930\text{ cm}^{-1}$ . Interestingly, HREEL spectra from cyclohexane on platinum nanoparticles do not resemble spectra from cyclohexane on Pt(111). Specifically, the additional  $\nu_{\text{C-H}}$  energy loss peak observed at  $2600\text{ cm}^{-1}$  for cyclohexane adsorbed on Pt(111) is not seen in the case of platinum nanoparticles.<sup>1,2</sup> In addition, the  $\nu_{\text{C-H}}$  energy loss peak from cyclohexane on platinum nanoparticles does not shift or decrease in intensity upon annealing to room temperature. Our results indicate that cyclohexane dehydrogenates upon adsorption to platinum nanoparticles at 170 K. This dehydrogenation temperature is lower than that on Pt(111), indicating that platinum nanoparticles supported on an alumina film are more catalytically active for the initial stages of dehydrogenation than Pt(111).

1. Land, D. P.; Erley, W.; Ibach, H., HREELS Investigation of the Orientation and Dehydrogenation of Cyclohexane on Pt(111). *Surface Science* **1993**, 289 (3), 237-246.
2. Saeys, M.; Reyniers, M. F.; Neurock, M.; Marin, G. B., Adsorption of cyclohexadiene, cyclohexene and cyclohexane on Pt(111). *Surface Science* **2006**, 600 (16), 3121-3134.

#### 11:40am SS-WeM12 Scanning Tunneling Microscopy Investigation of the Conversion of Propylene and Butylene to Carbon Clusters on Pt(111), G.F. Sun, S.S. Khan, A.B. De la Ree, J.C. Hemminger, University of California Irvine

Thermal dehydrogenation of propylene and butylene adsorbed on Pt(111) has been studied under ultra-high vacuum (UHV) conditions using scanning tunneling microscopy (STM). After heating to 700 K the alkenes dehydrogenated to form flat, uniform sized circular carbon clusters with less than a monolayer coverage. With cycles of continued adsorption and heating, particles grew in number but not in size. The catalytic activity stopped by the third saturation dose, leaving areas of bare Pt. Clusters of propylene and butylene were  $12 \pm 1.2\text{ \AA}$  and  $13 \pm 1.0\text{ \AA}$  in diameter, respectively. Propylene and butylene clusters contain an average of 44 and 51 carbons atoms per cluster, respectively.

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