# Wednesday Morning, November 11, 2009

**Surface Science**
**Room: N - Session SS2-WeM**

**Surface Chemistry and Dynamics**
**Moderator:** C.E. Sykes, Tufts University

**8:00am SS2-WeM1 Adsorption of Xenon on Vicinal Copper Surfaces**, *B. Holsclaw*, *A.J. Gellman*, Carnegie Mellon University

The adsorption of xenon was studied on Cu(111), Cu(221), Cu(643), and Cu(653) using temperature programmed desorption (TPD) of xenon and ultraviolet photoemission of adsorbed xenon (PAX). These experiments were performed to study the atomic and electronic structure of step-kinked, chiral copper surfaces. Xenon TPD and PAX were performed in an attempt to distinguish terrace, step-edge, and kink adsorption sites by adsorption energy (TPD) and local work function differences (PAX). The different adsorption sites could not be clearly differentiated using xenon TPD due to the complex behavior of xenon on these surfaces. Comparison of TPD spectra of *R*-3-methylcyclohexanone (R-3-MCHO) previously performed[1] on stepped and kinked copper surfaces suggests clear differences between Cu(643) and Cu(653) that are not apparent using xenon TPD. However, unique features of xenon adsorption on different copper surfaces were visually and numerically distinguishable using the PAX method. The PAX experiments on the copper surfaces demonstrate local work function differences between kink and step surface sites as well as step and terrace sites. A data fitting model was developed to analyze the PAX data for all four copper surfaces simultaneously. Kink sites were found to have a lower local work function than step sites, and steps, in turn, had a lower local work function than terrace sites. Step/kink adsorption of xenon is favored (for all surfaces studied at 50-70 K) at low coverages of xenon, but these sites do not saturate until monolayer coverage is reached. The results of this research provide several observations regarding the adsorptive behavior of xenon on vicinal copper surfaces.

[1]Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J., Enantioselective separation on a naturally chiral surface. *Journal of the American Chemical Society* **2004,** 126, (45), 14988-14994.

**8:20am SS2-WeM2 Effect of Surface Order and Thickness on the Adsorption Mechanism of NO on FePc**, *S.R. Bishop*, *N. Tran*, *A.C. Kummel*, University of California, San Diego

The diverse electronic properties, chemical and thermal robustness, and ease of deposition (spin coating and organic molecular beam epitaxy) make Metallophthalocyanine (MPc) materials an attractive and economical candidate for use in chemical sensors. The purpose of this study is to obtain an atomic level understanding of the fundamental mechanisms in which analytes interact with MPc thin films. MPc thin films investigated include ordered monolayer FePc, ordered multilayer FePc, and quasi-amorphous tetra-*t*-butyl FePc multilayer thin films. These experiments were further supported with density functional theory (DFT) of NO adsorption on FePc via simulated potential energy diagram. Exploration of how surface order and thickness affects NO adsorption was performed via King and Wells sticking measurements. The unique sticking profile features a sharp, downward spike, representing a short saturation time. For monolayer and ordered multilayer FePc/Au(111), NO adsorption onto FePc saturates at 3% of a monolayer suggesting that the final chemisorption site is confined to the iron metal centers. Furthermore, the saturation coverage is only 2% for the quasi-amorphous multilayer. The reduced saturation coverage in comparison to ordered FePc is attributed to the lower packing density of the tert-*t*-butyl FePc. At low surface temperature and low incident beam energy, the initial sticking probability is as great as 40% and decreases linearly with increasing beam energy and surface temperature. This is consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the organic periphery followed by diffusion to the Fe metal center, precursor-mediated chemisorption. For the multilayer ordered flat-lying film, the sticking probabilities are greater in comparison to the monolayer for the same incident beam energy and surface temperature. More efficient trapping onto the ordered multilayer film is consistent with NO having improved mass-matching with the multilayer FePc surface compared to monolayer. In addition, computations suggest that there are multiple available physisorption sites available within the organic periphery of the FePc films. The results strongly suggest the analyte adsorbs via a multiple pathway precursor-mediated chemisorption mechanism. A current study focuses on the analyte adsorption onto a totally amorphous film. MPc forms a β-polymorph on $SiO_2$ substrates which are no longer flat-lying, and planned sticking measurements of NO interaction with amorphous FePc will complete the study of the effect of surface order on analyte adsorption.

