### Monday Morning, October 25, 1999

### Surface Science Division Room 606 - Session SS1+EM-MoM

#### **Chemistry on Oxides**

Moderator: S.A. Joyce, Pacific Northwest Laboratory

#### 8:20am SS1+EM-MoM1 The Reactions of Maleic Anhydride Over TiO@sub 2@ (001) Single Crystal Surfaces, J.N. Wilson, D.J. Titheridge, H. Idriss, The University of Auckland, New Zealand

The reactions of maleic anhydride have been investigated on the stoichiometric and substoichiometric surfaces of TiO@sub 2@ by Temperature Programmed Desorption (TPD) and Scanning Kinetic Spectroscopy (SKS). SKS technique, showing complementary information to TPD, has been successfully applied to investigate the chemical pathways on this oxide material for the first time. Results from the maleic anhydride TPD and SKS show the desorption of a wide variety of products in several temperature domains. In addition to the decomposition pathway to CO, CO@sub 2@, acetylene, and ethylene, the desorption of coupling reaction products of two molecules of acetylene to vinylacetylene (m/e 52) and of three molecules of acetylene to benzene (m/e 78) is observed. Moreover, the potential desorption of both ends of the molecule, is discussed. The coupling pathways of the reactions of maleic anhydride on the substoichiometric surface were more accentuated.

## 8:40am SS1+EM-MoM2 S Adsorption on TiO@sub 2@(110) Studied with STM, XPS and LEED, *E.L.D. Hebenstreit*, *W. Hebenstreit*, *U. Diebold*, Tulane University

TiO@sub 2@ surfaces are well-known for their catalytic properties. Since sulfur is known as a catalyst inhibitor, its adsorption behavior on TiO@sub 2@ single crystal surfaces are of great interest. Measurements with a scanning tunneling microscope reveal the existence of two different adsorption sites, depending on the sample temperature during adsorption. Adsorption at room temperature leads to very mobile sulfur atoms sitting on titanium sites of TiO@sub 2@(110). Adsorption at 300°C causes the formation of more stable sulfur chains running along the [1-10] direction with an ordered (3x1) structure at saturation. In the latter case the sulfur atoms are located at the positions of oxygen surface atoms. X-ray-photoelectron-spectroscopy confirms the existence of two chemically different S species.

9:00am SS1+EM-MoM3 Spectroscopic Studies of Sorption Processes at Metal Oxide-Aqueous Solutions Interfaces, G.E. Brown, Jr., T. Kendelewicz, Stanford U.; P. Liu, LBNL; J.R. Bargar, Stanford Synchrotron Radiation Lab.; J.P. Fitts, A.L. Foster, J.D. Ostergren, G.A. Parks, A.H. Templeton, Stanford U.; H.A. Thompson, LANL; S.N. Towle, Intel Corp.; T.P. Trainor, Stanford U.; P. Eng, S. Sutton, Adv. Photon Source INVITED Chemical interactions at metal oxide-aqueous solution interfaces are of great significance in atmospheric and environmental chemistry. They help control many important processes including dissolution and crystal growth of natural solids and the sorption a nd desorption of aqueous metal ions, which can sequester or release heavy metal contaminants in atmospheric and aquatic environments. Metal oxide-water interfaces in natural systems

are extremely complex when viewed at the molecular level because of the many variable that must be accounted for and the difficulty in observing the products of interfacial reactions under in-situ conditions (i.e., with bulk water present). To make this problem more tractable, we have employed a reductionist approach in which interfacial reaction products are examined in simplified model systems under carefully controlled conditions using a combination of classical surface chemistry methods, synchrotron radiationbased surface science methods, and other spectroscopic and scanning force microscopy methods. The resulting information at macroscopic and atomic/molecular scales allows sorption behavior to be correlated with chemical species information, including the structure, composition, and mode of sorption of adsorbates, and, in selected cases, the types of reactive sites on adsorbent surfaces and the effect of aging time. In parallel model system studies, we have also examined the effects of common inorganic ligands, organic ligands, and biofilms on the sorption of metal ions at mineral-water interfaces, and we have used the results as a basis for studies of As and Pb speciation in contaminated soils and mine tailings. These studies have revealed the structure and composition of adsorbates, and for single-crystal adsorbents, have allowed us to place constraints on the stoichiometry of sorption reactions, including the types of reactive sites

to which the adsorbate binds. Selected examples of these studies will be presented.

# 9:40am SS1+EM-MoM5 Reactions of SeF@sub6@ with Iron and Iron Oxides, S.R. Qiu<sup>1</sup>, H.-F. Lai, H.T. Than, C. Amrhein, J.A. Yarmoff, University of California, Riverside

Concentrated levels of selenium in the groundwater of the western US have been found to cause the death and birth-deformation of wildlife. Zero valent iron has been used to immobilize many soluble toxic groundwater contaminants, including selenate (Se@super6+@), by a surface redox reaction in which aqueous contaminants are reduced to less mobile forms. Only limited success has been achieved in the field, however, as the understanding of the reaction mechanism at the liquid/solid interface is incomplete. In this work, the remediation process is modeled by the reaction of SeF@sub6@ with iron and iron oxide surfaces in ultra-high vacuum. Se in SeF@sub6@ is in the same oxidation state as in selenate, and a similar reduction is observed upon reaction with Fe. X-ray photoelectron spectroscopy (XPS) spectra collected following the exposure of a sputter-cleaned Fe foil to SeF@sub6@ show both Se and F on the surface. The Se is found to be directly bonded to Fe, with no bonds to F remaining, indicative of the complete dissociation of SeF@sub6@. The Fto-Se ratio is close to 6 to 1, showing that all of the products remain on the surface. The Fe 2p spectra show the formation of FeF@sub2@ as the major surface species formed. These results suggest that there is a high activation barrier to adsorption, but that once it occurs, the excess energy liberated by the exothermic reaction promotes complete dissociation. To ascertain the role of oxygen, SeF@sub6@ was exposed to both partially and fully oxidized Fe surfaces. Oxygen was found, in all cases, to inhibit the reaction. We are currently investigating this reaction employing clean and oxygen pre-covered single crystal Fe surfaces. Both XPS and scanning tunneling microscopy are being used to understand the chemical reaction mechanism and to ascertain the adsorption sites. The implications of our results on practical remediation methods will be discussed.

