

Friday Morning, October 24, 2008

Surface Science

Room: 207 - Session SS+AS+NC-FrM

Environmental Surfaces and Water Interaction with Oxide Surfaces

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS+AS+NC-FrM1 Heterogeneous Reactivity of O₃ and OH Radical with Potassium Iodide**, *M.A. Brown, T.M. McIntire, M.J. Krisch*, University of California, Irvine, *V. Johánek*, University of Virginia, *P.D. Ashby, Z. Liu*, Lawrence Berkeley National Laboratory, *A. Mehta*, Stanford Linear Accelerator Center, *D.F. Ogeltree, M. Salmeron*, Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California, Irvine

Sea salt aerosols are known to undergo heterogeneous reactions with atmospheric oxidants, resulting in halide depletion as they travel through polluted regions of the environment. The subsequent photochemistry of halide compounds (including halogenated oxides) strongly influences the chemical composition of the atmosphere. The results from uptake measurements of O₃ and OH radical on potassium iodide will be discussed. The reactivity of KI with O₃ and OH radical are remarkably different and result in reaction products of KIO₃ and KOH, respectively. We describe results from X-ray photoemission spectroscopy, X-ray diffraction, Atomic Force Microscopy and IR spectroscopy. In the case of O₃, under conditions in which the KI surface is devoid of adsorbed water molecules the reaction is self-passivating, and results in a thin layer of KIO₃ with an rms roughness of 3.6 nm. Subsequent exposure to water vapor mobilizes the KIO₃ oxide layer, revealing additional KI substrate that is readily available for further oxidation. As such, under conditions of low relative humidity the uptake of O₃ onto KI is not expected to be self-passivating. Under similar conditions, the reaction of OH radical with KI results in halide vacancies (iodide is released into the gas phase) created in the outermost surface lattice sites. The iodide vacancies are filled with OH- to generate a layer of KOH that is self-passivating following prolonged exposures. There is no spectroscopic evidence of stable oxidized iodide reaction products. AFM and IR results will also be discussed.

8:40am **SS+AS+NC-FrM2 Reactivity of Fe⁰ Atoms, Clusters and Nanoparticles with CCl₄ Multilayers on FeO(111)**, *G.S. Parkinson, Z. Dohnálek, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

There is currently much interest in the development of Fe⁰ nanoparticles as an agent for the destruction of chlorinated hydrocarbons in environmental remediation applications. However, the fundamental reaction pathways for the interaction of nano-Fe⁰ with such target molecules is unknown, and this presents a major obstacle to the design of improved particles. Our work utilizes a novel "atom dropping" technique where Fe⁰ atoms, clusters and nanoparticles are deposited into CCl₄ multilayers on FeO(111) at 30 K in ultra-high vacuum. A series of temperature programmed desorption and X-ray photoelectron spectroscopy experiments will be described which demonstrate an interesting size effect whereby isolated atoms and small clusters exhibit markedly different reactivity and product branching ratio to nanoparticles. The results will be discussed in the context of relevant theoretical calculations and the reaction pathways identified. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

9:00am **SS+AS+NC-FrM3 New Paradigms for Environmental Surfaces: Structure and Reductive Transformation at α -Fe₂O₃/Water Interfaces**, *K.M. Rosso, S.V. Yanina, S. Kerisit*, Pacific Northwest National Laboratory

INVITED

The semiconducting properties of a wide range of minerals are often overlooked in the study of their interfacial chemical behavior. As a case study, reductive transformation of α -Fe₂O₃ (hematite) in aqueous solutions is a central part of the natural iron cycle in the environment. The transformation involves reduction of surface Fe(III) to Fe(II) by electron transfer, followed by Fe(II) solubilization and precipitation of new phases. It is a long-held perception that locations of Fe(III) reduction at the interface with aqueous solution correspond directly to sites of Fe(II) release. However, hematite is a semiconductor with a propensity for moderate electron diffusivity in the surface and bulk. Hematite surfaces are also reactive with water and ions leading to surface charging behavior that is closely dependent on the crystallographic termination. Our recent focus has been on understanding how these qualities create unique conditions for the

interfacial electron transfer involved in reductive transformation. We show using atomic force microscopy and surface-specific potentiometry evidence that these qualities couple interfacial electron transfer reactions at hematite (001) surfaces with those occurring at crystallographic edge terminations such as (012) via current flow through the crystal bulk. At low pH, divergent charging behavior between (001) and (012) surfaces yield a surface potential bias across the crystal of several hundred millivolts capable of biasing diffusion of charge carriers. We examined this aspect in detail with atomistic simulations of electron diffusion in bulk hematite and at (001) and (012) surfaces using a small polaron hopping model. The model supports the experimentally evident reductive transformation process of net oxidative adsorption of Fe(II) at (001) surfaces coupled by bulk charge transport to net internal reductive dissolution of Fe(III) at edge surfaces. This new paradigm for hematite reductive transformation has important implications for our understanding of the natural iron cycle in the environment. More generally, the apparent importance of chemically induced bulk crystal conduction is likely to be generalizable to a host of naturally abundant semiconducting minerals playing varied key roles in soils, sediments, and the atmosphere.

