

Monday Morning, October 31, 2011

Surface Science Division

Room: 110 - Session SS2-MoM

Surface Chemical Dynamics

Moderator: L. Bartels, University of California, Riverside

8:20am SS2-MoM1 STM Dynamics Studies of Tip-Induced Reactions of Anthracene Derivatives on TiO₂(110), *D.V. Potapenko, R.M. Osgood*, Columbia University

In photocatalysis, reactions are driven by the charges that are generated in the bulk of the catalyst and then are transferred to the adsorbed molecules. Injection of electrons from the STM tip into the adsorbed molecules is a useful tool for surface dynamics studies as the energy the electrons as well as the adsorption state of the molecules could be precisely controlled. We have studied adsorption and tip-induced chemistry of anthracene and its derivatives on the TiO₂(110) surface. These molecules self-assemble on the rutile(110) surface at room temperature driven by electrostatic interaction. Applying electric pulses from the STM tip to individual molecules causes desorption and in some cases dissociation as indicated by the changes in the STM images. We have observed dissociative electron capture of 2-chloroanthracene molecules that leaves behind a surface chlorine atom. The energy threshold for dissociation found as ~ 3.1 V. We report on the dynamics of this tip-induced chemistry and propose a mechanism for the observed phenomena.

8:40am SS2-MoM2 Atom Specific Ultrafast Surface Chemistry using Soft X-ray Free Electron Laser: CO on Ru(0001), *M. Beye*, Helmholtz Zentrum Berlin, Germany, *R. Coffee*, SLAC Nat. Accel. Lab, *M. Dell'Angela*, Univ. of Hamburg, Germany, *A. Foehlich*, Helmholtz Zentrum Berlin, Germany, *J. Gladh*, Stockholm Univ., Sweden, *T. Katayama*, *S. Kaya*, *O. Krupin*, *A. Nilsson*, *D. Nordlund*, SLAC Nat. Accel. Lab, *H. Oberg*, Stockholm Univ., Sweden, *H. Ogasawara*, SLAC Nat. Accel. Lab, *H. Ostrom*, *L.G.M. Pettersson*, Stockholm Univ., Sweden, *W.F. Schlott*, *J.A. Sellberg*, SLAC Nat. Accel. Lab, *F. Sorgenfrei*, Univ. of Hamburg, Germany, *J.J. Turner*, SLAC Nat. Accel. Lab, *M. Wolf*, Fritz-Haber-Inst., Germany, *W. Wurth*, Univ. of Hamburg, Germany

New possibilities for the study of chemical reactions on surfaces using X-ray free-electron lasers (Linac Coherent Light Source, or LCLS, at SLAC National Accelerator Laboratory) will be presented. We induced the hot electron mediated excitation of CO on Ru(0001) with synchronized excitation by a femtosecond optical laser pulse. We have followed the ultrafast evolution of the bond distortions, weakening and breaking, using x-ray emission spectroscopy resonantly tuned to the oxygen core level with ultrashort x-ray pulses delivered from LCLS. We can directly study the time evolution of the molecular orbitals in an atom-specific way on a subpicosecond timescale. Different adsorption configurations explored have been characterized by comparing the measured time dependent energy shifts of the molecular orbitals in the valence band with theoretical results.

This research was carried out on the SXR Instrument on the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory. The SXR Instrument is funded by a consortium whose membership include the LCLS, Stanford University through the Stanford Institute for Materials Energy Sciences (SIMES), Lawrence Berkeley National Laboratory (LBNL), University of Hamburg through the BMBF priority program FSP 301, and the Center for Free Electron Laser Science (CFEL). The LCLS is funded by the U.S. Department of Energy's Office of Basic Energy Sciences.

9:00am SS2-MoM3 The Oxidation of Benzyl Alcohol on Gold and its Implications Towards a Gold-Mediated Conversion of Hydrocarbons, *J.C. Rodriguez-Reyes*, *C.M. Friend*, *R.J. Madix*, Harvard University