**8:40am SS2-WeM3 Interfacial Bonding of Thiophene and Aromatic Isocyanide on Au(111)**, *J. Zhou*, *Y. Yang*, SUNY Stony Brook, *P.J. Liu*, *N. Camillone*, Brookhaven National Laboratory, *M. White*, Brookhaven National Laboratory & SUNY Stony Brook

The electronic structures of thiophene and 1,4-phenylene diisocyanide (PDI) adsorbed on Au(111) are investigated by two-photon photoemission (2PPE) spectroscopy and density functional theory (DFT) calculation. The adsorption of thiophene lowers the work function by 0.88 eV for Au(111) exposed to 4.0 L thiophene, due to the electron donation from the thiophene to the substrate. With thiophene adsorbed on Au(111), a localized σ* state forms with increasing thiophene exposure on Au(111). This state is attributed to the σ* antibonding orbital of a Au-S bond and is evidence of an orientational phase transition of adsorbed thiophene. For PDI adsorbed on Au(111), a bonding state located at 0.8 eV below the Fermi level forms at the interface. The temperature dependence of work function change of PDI/Au(111) provides an evidence for molecular crystallization on the surface. Adsorption of 1 monolayer of PDI on Au(111) lowers the work function by 0.25 eV. Upon annealing to 300 K, the work function decreases by 1.45 eV due to amplified charge transfer or dipole effects which induced by the formation of a crystallized layer.

**9:00am SS2-WeM4 Identification of $C_2H_x$ Intermediates on Pt(111) through the Combined Use of Low Temperature Scanning Tunneling Microscopy and Reflection Absorption Infrared Spectroscopy**, *T. Okada*, *Y. Kim*, *M. Kawai*, RIKEN, Japan, *M. Trenary*, University of Illinois at Chicago

Various $C_2H_x$ surfaces intermediates formed through the thermal decomposition of acetylene and ethylene on the Pt(111) surface were identified and their stabilities characterized through complementary studies using the techniques of low temperature scanning tunneling microscopy (LT-STM) and reflection absorption infrared spectroscopy (RAIRS). By providing high-resolution vibrational spectra of surface species, RAIRS data is highly sensitive to the chemical identity of those species. However, it does not provide information on the relative coverages of adsorbed molecules and many important stable intermediates are invisible to RAIRS. In contrast, with a LT-STM operated at 4.7 K, individual molecules are observable and their absolute coverages are readily obtained simply by counting, yet their chemical identities cannot be directly determined from the STM images alone. In the case of acetylene, both RAIRS and LT-STM indicate that it adsorbs in a single form at low temperature in which the CC bond is positioned over a three-fold hollow site, and that the interaction with the surface occurs through both di-σ and π bonding. On warming to 250 K in the presence of coadsorbed hydrogen, RAIRS provides strong evidence for the partial hydrogenation of acetylene to form an adsorbed vinyl ($CHCH_2$) species. The LT-STM images following a 250 K anneal in the presence of coadsorbed hydrogen show a marked increase in the coverage of a species that is identified as vinyl, based on the RAIRS results. Both techniques indicate that adsorbed acetylene is stable up to 300 K. A third species, in addition to adsorbed acetylene and vinyl, is also observed with the LT-STM after a 300 K anneal, which is identified as vinylidene, $CCH_2$. However, the RAIRS evidence for a vinylidene species is not definitive. In the case of ethylene adsorption at low temperature, RAIRS provides clear evidence for a di-σ bonded form of ethylene at low temperatures that coverts to ethylidyne at 280-420 K. The LT-STM images show that ethylene exists in both π-bonded and di-σ bonded forms at low temperature and that the two forms can be easily interconverted using electron pulses from the STM tip. On the basis of RAIRS experiments, it was found that surface carbon formed through the complete dehydrogenation of acetylene could be hydrogenated to form ethylidyne ($CCH_3$), from which it was inferred that the surface carbon was in the form of $C_2$ molecules. A form of surface carbon that can be hydrogenated to ethylidyne was also identified with LT-STM. Other surface species that have been investigated with the two techniques include ethynyl (CCH), ethylidene ($CHCH_3$), and methylidyne (CH).

**9:20am SS2-WeM5 Dehydrogenation of Single Ammonia Molecules on Ruthenium**, *I. Stass*, *S. Maier*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Ammonia ($NH_3$) can be potentially used for hydrogen storage, because the dissociation of ammonia molecules generates hydrogen. Although Ruthenium is the best elementary metallic catalyst for ammonia synthesis, the exact reaction mechanisms at the atomic scale of both synthesis and dissociation over the Ruthenium surface have yet to be understood. Previously, the dehydrogenated products were obtained by annealing the sample and characterized by spectroscopic methods.