9:40am **SS+AS+NC-FrM5 Molecular Beam Studies of Supercooled Mixtures of Methanol and Water**, *J. Matthiesen, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Molecular beams, temperature programmed desorption, and infrared spectroscopy were used to study the diffusive intermixing of amorphous water and methanol nanoscale films. Composite films with initially separated layers were created by sequential dosing at 25 K in UHV. The films were then heated and the extent of intermixing was determined by the onset of desorption of the underlayer species and changes in the infrared spectra. Both linear ramp and isothermal experiments were conducted. In a series of experiments the layer thickness, film composition, and heating rate were varied to extract quantitative temperature dependent diffusivities. Isotopically labeled methanol was used to mimic tracer-type experiments. These results compare favorably to the results obtained from separated layer experiments. Numerical simulations of the diffusive intermixing were used to quantitatively model the experimental results. The details of the experiment and the interpretation of the results will be discussed in detail. The research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

10:00am **SS+AS+NC-FrM6 DFT Study of Water Adsorption on SrTiO₃ (001) Bulk Termination and 2x1 Reconstruction**, *A.E. Becerra-Toledo, L.D. Marks*, Northwestern University

Strontium titanate, SrTiO₃, has been studied extensively as a model perovskite system. Among other advances, its variety of cation oxidation states has provided critical insights into oxide surface reaction mechanisms. Understanding the reaction of ubiquitous water molecules with SrTiO₃ surfaces is of great importance to environmental science and catalysis. Density functional theory (DFT) calculations were performed to study the adsorption of water molecules on two different SrTiO₃ (001) surfaces. A repeated slab model was employed to study both a bulk-like TiO₂ surface termination and a 2x1 surface reconstruction. While similar studies have been carried out in the past, our treatment using a full-electron potential and a linear augmented plane wave plus local orbital (LAPW+lo) basis more accurately models the spatial character of single-particle wavefunctions. Two different exchange-correlation functionals were employed: the PBE¹ generalized gradient approximation (GGA) and the TPSS² meta-GGA. On the TiO₂-terminated surface, both molecular and dissociative adsorption of water were modeled. The results did not show a significant dependence on the choice of exchange-correlation functional. Most importantly, the adsorption energies for molecular and dissociative adsorption were more similar than has been previously reported,³ and therefore favor the coexistence of hydroxyl groups and molecular water on the surface. On the 2x1 surface reconstruction, which was solved by Erdman et al.⁴ and is typically formed under oxidizing conditions, dissociative adsorption was studied with several distinct stable structures considered. The most stable of these showed an adsorption energy (per H₂O molecule) much larger than that observed for the bulk TiO₂ termination. In all cases we observe the effect of hydrogen bonding between adsorbate and surface anions on the stabilization of the structures.

¹ Perdew, J.P. et al. Phys.Rev.Lett. 77, 3865 (1996).

² Tao, J. et al. Phys.Rev.Lett. 91, 146401 (2003).

³ Evarestov, R.A. et al. Surf.Sci. 601, 1844 (2007).

⁴ Erdman, N. et al. Nature 419, 55 (2002).

10:20am **SS+AS+NC-FrM7 Unraveling a Reaction on an Oxide Surface Step by Step: Formation of Water from Oxygen through Successive H Transfer Reactions on TiO₂(110).** *F. Besenbacher, J. Matthiesen, S. Wendt, J.Ø. Hansen, E. Laegsgaard, B. Hammer*, University of Aarhus, Denmark

By means of high-resolution scanning tunneling microscopy (STM) measurements and density functional theory (DFT) calculations we studied the reaction between O₂ and H adatoms on reduced rutile TiO₂(110). We identified chemisorbed OH₂O species as the initial intermediate that is produced by H transfer reactions to O₂ molecules, which concomitantly dissociate. Through further successive H transfer reactions, mediated by co-adsorbed water, the OH₂O species are finally transformed into water dimers. Our data exemplify how time-lapsed STM imaging, in combination with DFT calculations, can be successfully used to unravel reactions on surfaces with a high number of intermediates.

