Monday Morning, November 4, 2002

Surface Science
Room: C-108 - Session SS1-MoM

Adsorption and Chirality
Moderator: B.E. Koel, University of Southern California

8:20am **SS1-MoM1 STM Studies of the Role of Copper in Chlorosilane Desorption Mechanisms from Cl-exposed Cu/Si(111) Surfaces**, ***D.V. Potapenko***, *S.E. Sysoev, A.V. Ermakov, D. Maithil, B.J. Hinch*, Rutgers University

TPD experiments show that the presence of copper on a Si(111) surface significantly influences the desorption kinetics of chlorosilanes from chlorine-exposed Si(111) surfaces. The major desorption peak (of $SiCl_2$) occurs at ~600°C from Cl-covered Cu/Si(111) surfaces, and complex desorption kinetics are exhibited that indicate an active role of chlorine-free sites in the $SiCl_2$ desorption process. In contrast, $SiCl_2$ desorption from Si(111) 7x7 surfaces is observed at ~650°C and this follows comparatively simple second-order kinetics. Here we report on STM studies of the Cl-covered Cu/Si(111) surfaces, following low temperature (~450°C) restructuring and at the onset of chlorosilane desorption at 600°C. We will display evidence for the direct role of copper in the aggregation of Cl in compact Cl-containing regions during the high temperature chlorosilane desorption process. We will also discuss possible mechanisms of Cu-catalyzed desorption of chlorosilanes from the Si(111) surface.

8:40am **SS1-MoM2 Dynamics of Oligomer Desorption from Surfaces**, *A.J. Gellman*, ***K.R. Paserba***, *N. Vaidyanathan*, Carnegie Mellon University

A study of the desorption of long chain oligomers from surfaces has revealed that the measured desorption energies are non-linear in the oligomer chain length. This work has used alkanes, polyetheyleneglycols, and polyethyleneglycol dimethylethers with chain lengths in the range 5 to 60 atoms. These have been adsorbed on the surface of graphite at low temperature and the kinetics of desorption have been measured using temperature programmed desorption. Empirically we find that the desorption energies scale as the square root of the chain length. A model has been proposed for oligomer desorption that accurately accounts for the observed dependence of the desorption energy on chain length. The adsorbed oligomers can be considered to consist of segments that are attaching to and detachng from the surface independently. Within the context of transition state theory these partially detached oligomers are in equilibrium with a transition state to desorption which is fully detached from the surface. The energy of each of the detached states is simply proportional to the number of detached segments. The entropy is given by the number of ways of detaching segments and by the partition function for trans-gauche conformations about each detached bond. These energies and entropies determine the equilibrium constants for each of the partially detached species. These considerations can be formulated into an analytical expression for the measured desorption energy that accurately reproduces the experimental results. One of the interesting insights that our model provides is that the analytical expression for oligomer desorption energies exactly matches the predictions of Tolman's theorem. Because the oligomers on the surface can adopt a huge number of conformations this leads to a substantial non-linearity in the desorption energy as a function of chain length.

9:00am **SS1-MoM3 D Abstraction by H on Si(111) Surfaces: Temperature and Coverage Dependence**, ***F. Khanom***, *F. Rahman, A. Aoki, A. Namiki*, Kyushu Institute of Technology, Japan

Influences of surface temperature T_s and D adatom coverage on direct abstraction (ABS) as well as collision-induced-desorption (CID) of surface D adatoms by H atoms have been studied on Si(111). We found that D_2 CID as a result of reaction H + D/Si --> D_2 , obeys a third-order kinetics with respect to θ_D, ruling out the so-called hot atom mechanism. D_2 CID rate versus T_s curves were found to exhibit a close similarity in spectral line shape with a β_2 temperature-programmed-desorption (TPD) spectrum arising from a dideuteride phase. The spectral similarity between CID and TPD suggests that D_2 CID obey the same mechanism as for the β_2 TPD. In order to understand the underling mechanism we measured reaction order of the β_2 TPD. As a consequence, 1.5th-reaction order was obtained with respect to dideuteride coverage. The 1.5th reaction order suggests that three D atoms are involved in a single D_2 desorption, which rationalizes the third-order reaction observed in D_2 CID. Regarding ABS to form HD molecules, HD rates were determined for various θ_D. As a result, we found that a first-order kinetics prevails the HD ABS for low D coverage regime below 0.5ML, but strangely enough, a second-order kinetics becomes dominant for high coverage regime around 1.0 ML. The second-order kinetics suggests that a direct Eley-Rideal reaction mechanism as well as hot atom mechanism are ruled out. We propose a new mechanism of hot complex mediated ABS and CID: the incident H atoms form a complex with D-Si system in the very early stages of sticking. ABS and dihydride formation occur competitively during the relaxation process of the hot complex.

