Surface Science
Room 210 - Session SS3-TuA
Water/Surface Interactions

Moderator: E.M. Stuve, University of Washington

2:00pm **SS3-TuA1 Alumina-Water Interactions from First Principles***, **K.C. Hass**, W.F. Schneider, C.M. Wolverton,* Ford Motor Company **INVITED**

The chemical formula for aluminas is often written explicitly as Al@sub 2@O@sub 3@@sup .@nH@sub 2@O to emphasize the key role that water plays in this important class of materials. To date, there is little microscopic understanding of this role, despite its clear relevance to fields ranging from catalysis, corrosion, and adhesion to geology, microelectronics, and atmospheric chemistry. This talk will summarize recent progress on two aspects of this problem: (1) the hydroxylation of @alpha@-Al@sub 2@O@sub 3@ (0001)@footnote 1@, and (2) the bulk structure and phase stability of @gamma@- and other transitional aluminas that are produced by the dehydration of boehmite (@gamma@-AlOOH). Both studies are based on accurate planewave pseudopotential, density functional theory methods. Comparisons to related recent work and future prospects and challenges will also be discussed. @FootnoteText@ @footnote 1@ K. C. Hass, W. F. Schneider, A. Curioni, and W. Andreoni, Science 282 (1998) 265, and to appear in J. Phys. Chem. (2000).

2:40pm **SS3-TuA3 The Effect of Boron on Water Dissociation and Surface Diffusion of Atomic Hydrogen on Single Crystal Ni@sub3@(Al, Ti) (110)***, **J. Wang**, Y.-W. Chung,* Northwestern University

Polycrystalline Ni@sub3@Al alloys are severely embrittled in a moist environment at room temperature. Ductility measurements showed that addition of boron suppresses this moisture-induced embrittlement. Previous results indicated that water dissociates on clean Ni@sub3@(Al, Ti) (100) and (110), resulting in hydrogen evolution at ~350 and 400 K respectively. To explore the effect of boron on water dissociation, we first dosed the surface of clean Ni@sub3@(Al, Ti) (110) with controlled amounts of boron, using a specially designed low-energy negative boron ion source, followed by low-temperature exposure to D@sub2@O. The interaction between water vapor and boron-modified Ni@sub3@(Al, Ti) (110) was investigated using temperature-programmed desorption, X-ray photoemission and Auger electron spectroscopy. Auger and X-ray photoemission studies on boron-modified Ni@sub3@(Al, Ti) (110) show that boron reacts with water to form hydroxyls at 130~190 K. Hydrogen desorption occurs at ~950 K from boron-modified Ni@sub3@(Al, Ti) (110), indicating strong B-H bonding. After water dosing at ~130 K, the surface diffusion coefficients of atomic hydrogen on clean and boron-modified Ni@sub3@(Al, Ti) (110) surfaces were measured at 270 K with electron stimulated desorption. The surface diffusion of atomic hydrogen on 0.05 monolayer boron-modified surface is about 10 times slower than that on clean boron-free surface. Therefore, the strong B-H bonding suppresses both hydrogen desorption and the surface diffusion of atomic hydrogen to the crack tip at room temperature. These results may explain the suppression of moisture-induced embrittlement of Ni@sub3@Al and related alloys by boron.

3:00pm **SS3-TuA4 Physicochemical Properties of Water and Ammonia Ice Thin Films***, **D.J. Safarik**, R.J. Meyer, C.T. Reeves, C.B. Mullins,* University of Texas at Austin

We have studied the physical and chemical properties of water and ammonia ice films utilizing surface science techniques. Ultrathin films of amorphous solid water (ASW) and crystalline ammonia ice were grown via supersonic molecular beam on an Ir(111) substrate and characterized with temperature programmed desorption (TPD) and low energy electron diffraction (LEED). Overlayers of ASW dramatically alter the desorption of ammonia, resulting in a TPD spectrum that is distinctly different than free ammonia desorption yet unlike the desorption of carbon tetrachloride through water overlayers (the "molecular volcano") as reported by Smith et al.@footnote 1@ Whereas uncovered ammonia multilayers desorb with zero order kinetics at approximately 100 K, covered films desorb in a sequence of one to three distinct and rapid bursts. The number of ammonia releases, the temperature at which they occur, and their intensity varies with the thickness of both the ASW and ammonia ice films. These phenomena cannot be completely explained by a diffusional model. The overlying water film desorbs with zero order kinetics at approximately 160 K, apparently unaffected by the ammonia discharge. However, TPD, isothermal desorption, and LEED experiments indicate that the ammonia underlayer accelerates the kinetics of ASW crystallization and reduces the volatility of the remaining solid water. @FootnoteText@ @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay. The Molecular Volcano: Abrupt CCl4 Desorption Driven by the Crystallization of Amorphous Solid Water. Phys. Rev. Lett. 79, 909-912 (1997).