10:40am **SS+AS+NC-FrM8 Water Dissociation on Single Crystalline Anatase TiO₂(001) Studied by Core Level Photoelectron Spectroscopy.** *A. Sandell*, Uppsala University, Sweden, *J. Blomquist*, Lund University, Sweden, *L.E. Walle*, NTNU, Norway, *P. Uvdal*, Lund University, Sweden, *A. Borg*, NTNU, Norway

The interaction of water and TiO₂ surfaces has been intensely studied since the discovery of photoinduced splitting of water into hydrogen and oxygen on a rutile TiO₂ single crystal in 1972.¹ However, even though the anatase TiO₂ polymorph is more widely used as photocatalyst than rutile studies of the adsorption of water on well-defined anatase TiO₂ surfaces are scarce. So far, the efforts have mainly been theoretical. Based on calculations it has been proposed that molecular water adsorption is favored on the (101) surface, whereas water dissociation is favored on the (001) surface.^{2,3} This implies that the (001) surface may be very important in spite of it being the minority surface termination of anatase crystallites. In this contribution, we present the first study on the coverage dependent adsorption of water on the anatase TiO₂(001)-(4x1) surface using core level photoemission spectroscopy. Data with high surface sensitivity were recorded at the MAX-lab synchrotron radiation source. Two types of anatase TiO₂(001)-(4x1) surfaces were prepared: One by MOCVD growth on a lattice matched substrate [SrTiO₃(001)] and one by cleaning of a natural single crystal. Our results confirm that water dissociate on the anatase TiO₂(001)-(4x1) surface. We can define two adsorption phases: Phase 1 consists only of dissociated water, observed as OH-groups. This phase is found at low coverage at low temperature (190 K) and is the only state of adsorbed water above ~230 K. The saturation coverage of phase 1 agrees with the number of four-fold coordinated Ti ridge atoms of the (4x1) surface reconstruction. Phase 2 is found at higher coverage, reached at low temperature. It consists of a mixture of dissociated and molecular water with a ratio of 1:1 at 170 K. The hydroxyl coverage of phase 2 is approximately two times that of phase 1.

¹ A. Fujishima and K. Honda, *Nature (London)* 238, 37 (1972).

² A. Vittadini, A. Selloni, F. P. Rotzinger, and M. Grätzel, *Phys. Rev. Lett.* 81, 2954 (1998).

³ X.-Q. Gong and A. Selloni, *J. Phys. Chem. B* 109, 19560 (2005).

11:00am **SS+AS+NC-FrM9 Study of the Oxidation of Titanium and the Adsorption of Biomolecules on Titanium by Means of Electrochemical Quartz Crystal Microbalance with Dissipation Supported by X-ray Photoelectron Spectroscopy.** *I. Van De Keere*, Vrije Univ. Brussel, Belgium, *S. Svedhem*, *A. Kunze*, Chalmers Univ. of Tech., Sweden, *J. Vereecken*, Vrije Univ. Brussel, Belgium, *B. Kasemo*, Chalmers Univ. of Tech., Sweden, *A. Hubin*, Vrije Univ. Brussel, Belgium

Titanium is frequently used as a biomaterial in orthopaedics and cardiovascular devices. The metal is covered with a native oxide layer of a few nm, which contributes to the high biocompatibility of Ti implants. One of the surface properties of a biomaterial, which plays an important role in the interaction with biomolecules is electrostatic interaction at the surface. By varying the potential of Ti, the surface charge of Ti changes, and electrostatic interactions are likely to be influenced. The goal of the present study is to investigate the influence of an electric field on the adsorption of biomolecules, such as proteins and lipids, onto Ti surfaces and their conformational changes with electrochemical quartz crystal microbalance with dissipation (ECQCMD). QCMD is a well-established technique for monitoring mass and film thickness (through the frequency shift) and to obtain information about the viscoelastic properties of the adsorbed layers (through the dissipation shift). It has recently become possible to carry out combined QCMD and electrochemical measurements using a specially designed flow cell. This combination is valuable for adsorption studies under the influence of external fields and/or where one wants to in situ change the oxide layer thickness. A difficulty arises upon using Ti compared to other model substrates as gold since the surface of Ti is always covered with a native oxide layer, which may grow upon application of an external potential to the Ti surface. Firstly, the oxidation of Ti in buffer under the influence of an electric field was investigated, because a stable oxide layer was desired before investigating the interaction of biomolecules