In order to understand alcohol conversion on gold, we have explored the mechanism of the oxidation of benzyl alcohol (C₆H₅-CH₂OH) on a Au(111) surface - a test reaction commonly used to determine the efficiency and selectivity of novel gold-based catalysts. Using adsorbed atomic oxygen as the active oxidizing species, we find that a high selectivity towards the conversion to aldehyde (benzaldehyde, C₆H₅-CHO) is achieved at low oxygen coverages. However, in excess oxygen the selectivity decreases dramatically, and benzaldehyde is readily transformed to adsorbed benzoate, which is eliminated as benzoic acid (C₆H₅-COOH) and CO₂. In addition, we show that the production of the ester produced by self-coupling (benzyl benzoate) does not require the separate presence of acid, as might be expected from acid-alcohol condensation reactions. These surface transformations are extremely facile and exhibit small kinetic barriers of the rate-limiting steps. Lastly, by comparing the mechanism of benzyl alcohol

oxidation to that of toluene oxidation, we extract information of a model hydrocarbon-to-alcohol reaction (toluene to benzyl alcohol, C₆H₅-CH₃ to C₆H₅-CH₂OH). Our results suggest that due to the relatively large kinetic requirements for toluene conversion, the alcohol cannot be selectively produced on a gold surface; indeed, preliminary TPRS data indicates that the gold-mediated conversion of toluene yields benzoic acid and combustion gases.

9:20am SS2-MoM4 Determination of the Structure and Vibrational Dynamics of Methyl-Terminated Si(111) Using Helium Atom Scattering, *R.D. Brown*, *S.J. Sibener*, University of Chicago

MMethyl-terminated Si(111) interfaces are of great interest in the fields of solar energy, solar fuels, and electronics due to their superior electrochemical stability and device performance. Recent advances in synthetic techniques allow for the fabrication of high-quality, passivated organic-semiconductor hybrid interfaces on single-crystalline silicon substrates. This termination maintains the bulk electronic behavior of the underlying silicon, but eliminates surface trap states which hinder the performance of any device. We directly examined the structural and dynamical characteristics of the CH₃-Si(111) and CD₃-Si(111) interfaces using helium atom scattering. Helium atom scattering is a uniquely surface-sensitive technique which probes both atomic structure and dynamics. These results are the first measurements of this nature for an organic-semiconductor hybrid interface. Helium atom diffraction confirmed a high quality (1x1) methyl termination of the Si(111) substrate. We observed unusual dynamical characteristics for these interfaces through Debye-Waller attenuation measurements of helium atom diffraction peaks. These measurements characterized the thermal motion of the interface, and elucidated the surface Debye temperature and gas-surface interaction well depth. The Debye Waller measurements yielded temperature dependencies of the surface mean-square displacements displaying polarization dependence, and were similar to the thermal motion of local molecular vibrational modes. The effective surface Debye temperatures were much higher than expected, and correspond to the local vibrational modes of the C-Si bond. These two unusual results indicate that termination with the simplest monolayer organic film initiates a transition away from phonon dominated surface dynamics to dynamics dominated by local molecular vibrational modes. We also performed a series of high precision inelastic time-or-flight measurements to characterize the phonon band structure of these interfaces. Our measurements have clearly resolved multiple single phonon surface modes on CH₃-Si(111), and are the first observations of this nature on an organic-semiconductor hybrid interface.

9:40am SS2-MoM5 STM Insights into Single-Molecule Dynamics, *K. Morgenstern*, Leibniz University of Hannover, Germany **INVITED**

The development of molecular switches on the single molecule level is a major challenge on the path towards incorporating molecules as building units into nanoelectronic circuits. With a scanning tunneling microscope (STM) it is possible to induce chemical reactions on a single molecule basis by electrons tunneling inelastically from the STM tip into a molecule. The method is based on high-resolution imaging at low-temperature (5K) that allows us to identify different groups within the molecule. Chemical reactions are induced by injecting selectively electrons into specific parts of the molecule. The success of the manipulation is visualized in the recorded tunneling current during the manipulation and in STM images taken afterwards. We investigate isomerization of individual molecules adsorbed on metal surfaces. For chlorobenzene and azobenzene derivatives, the effects of different substitutional groups and different substrates are explored.

10:40am SS2-MoM8 State-resolved Reactivity of Methane (v_2+v_4) on Ni(111), *N. Chen*, *Y. Huang*, *A. Utz*, Tufts University

Methane dissociation on transition metal surfaces is the rate-limiting step in the steam reforming reaction, which is the principal route for converting CH₄ to H₂. Understanding the dynamics of energy flow during this process has both fundamental and practical impact. Experiments that measure the reactivity of methane prepared in select vibrational states reveal how specific nuclear motions promote methane dissociation. State-resolved measurements for methane reactivity on Ni and Pt surfaces show that molecules prepared in vibrationally excited states are more reactive than those without laser excitation, and the efficacies of vibrational energy in different excited states can differ significantly.