3:20pm **SS3-TuA5 Water Ion Cluster Formation in High Electric Fields at and Near a Pt Emitter Tip***, **C.J. Rothfuss**, V.K. Medvedev, E.M. Stuve,* University of Washington

Water ion cluster formation in high electric fields has been characterized on a field cleaned Pt emitter tip over temperatures ranging from 110K to 300K. The ion clusters were mass resolved using either an ExB filter or time of flight mass spectroscopy, or imaged directly using Field Ion Microscopy (FIM). Experimental results explain the qualitative trends observed in previous studies of this nature. For H@super +@(H@sub 2@O)@sub n@ cluster formation, the onset potential was found to be dependent upon the value of n and is lower for large masses. This dependency follows from a consideration of the thermodynamics of dissociative ion formation and proton solvation by nearby water molecules. However, the formation of large clusters is entropically unfavorable at high temperatures for low concentrations of water molecules on the surface and dynamically unfavorable at low temperatures. As a result high local concentrations and surface mobility are needed for creation of large n clusters. This local concentration has been experimentally imaged on the surface using FIM, under conditions favoring large n cluster formation, but is absent in the direct field ionization of water (H@sub 2@O@super +@) in space near the surface. With increasing field, each successive (n-->n-1) cluster becomes energetically accessible and becomes the dominant species due to its kinetic advantage. Above the condensation point for water on Pt (~165K), the limiting factor for determining the maximum n in field adsorbed cluster formation is the surface residence time of the water. As temperature increases, the residence time decreases and the propensity for forming large n clusters diminishes. Activation energies for ion cluster desorption were found to be 0.85 eV, 0.76 eV and 0.55 eV for n=3, 4 and 5, respectively. Below the condensation point, surface diffusion limits the supply function for large cluster formation, so lower temperatures result in decreased ion signal for large n clusters.

3:40pm **SS3-TuA6 Interactions of Methanol with Water and Hydrogen in Electrolytic Adlayers on Pt(111)***, **D.S.W. Lim**, E.M. Stuve,* University of Washington

To model the interactions of methanol with water and hydrogen at electrolye/electrode interface, thermal desorption experiments of the co-adsorbed system were performed on Pt(111). In electrochemical environments, adsorption of methanol on Pt(111) is inhibited by chemisorbed hydrogen, and water competes with methanol for available Pt sites. In ultra-high vacuum, methanol desorbed from Pt(111) in a multilayer state B@sub m@ at 142 and a monolayer state A@sub m1@ at 180 K. However, when the surface was pre-adsorbed with hydrogen, the desorption temperature of the methanol monolayer state, A@sub m1@, was lowered by as much as 20 K. The reduction in desorption temperatures was attribited to weakened interactions between methanol and the surface due to chemisorbed hydrogen. When methanol was co-adsorbed with water, mutual displacement between the methanol monolayer and water bilayer occurred on the surface. Water molecules in direct contact with Pt(111) surface form bilayer structure that desorbs at 173 - 178 K. A realistic simulation of the electrolytic adlayers was to co-adsorb all three species: methanol, water and hydrogen on Pt(111). In a water-lean adlayer system, the methanol monolayer state was destabilized by chemisorbed hydrogen. However, with the introduction of a sufficient amount of water, methanol was re-stabilized and, the effects of hydrogen-induced destabilization were completely erased when excess water was added to the adlayer. Methanol behaved as if it was only interacting with water. The results of these experiments illustrate that there is a delicate balance of hydrogen-induced destabilization and water-promoted stabilization in the electrolytic adlayers on Pt(111), and behavior of methanol interactions with co-adsorbed hydrogen and water followed that observed in electrochemical environments.

4:00pm **SS3-TuA7 From Gases to Dust: Ice Chemistry in the Interstellar Environment***, **H.J. Fraser**,* University of Nottingham, UK, NL*; M.R.S. McCoustra,* University of Nottingham, UK*; D.A. Williams,* University College London, UK

It has become clear in the last decade that gas-phase reaction schemes cannot soley account for the variety and richness of chemistry in the Interstellar Medium (ISM). In such environments, gas-dust interactions play a key role. In dense molecular regions, H@sub 2@O is the most abundant ice: it is vital to understand the freeze out, reactivity and desorption processes of atomic and molecular species on such ice surfaces to fully evaluate the chemical evolution of the ISM. A novel surface science experiment has been constructed that simulates the harsh conditions in the ISM. Traditional surface science techniques such as TPD and RAIRS have been combined with a Quartz Crystal Microbalance sample stage, capable of operating below 10 K. The experiment is equipped to study several aspects of the gas-dust interaction that are central to astrophysics, measuring sticking probabilities and rates of desorption empirically and accurately, as well as identifying the nature of the surface bound states. We will present the first results from this experiment, characterising a number of thin molecular ice films prepared under a variety of conditions to reflect a range of substrate morphologies. We will report measurements of the interaction of simple molecular species with these H@sub 2@O ices, concentrating on the behaviour of such systems between 10 and 150 K. The implications of these results to the chemistry and astrophysics of the ISM will be mentioned.