with Ti under applied external potential. With ECQCMD, quantitative information on the growth behaviour and the thickness of the Ti oxide layer was obtained. The calculated thickness from ECQCMD was correlated with the depth profiles obtained from X-ray Photoelectron Spectroscopy (XPS). Secondly, the adsorption of biomolecules on Ti was studied. The influence of an external potential applied to the Ti-surface on the formation of supported lipid bilayers of DOEPC (positively charged phospholipid) is pronounced. The moment of vesicle rupture, which precedes the formation of bilayers, is delayed significantly upon application of a potential of 0 V vs SHE, compared to open circuit potential and 0.6 V vs SHE. For these two potentials, the rupture of vesicles occurs faster and at the same moment.

11:20am **SS+AS+NC-FrM10 Acidic Dissolution Mechanism, pH-dependent Stabilization and Adhesion of Single Molecules on Single Crystalline ZnO(0001)-Zn Model Surfaces Studied by in-situ AFM and DFT Simulations.** *M. Valtiner*, Max-Planck-Institut für Eisenforschung, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry at oxide/water interfaces is a key issue in adhesion science and related areas such as corrosion science. De-adhesion processes as well as corrosion processes are often accompanied by a change of the pH at the interface. Hence an atomistic understanding of oxide dissolution promoting effects of H⁺, OH⁻ and anions, as chlorides or sulfates, are an important aspect of de-/adhesion, metal corrosion and its inhibition. In this context, experimental results on single crystalline ZnO(0001)-Zn model surfaces and DFT-based ab-initio studies will be discussed. First, it will be shown that single crystalline ZnO(0001)-Zn model surfaces can be prepared easily and surprisingly clean under ambient conditions by introducing hydroxide stabilization via a wet chemical etching step. The prepared model surfaces will be discussed by AFM, LEED, angle resolved XPS, ToF-SIMS and Auger spectroscopy data.¹ Secondly, the stability of these ZnO(0001)-Zn surfaces in electrolyte solutions will be demonstrated by a combined approach of in-situ AFM imaging and ex-situ LEED investigations. It will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline in aqueous solutions within a wide pH range due to hydroxide stabilization. An in-situ AFM study of the acidic dissolution allowed an imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported.² Moreover, Single Molecule Adhesion studies - by means of single molecule desorption of polyelectrolyte molecules - on these surfaces at variation of the pH level will be presented. Finally, the potential of a synergistic combination of these approaches with ab-initio based simulation methods will be highlighted.

¹M. Valtiner, S. Borodin, G. Grundmeier, *Physical Chemistry Chemical Physics*, 9(19), (2007) 2406-2412.

²M. Valtiner, S. Borodin, G. Grundmeier; *Langmuir* (2008), ASAP Article: 10.1021/la7037697.

11:40am **SS+AS+NC-FrM11 The Adsorption of Water on a PdO(101) Thin Film on Pd(111).** *H.H. Kan*, *R.J. Colmyer*, *J.F. Weaver*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of hydrocarbons and CO under oxygen-rich conditions. Unfortunately, however, many fundamental questions about the surface chemistry of PdO have remained unanswered since it has been challenging to prepare well-defined PdO surfaces for detailed experimental investigations. In this talk, I will discuss our recent experimental study of the adsorption of water on a PdO(101) thin film that was grown in ultrahigh vacuum by oxidizing Pd(111) using an oxygen atom beam. From temperature programmed desorption (TPD) measurements, we find that water can populate several adsorbed states on PdO(101). Physisorbed water molecules populate both monolayer and multilayer states on PdO(101), with desorption from these states yielding TPD peaks at 150 and 197 K, respectively. The desorption temperature from the physisorbed monolayer is about 35 K higher for PdO(101) compared with Pd(111), which suggests that hydrogen-bonding enhances the physisorption bond strength on the oxide. We also observe a relatively broad desorption feature of water from PdO(101) that appears to consist of two components centered at 320 K and 350 K. We present evidence that these components arise from distinct states of molecularly and dissociatively chemisorbed water, respectively, and that both forms of chemisorbed water bind to coordinatively unsaturated Pd cations that are prevalent on the PdO(101) surface. Finally, although the dissociative chemisorption of water presumably involves hydrogen transfer to an oxygen anion of the oxide, we observe only small amounts of oxygen exchange between water and the oxide in experiments with oxygen-labeled water. This finding suggests that water dissociation produces inequivalent hydroxyl groups on PdO(101).

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