9:20am **SS1-MoM4 Adsorption and Abstraction of H Atoms on the Graphite (0001) Surface**, ***T. Zecho***, Max-Planck-Institut für Plasmaphysik (EURATOM Association), Germany, *A. Güttler, C. Drummer,* Universität Bayreuth, Germany, *X. Sha, B. Jackson,* University of Massachusetts, *J. Küppers*, Max-Planck-Institut für Plasmaphysik (EURATOM Association), Germany

The interactions of hydrogen atoms with graphite surfaces are of interest for many areas like astrophysics, plasma surface interactions in controlled fusion devices and diamond synthesises. Nevertheless most of the knowledge up to now is deduced from theoretical work and without experimental evidence. The present study has been performed in order to verify recent theoretical results on the interactions of hydrogen atoms with the graphite basal plane. Highly oriented pyrolytic graphite (HOPG-ZYH) was used and characterised by scanning electron microscopy (SEM) prior to the experiments. Hydrogen atoms were generated by thermal dissociation of hydrogen molecules in a tungsten capillary heated to 2000 K. Adsorption and abstraction were investigated by thermal desorption spectroscopy (TDS), electronic and vibrational energy loss spectroscopy (EELS, HREELS) and in situ measurment of the abstraction products. Admission of hydrogen atoms at low temperatures (100 K-300 K) leads to adsorption of hydrogen on graphite up to coverages of about 0.5 monolayer. In EEL spectra the intensity of the π-plasmon of graphite decreases upon hydrogen adsorption indicating a decreasing sp^2 character of surface carbon 2sp electrons. HREEL spectra allowed to determine the C-H normal and parallel vibrational frequencies which are close to theoretical predictions. Heating of H(D) covered graphite surfaces leads to desorption of hydrogen (deuterium) molecules with peaks between 300 K and 600 K. The thermal desorption peak maxima show a large isotope effect of about 50 K. The admission of deuterium atoms to H covered graphite surfaces leads to the release of HD and a very small amount of H_2. The abstraction reaction shows a coverage dependent cross section which decreases from about 16 $Å^2$ at low coverages to about 4 $Å^2$ close to saturation.

9:40am **SS1-MoM5 Experimental and Theoretical Characterization of the Vibrational Properties of Aminocarbyne Surface Intermediates**, *B. Chatterjee, D.H. Kang,* University of Illinois at Chicago, *P. Mills,* North Central College, ***M. Trenary***, University of Illinois at Chicago

Density functional theory (DFT) calculations and measurements using reflection absorption infrared spectroscopy have been used to characterize aminocarbynes on a Pt(111) surface. The three aminocarbynes considered are CNH_2, $CNHCH_3$ and $CN(CH_3)_2$. The CNH_2 species, known simply as aminocarbyne or as aminomethylidyne, is formed from HCN, methyl amine, or the hydrogenation of surface CN. Methylaminocarbyne, $CNHCH_3$, can be formed from the N-protonation of methyl isocyanide ($CNCH_3$) or from the partial dehydrogenation of dimethyl amine, $HN(CH_3)_2$. Dimethylaminocarbyne, $CN(CH_3)_2$, is formed from the decomposition of trimethylamine, $N(CH_3)_3$. The DFT calculations were based on a model consisting of only two Pt atoms, as would be appropriate for bonding at a two-fold bridge site. Gaussian 98 with the B3LYP functional and a 6-311G** basis set along with effective core potentials for the Pt atoms was used. The calculations converged and optimized to reasonable geometries. For example, Pt_2CNH_2 converged to a C_{2v} symmetry structure with a CN bond length of 1.32 Å with calculated frequencies (using the appropriate scale factor of 0.9613) for the ν(CN), δ(NH_2), and ν_s(NH) fundamentals of 1393, 1564, and 3407 cm^{-1}, respectively, compared to experimental values for CNH_2 on Pt(111) of 1323, 1567, and 3363 cm^{-1}. The calculations successfully reproduce not only the measured vibrational frequencies, but also the relative intensities and the measured shifts that occur with various isotopic substitutions. Calculations using larger Pt clusters, which are much more time consuming, lead to only modest improvements. The results suggest that the internal vibrations of polyatomic adsorbates can be successfully calculated using models of the surface that are surprisingly simple.