4:20pm **SS3-TuA8 Diffusion of Organic Molecules in Ice Measured Using Laser Resonant Desorption Depth-Profiling***, **F.E. Livingston**, S.M. George,* University of Colorado

Knowledge of the diffusion of organic molecules in ice is important for understanding the history of the Earth's atmosphere preserved in ice cores. Molecular diffusion in ice is affected by chemical and physical properties such as hydrophilicity, size and geometry. To explore these properties, we have measured the diffusion rates of different organic molecules such as carboxylic acids and alcohols. Diffusion was measured using an infrared laser resonant desorption (LRD) technique to depth-profile into the ice. LRD was accomplished using a Q-switched Er:YAG laser that emits light at @lambda@=2.94 µm. The laser radiation is resonantly absorbed by the O-H stretching vibration of H@sub2@O molecules and thermalized to facilitate desorption in the surface region. We have employed LRD depth-profiling to study the diffusion kinetics of formic (HCOOH) and acetic (CH@sub3@COOH) acid. LRD analysis revealed that acetic acid diffuses ~3 times faster than formic acid. The diffusion coefficients for formic acid vary from D~2 x10@super-13@ cm@super2@/s at T=175 K to D~2x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded a diffusion activation energy of E@subA@~24 kcal/mol and a diffusion preexponential D@subo@~4x10@super16@ cm@super2@/s. For acetic acid, the measured diffusion coefficients range from D~7x10@super-13@ cm@super2@/s at T=170 K to D~7x10@super-10@ cm@super2@/s at T=195 K. Arrhenius analysis yielded diffusion kinetic parameters of E@subA@~18 kcal/mol and D@subo@~1x10@super11@ cm@super2@/s. The faster diffusion for acetic acid argues that the lower hydrophilicity and larger size of acetic acid does not reduce its diffusion relative to formic acid.

4:40pm **SS3-TuA9 Can Clustering Lower the Barrier to Dissociation of Water on Nickel Surfaces?***, L. Mao, **K. Griffiths**, P.R. Norton,* University of Western Ontario, Canada

The interaction of water with Ni(110) surface has been extensively explored in this group due to its fundamental and practical importance in the fields of heterogeneous catalysis, electrochemistry as well as corrosion. At temperatures ï€¤ 400K, water molecules react rapidly with Ni(110) producing adsorbed O and H2(g). Reaction probabilities can reach as high as 0.24 and our studies indicate that the reaction mechanism involves single water molecules. Dissociation of water can also occur at low temperatures (ï€£220K) provided that we begin with an adsorbed chemisorbed layer. The activation energy for the dissociation reaction is believed to be lowered by some means which involves a cluster of at least two water molecules. The exact mechanism is still speculative at this stage. Between these two temperatures, the Ni surface appears to be inert towards the dissociation of water. Under normal UHV dosing conditions, the surface is sufficiently hot to prevent an appreciable dynamic coverage of dimers. At the same time, the activation energy barrier for the unimolecular , high temperature mechanism cannot be overcome. The aim of this study is to investigate the reaction between water and Ni(110) in this >inert= temperature regime. In this study, we have produced locally relatively high pressures at the surface using a capillary doser to demonstrate that there is a non-linear dependence of reaction rate on dosing pressure. The absolute number of impinged water molecules as well as the instantaneous coverage of water (governed by the dosing pressure) determines the extent of reaction.

5:00pm **SS3-TuA10 Surface and Near Surface Reactions in Aqueous Solution Exposed Na@sub 2@O-Al@sub 2@O@sub3@-SiO@sub 2@ Glasses***, **V. Shutthanandan**, S. Thevuthasan, D.R. Baer, J.P. Icenhower, M.H. Engelhard, B.P. McGrail,* Pacific Northwest National Laboratory

Glass and ceramic waste forms are proposed for the stabilization and immobilization of nuclear wastes. Recent findings show that Na ion exchange reaction control the release of radionuclides from the glass matrix. As part of understanding the processes leading to sodium release and ion exchange, the surface and near surface reaction regions on several specimens of Na@sub 2@O-Al@sub 2@O@sub 3@-SiO@sub 2@ glasses with fixed Na@sub 2@O and variable Al@sub 2@O@sub 3@ (10 mole % and 15 mole %) concentrations have been examined after exposures to isotopicaly labeled aqueous D@sub 2@@super 18@O solutions. The sodium removal and the deuterium and oxygen uptake in the glass samples were measured using Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) and nuclear reaction analysis (NRA). The results show that the Na exchange rate is much higher than the matrix dissolution rate. Although the sodium concentration is decreased in the near surface region, it is not totally removed from the outer surface. In this same region, there is also a significant amount of @super 18@O incorporated demonstrating considerable interaction between the water and the glass. On the basis of the depth distributions of Na, D and @super 18@O, different regions including reaction, transition and diffusion zones were identified in both samples. The glass samples with higher amounts of Al content have a significantly narrower reaction zone than the low Al materials.

Author Index

Bold page numbers indicate presenter