We studied the dehydrogenation of single ammonia molecules adsorbed on a Ru(0001) surface, by means of scanning tunneling microscopy (STM) at low temperature. The sudden change in tunneling current during the dissociation process allows us to study the dissociation mechanism and rate of single molecules in detail. We observe the different dehydrogenation steps after selectively applying voltage pulses in the order of a few volts between STM tip and an adsorbed ammonia molecule. The various dissociation products show a distinct imaging contrast. Together with the assignment of the adsorption site, this leads to the identification of the dissociation products. We will discuss to what extent electron induced and electric field driven processes, respectively, are affecting the dissociation mechanism of ammonia and its dissociation products.

**9:40am  SS2-WeM6  The Ca / MEH-CN-PPV Interface: Ca Adsorption Calorimetry, LEIS and XPS**, *J.C. Sharp, J.H. Baricuatro,* University of Washington, *F. Bebensee, H.-P. Steinrueck, J.M. Gottfried,* Universitaet Erlangen-Nuernberg, Germany, *C.T. Campbell,* University of Washington

Conjugated polymers are of interest for use in photovoltaics and OLEDs because of the tunability of their band gap and ease of processing them into devices. Poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene) (MEH-CN-PPV) has high photoluminescence efficiency and thus has potential use in OLEDs. The interaction between the conjugated polymer and metal electrode is critical to the performance of these devices. The energetics and structure of calcium growth on MEH-CN-PPV was studied using adsorption microcalorimetry and low-energy ion scattering spectroscopy (LEIS) in ultrahigh vacuum. At 300 K the integrated Ca LEIS peak area grew slowly until ~1.5 ML and the rate of growth increased until a continuous film of Ca was formed by ~15 ML. The slow initial growth rate is due to calcium diffusing subsurface. After ~1.5 ML, Ca forms 3-D islands on the surface. At 130 K, the transitions from subsurface diffusion to 3D cluster growth to film formation occur at lower coverages. The initial heat of adsorption of Ca on MEH-CN-PPV at 300 K is 436 kJ/mol. The heat of adsorption increases to 464 kJ/mol at ~0.1 ML and then decreases to the heat of sublimation of Ca by 4 ML. Similar behavior is seen at 130 K with the initial heat of adsorption being 326 kJ/mol and increasing to 331 kJ/mol at ~0.1 ML and decreasing to the heat of sublimation already by 1.25 ML. The sticking probability (S) at 300 K was 0.70 initially and increased to 0.75 at ~0.1 ML of Ca coverage. After ~0.1 ML, S decreased to 0.64 by ~1.5 ML, then gradually increases to unity. The initial sticking probability at 130 K was 0.92 and increased toward unity. The thermodynamic, sticking and growth behavior below 1.5 ML, where Ca is interacting strongly with specific adsorption sites on the polymer, will be discussed

**10:40am  SS2-WeM9  STM Tip Induced Surface Reactions on TiO$_2$(110)**, *D.V. Potapenko, R.M. Osgood,* Columbia University

Chemistry on the surfaces of photocatalytic materials, including TiO$_2$, is driven by the charge carriers that are created in the bulk of the catalyst by light adsorption. The tip of a scanning tunneling microscope may serve as an alternative source of both free electrons and holes in a semiconductor. We have studied adsorption and tip-induced surface chemistry of 4-bromobiphenyl on the TiO$_2$(110) surface. The adsorbed molecules could be identified in the STM images at the limit of low coverages. The response of the surface to the adsorbed substance was characterized with in situ temperature program desorption. Passing the electric current from the STM tip through molecules caused dissociation of the molecules as was indicated by the changes in the STM images. We report on the conditions of the tip-induced chemistry and propose mechanistic explanation of the observed phenomena. An important follow on experiment to this work will be to examine reactions on nanocrystal TiO$_2$.

**11:00am  SS2-WeM10  H$_2$O Interaction with Oxygen Adatoms on TiO$_2$(110)**, *Y. Du, A. Deskins, Z. Zhang, Z. Dohnalek, M. Dupuis, I. Lyubinetsky,* Pacific Northwest National Laboratory

Water and oxygen interactions on the catalytically important TiO$_2$ surfaces have attracted great interest from both fundamental and technological points of view. In this work, surface chemistry of water on oxidized TiO$_2$(110) surfaces is investigated by scanning tunneling microscopy studies and density functional theory calculations. We show that oxygen adatoms (O$_a$), generated during oxygen dissociation, alter the water dissociation and recombination chemistry through two distinctive pathways. Depending on whether H$_2$O and O$_a$ are on the same or adjacent Ti$^{4+}$ rows, O$_a$ facilitates H$_2$O dissociation and proton transfer to form a terminal hydroxyl pair, positioned along or across the Ti$^{4+}$ row, respectively. The latter process involves proton transfer through a bridging oxygen atom where H$_2$O is considered to be in a ''pseudo-dissociated'' state. In both pathways, the reverse H transfer results in H$_2$O reformation and statistical O scrambling, as manifested by an apparent along- or across-row motion of O$_a$'s.