10:00am **SS1-MoM6 Adsorption and Adhesion Energies of Pb on (1x1)-MoC/Mo(001) by Single-crystal Adsorption Calorimetry**, ***M.H. Smedh***, *S.F. Diaz, C.T. Campbell*, University of Washington

The heat of adsorption, sticking probability and film growth mode of Pb adsorption was studied on a thin, ordered MoC film at 300 K. A several layers thick film of MoC displaying a (1x1) LEED pattern was grown by dissociating ethylene on hot Mo(100), following Frühberger.[1] The Pb atoms were deposited in a chopped molecular beam, with 0.1 s pulses containing 0.015 ML Pb every 2 s. The Pb beam flux was determined using a quartz crystal microbalance. The heat of Pb adsorption was measured by single-crystal adsorption microcalorimetry, based on King's approach,[2] with a different heat detection scheme. The adsorption of a Pb pulse causes a transient heat input and temperature rise, detected by a pyroelectric polymer ribbon in contact with the backside of the sample.[3] An initial heat of adsorption of 245 ± 5 kJ/mol was found. It stayed constant up to ~0.5 ML, then dropped smoothly up to 1 ML to ~195 kJ/mol, within a few percent of the heat of sublimation for Pb, where it remained constant up to ~ 8 ML. The implications of these results with respect to Pb-Pb repulsions and Pb mobility in the adlayer will be discussed. From the integral heat of adsorption at 8 ML, a Pb/MoC adhesion energy of ~180 µJ/cm^2 was obtained. This will be compared to results obtained from the contact angle of molten Pb drops. The sticking probability was found to be 0.96 initially, increasing linearly up to ~1 ML to 0.994 ± 0.003, where it remained for higher coverages. The growth mode of Pb on (1x1)-MoC/Mo(100) was further investigated by comparing the behavior of the Pb and Mo AES intensities as a function of the Pb coverage to different growth models.

[1] B. Frühberger and J.G. Chen, Surf. Sci. 342 (1995) 38.

[2] C.E. Borroni-Bird and D.A. King, Rev. Sci. Instrum. 62 (1991) 2177

[3] J.T. Stuckless, N.A. Frei, and C.T. Campbell, Rev. Sci. Instrum. 69 (1998) 2427.

10:20am **SS1-MoM7 Enantioselectivity on Naturally Chiral Surfaces**, ***A.J. Gellman***, *J. Horvath*, Carnegie Mellon University **INVITED**

Chirality is an omnipresent feature of the biochemical and biophysical world. The handedness of the molecules that form the basis of life creates the need for enantiomeric purity in the chemicals used for pharmaceutical and other bio-active purposes. Many of the processes used for synthesis and preparation of enantiomerically pure compounds rely on the use of chiral surfaces. The high Miller index surfaces of metals have chiral structures and can, in principle, be used for to control enantioselectivity in chemical processes. The kinked step structures of such surface are chiral and thus serve as chiral binding sites for a number of enantiospecific adsorption, desorption and surface reactions. As an example, the orientation of chiral molecules on chiral surfaces can be shown to depend on the relative handedness of adsorbate and substrate. This has been shown by study of the infrared reflection absorption spectra of 2-butanoxy groups on the Ag(643) surface. The intensities of the absorptions by R- and S-2-butanoxy groups are dependent on the handedness of the Ag(643) substrate. Similarly, the heats of adsorption of small chiral molecules such as R- and S-propylene oxide (CH3CH(O)CH2) and R-3-methylcyclohexanone are sensitive to the handedness of surfaces such as Cu(643). This has been observed using thermally programmed desorption measurements which reveal that the desorption kinetics of these chiral molecules are enantiospecific on chiral surfaces. They do not exhibit enantiospecificity on achiral surfaces such as Cu(111). In the course of this work we have been able to identify chiral adsorption sites on high Miller index metal surfaces. Most recently we have been able to demonstrate an enantioselective separation using such surfaces to purify a racemic mixture of 3-methylcyclohexanone. Understanding and controlling these enantiospecific properties poses some extremely interesting challenges for surface chemistry and surface physics.

11:00am **SS1-MoM9 Self-assembly of Chiral Nanoclusters of Cysteine on Au(110)-(1x2)**, ***A. Kühnle***, *T.R. Linderoth, L. Molina, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark

We have performed a comprehensive STM-based study of the adsorption of the chiral amino acid cysteine, HS-CH$_2$CH(NH$_2$)-COOH, onto the missing-row reconstructed Au(110)-(1x2) surface under UHV conditions. In experiments where we deposit cysteine either as the pure enantiomeric forms or as the racemic mixture, we have identified a rich variety of chiral adsorption phenomena. The results are interpreted with the aid of density functional theory calculations. Previously, we have reported on the enantioselective dimerization of cysteine into homochiral molecular pairs and identified the atomic-scale interactions responsible for this intermolecular chiral recognition.[1] Here, we focus first on supramolecular chain-like assemblies of cysteine molecules that coexist with the molecular pairs. The chiral chains extend over several hundred Ångström and consist of two adjacent rows of cysteine molecules. Formation of these chains is accompanied by a pronounced surface reconstruction, involving the removal of two close-packed rows of gold atoms underneath each molecular double row, and is driven by the formation of hydrogen bonds between the carboxylic groups of the cysteine molecules in the rows. Secondly, we discuss the self-assembly of molecular nanoclusters of cysteine. When cysteine is deposited at a substrate temperature of 120 K, small, irregular agglomerates of molecules are formed. A remarkable transition is seen upon annealing to 270 K, where the molecules self-assemble into completely identical clusters with a size of 18 by 24 Å. The molecules appear to segregate into homochiral clusters when the racemic mixture is deposited.

[1] A. Kühnle, T.R. Linderoth, B. Hammer and F. Besenbacher, Nature 415, 891 (2002).

11:20am **SS1-MoM10 Towards Epitaxial Growth of Chiral Metal Films on Metal Oxide Substrates**, ***D.S. Sholl***, *A. Asthagiri, A.J. Francis, C. Niederberger, L.M. Porter, P. Salvador*, Carnegie Mellon University

Although intrinsically chiral metal surfaces have been demonstrated to have intriguing enantiospecific adsorption and electrochemical properties, current studies of these materials are performed using small single-crystal samples. To move towards practical applications of these surfaces, techniques for substantially increasing the surface area of these chiral films need to be developed. One avenue towards this goal is the controlled growth of thin metal films on suitable chiral metal oxide substrates. We will report theoretical and experimental results for the growth of Pt films on SrTiO$_3$ substrates. This metal/metal-oxide pair was chosen because of the catalytic properties of Pt, the close lattice match between Pt and SrTiO$_3$, and the availability of SrTiO$_3$ as single crystal substrates. To control metal film growth on stepped metal oxide substrates it is necessary to understand the growth modes on the relevant atomically flat surfaces. We have studied Pt deposition on the non-polar SrTiO$_3$(100) surface and the polar SrTiO$_3$(111) surfaces using various experimental probes and ab initio Density Functional Theory. Our results identify the preferred binding geometries and film orientations of Pt films on these substrates. X-ray diffraction and low energy electron diffraction confirmed epitaxial growth of the Pt films, with the number of in-plane orientations dependent on both the substrate temperature and the nature of the substrate surface. We are currently extending our studies to the deposition of Pt on intrinsically chiral SrTiO$_3$ substrates and will discuss the prospects for creating robust chiral metal films with this process.

11:40am **SS1-MoM11 Novel Low-Temperature Reactivity of Model Bimetallic Surfaces with Monolayer Coverages**, ***N.A. Khan***, *J.G. Chen*, University of Delaware

Bimetallic surfaces have gained considerable interest in fundamental surface science research because of their unique catalytic activity and electronic properties. By studying these surfaces at an atomic level, we can gain more insight into the origin of these novel properties. In this study, we have used various surface science techniques (TPD, HREELS, NEXAFS, and XPS) to investigate the properties of model bimetallic surfaces. We have shown that the one monolayer Ni/Pt(111) surface exhibits novel chemical reactivity, unlike the pure Ni(111) or Pt(111) surfaces. Temperature-programmed desorption (TPD) results indicate that hydrogen has a lower binding energy to the 1 ML Ni/Pt(111) surface than on the other two surfaces.[1,2] In principle, a weak metal - hydrogen interaction should lead to an increase in the hydrogenation activity of other species on the surface. We have used other catalytically important probe molecules, such as cyclohexene and thiophene to further investigate this hydrogenation activity. XPS and NEXAFS also showed that the oxidation state and density of unoccupied states of one monolayer Ni/Pt(111) are similar to that of bulk Ni(111). In addition to studying the Ni/Pt(111) surface, we have also investigated the Ni/W(110) surface for comparison. On the Ni/W(110) surface, the probe molecules also undergo hydrogenation at a low temperature. However, the maximum activity occurs at about 0.4 ML Ni. At this coverage of Ni, Schmidthals, et. al. have found a large amount of surface strain.[3] We will attempt to correlate this lattice mismatch to a novel chemical reactivity seen on the 0.4 ML Ni/W(110) surface.

[1] H.H. Hwu, J. Eng Jr., J.G. Chen, J. Am. Chem. Soc. 124 (2002) 702.

[2] N.A. Khan, H.H. Hwu, J.G. Chen, J. Catal. 205 (2002) 259.

[3] C. Schmidthals, et. al. Surf. Sci. 402-404 (1998) 636.

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