Here, we present state-resolved reactivity measurements of the v_2+v_4 bending combination vibration of CH₄ on Ni(111) as a function of translational energy. This state is a member of the pentad of vibrational states that can play an important role in the thermal activation of methane. We are able to quantify the state-resolved reactivity of methane in this

particular vibrational state over a wide range of translational energies. We compare the efficacy for v_2+v_4 bend with that of the v_3 stretching and $3v_4$ bending states to gain insight into the ability of v_2 excitation to promote dissociative chemisorption. The result permits a detailed comparison of the role of stretch and bend excitation of methane dissociative chemisorption on Ni(111).

11:00am **SS2-MoM9 Molecular Beam Scattering of CO and CO₂ on CuO_x Nanoclusters Supported on Silica Fabricated by Electron Beam Lithography**, *M. Komarneni, U. Burghaus*, North Dakota State University

Adsorption dynamics of CO and CO₂ on 12 nm CuO_x nanoclusters supported on silica are studied by molecular beam scattering. Samples are fabricated by electron beam lithography. Scanning electron microscopy, auger electron spectroscopy, and x-ray photoelectron spectroscopy are used to characterize the sample. Cu clusters which are nearly metallic, partially oxidized, and fully oxidized are prepared by varying the sample treatment. The initial adsorption probability, S_0 , of both CO and CO₂ decreased with an increase in impact energy, E_i , and adsorption temperature, T_s , which is consistent with non-activated molecular adsorption. S_0 of CO approaches the values obtained for copper single crystals for E_i of 0.4 eV. This is a result of the so-called capture zone effect, where CO molecules are trapped on the support and subsequently diffuse to the metal clusters. S_0 of CO₂ is larger than for single crystals. The differences in S_0 for metallic and oxidic clusters can be explained by deviations in the mass matching. In-contrast with CO₂, S_0 of CO on metallic clusters is slightly larger than that of oxidic clusters. At low E_i and T_s , coverage dependent adsorption probabilities, $S(\theta)$, of CO and CO₂ on metallic clusters obeyed precursor-mediated Kisliuk-like dynamics. At large E_i , Langmuirian-like dynamics is seen for CO which is less pronounced for CO₂ on metallic clusters.

11:20am **SS2-MoM10 Precursor-Mediated Reactivity of Vibrationally Hot Molecules**, *D. DelSesto, E. Peterson, E. Dombrowski, A. Utz*, Tufts University

Methane's dissociative chemisorption is highly activated on a range of transition metal surfaces. Internal-state-averaged and state-resolved beam-surface scattering experiments show that vibrational energy (E_{vib}) can be highly effective in promoting dissociative chemisorption via a direct mechanism, but evidence for E_{vib} activation via a precursor-mediated mechanism on a metal surface remains scarce. We will present recent experimental results from our lab that demonstrate the ability of E_{vib} to promote methane dissociation via both direct and precursor mechanisms on Ir(111). These results build on prior studies of trapping-mediated reactivity on Ir(111) by exploring how E_{vib} in the incident methane molecule promotes reactivity, and they are consistent with the timescales and pathways of vibrational energy flow and damping on these surfaces.

1. Seets, D. C., C. T. Reeves, et al. (1997). "Dissociative chemisorption of methane on Ir(111): Evidence for direct and trapping-mediated mechanisms." *J. Chem. Phys.* **107**(23): 10229-10241.

11:40am **SS2-MoM11 Three-Dimensional Spatial Distribution of Desorbing N₂ and N₂O from Pd(211)**, *M. Sakurai, T. Kondo, J. Nakamura*, University of Tsukuba, Japan

Spatial distributions of N₂ and N₂O desorbing from Pd(211), Pd(S)-[3(111)×(100)], in temperature programmed desorption (TPD) were measured after the N₂O dosing on the surface at 60 K. About one-third of N₂O molecules on the surface are found to desorb as N₂ by the decomposition with sharp concentration to 25° ($\theta = -25^\circ$) (100) side from the normal direction of (211) plane at 108 K in the parallel plane to [211] and [-111] directions at N₂O coverage of 1.0 ML. This indicates that N₂ desorbs without thermal equilibration by N₂O decomposition on Pd(211). From the preferential desorption direction ($\theta = -25^\circ$), the adsorption structure of N₂O just before the desorption is assigned as the bridge-structure at step-site, where O and terminal-N bonded with Pd at ontop (100) and 3fold hollow(111), respectively along the [-111] directions. On the other hand, the spatial distribution of desorbing N₂O obeyed cosine distribution directing the normal direction to the (211) plane, suggesting the existence of pre-desorption state on the surface.

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