**11:20am  SS2-WeM11  Sulfur Adsorption on Ag(111) and Ag(100): Structures and Surface Dynamics**, *D.-J. Liu, M. Shen, S. Russel, C.J. Jenks, J.W. Evans, P.A. Thiel,* Iowa State University

Exposure to sulfur (S) of Ag(111) and Ag(100) produces ordered surface structures as observed by STM. On Ag(111), a self-organized dot-row structure forms at around 200 K [1]. The dots, likely Ag$_3$S$_3$ clusters, can rearrange and form other more closed-packed structures at higher S coverages. On Ag(100) at 230 K, a √17 reconstruction structure appears for S coverage above 0.25 ML, together with a p(2x2) structure. STM studies also reveal that exposure to sulfur generally accelerates coarsening of 2D Ag nanoislands preformed on the surface by Ag deposition. For Ag(111), since steps serve as sinks for S, dramatic enhancement of Ostwald ripening only occurs above a threshold (step saturation) coverage of S [2]. For Ag(100), Ostwald ripening is activated with a rate increasing gradually with increasing S coverage. Possible acceleration mechanisms include AgnSm complex mediated mass transport, or S-catalyzed attachment-detachment. We perform a detailed analysis of the stability and formation energies of various structures and Ag-S complexes using DFT. Many aspects of the observed structures and mechanisms for mass transport during coarsening are elucidated based on these DFT energetics together with kinetic modeling.

[1] Shen *et al.* J. Phys. Chem. C **112** (2008) 4281

[2] Shen *et al.* J. Chem. Phys. **130** (2009) 094701

**11:40am  SS2-WeM12  Ionicity of Adsorbates: Dependence on Coverage, Site, and Substrate**, *P.S. Bagus,* University of North Texas, *Ch. Wöll,* Ruhr-Universitaet Bochum, Germany, *A. Wieckowski,* University of Illinois at Urbana-Champaign

We present detailed theoretical analyses of nominally anionic Iodine and nominally cationic Cs adsorbed on Cu(111) and Pt(111) surfaces. We consider the consequences of the coverage, the choice of on-top or three-fold sites, and the differences between Cu and Pt substrates on the degree of ionicity and on other properties of the interaction. This work extends our earlier studies of I and Cs on Cu(111)[1] and of I/Pt(111).[2] There we demonstrated that, although both Cs and I were dominantly ionic adsorbates, the properties of the adsorption, including work function changes, $\Delta\Phi$, and photoemission binding energy shifts, $\Delta$BE, depended on other factors besides the adsorbate ionicity. However in this earlier work, only a single I or Cs adsorbate was explicitly treated and we neglected both direct and indirect, substrate mediated, adsorbate-adsorbate interactions. Now, we use models where several adsorbates are included, thus explicitly modeling lower and higher coverages. In particular, we examine whether the coverage dependent departures from ideal ionicity are different for cations and anions. Furthermore, we examine how $\Delta\Phi$ depends on the adsorbate-adsorbate interaction and compare our predictions with measurements of $\Delta\Phi$ as a function of coverage. This is relevant for the modification of charge transport barriers, which is key for the design of organic electronics.[3] The distance of I above Pt(111) is quite different for on-top and three-fold sites,[2] which has important consequences for $\Delta\Phi$ and $\Delta$BE. Here, we examine the generality of different heights of ionic adsorbates at these sites and how this difference is affected by the sign of the ionicity and the substrate. Our theoretical methodology uses wavefunctions for cluster models of the surface since this allows us to determine the quantitative importance of the individual physical and chemical mechanisms that contribute to the interaction. Our present work marks the first time that these methods have been applied to study the influence of coverage for halogen and alkali metal adsorbates.

[1]P. S. Bagus, D. Käfer, G. Witte, and C.Wöll, Phys. Rev. Lett., **100**, 126101 (2008).

[2]P. S. Bagus, C. Wöll, and A. Wieckowski, Surf. Sci. **603**, 273 (2009).

[3]G. Witte, S. Lukas, P. S. Bagus, and C. Wöll, Appl. Phys. Lett., **87**,263502 (2005).

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