# 10:00am SS1+EM-MoM6 Interactions of HCOOH with Stoichiometric and Defective SrTiO@sub 3@(100) Surfaces, L. Wang, F. Ferris, H. Engelhardt, Pacific Northwest National Laboratories

Interactions of HCOOH with stoichiometric (nearly defect-free) and defective SrTiO@sub 3@(100) surfaces have been studied using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and electronic structure calculations. Two reaction pathways were observed for formaldehyde formation from formic acid on SrTiO@sub 3@(100) surfaces. On stoichiometric surfaces, formaldehyde was produced through bimolecular coupling of two formates. However, on Ar+ sputtered surfaces, formaldehyde formation involves the reduction of surface formate by the oxidation of reduced Ti cations. XPS results show that surface defects on sputtered SrTiO@sub 3@(100) surfaces were reoxidized significantly upon exposure to 30 L HCOOH at 300 K, in contrast to defects on sputtered TiO@sub 2@(110) surfaces where no reduction in defect intensity was observed under the same condition. The fact that surface formate was reduced at 300 K on SrTiO@sub 3@(100) is clearly evident in TPD data where the desorption peak of formaldehyde is shifted to a lower temperature and broadened significantly down to 300 K for Ar+ sputtered SrTiO@sub 3@(100) surfaces as compared with stoichiometric surfaces. Electronic structure calculations have been used to investigate the adsorptive interactions for formate and formaldehyde on the cation sites of both stoichiometric and defective SrTiO@sub 3@(100) surfaces. The results for formate indicate a strong adsorptive interaction consistent with the experimental observations, with significant charge redistribution. Further results will be discussed in terms of potential reaction mechanisms.

10:20am SS1+EM-MoM7 The Structure of the CeO@sub 2@(001) Surface and its Reactions with D@sub 2@O, G.S. Herman, Pacific Northwest National Laboratory; Y.-J. Kim, Taejon National University of Technology, Korea; S.A. Chambers, C.H.F. Peden, Pacific Northwest National Laboratory Angle-resolved mass-spectroscopy of recoiled ions (AR-MSRI) has been used to determine the surface structure of CeO@sub 2@(001). The results indicate that the surface is terminated with 0.5 monolayers of oxygen which gives rise to a zero dipole moment and, thus, a stable surface. The interaction of D@sub 2@O with the CeO@sub 2@(001) surface was studied with temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). It was found with TPD that D@sub 2@O desorption occurs in three states with temperatures of 152, 200, and 275 K which are defined as multilayer D@sub 2@O, weakly bound surface D@sub

1

### Monday Morning, October 25, 1999

2@O, and hydroxyl recombination, respectively. O 1s XPS measurements for high D@sub 2@O exposures, where multilayer water desorption was observed in the TPD, resulted in emission from only the substrate and surface hydroxyls. This is likely due to a non-wetting behavior of D@sub 2@O on this surface with the formation of nanosized clusters. An analysis of the O1s XPS data indicates that the surface has a hydroxyl coverage of 0.9 monolayers for large water exposures at 85 K. This is consistent with a model in which the polar CeO@sub 2@(001) surface can be stabilized by a reduction of the dipole in the top layer by the formation of full monolayer of hydroxyls. @FootnoteText@ Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

10:40am SS1+EM-MoM8 The Correlation Between MgO (100) Surface Morphology and Chemical Reactivity, S.S. Perry, University of Houston, US; S. Imaduddin, O. El-bjeirami, P.B. Merrill, S.M. Lee, H.I. Kim, University of Houston

A critical ingredient of any surface science study is the preparation of the surface so as to present a uniform and homogeneous distribution of surface sites. For metals, the nature of adsorption site is determined by the crystal face exposed and the local coordination of the different metal atoms at the surface. For compound semiconductors and oxide based materials, the situation can be much more complex as the crystal face and coordination now applies to more than one type of element. The preparation of such materials can be further complicated by the possibility of preferential sputtering of one component of the surface. In this study we have used a combination of microscopy, ex-situ processing, ultrahigh vacuum (UHV) processing and UHV surface analysis to correlate the chemical reactivity of a model metal oxide (MgO) with the nature of surface structure and morphology. Atomic force microscopy, low energy electron diffraction, and reflection high energy electron diffraction studies together have allowed the distinction between amorphous and crystalline surfaces as well as the length scale of surface order. Single crystal MgO(100) surfaces have been prepared by a number of procedures including acid etching, high temperature annealing in ambient pressures of oxygen, UHV annealing, and ion bombardment. The compositional changes of the surface region with respect to these procedures have been followed with X-ray photoelectron spectroscopy. Finally, the chemical reactivity of the MgO(100) surface has been studied using temperature programmed desorption, investigating the desorption properties of water, methanol and carbon monoxide. Together, these studies have generated a complete picture of the relationship between microscopic surface morphology and chemical reactivity for this model metal oxide surface and have highlighted several critical aspects involved in the preparation of single crystal metal oxide surfaces for UHV surface science studies.

## 11:00am SS1+EM-MoM9 Photoconversion of Adsorbed Oxygen States On TiO@sub 2@(110), C.L. Perkins, M.A. Henderson, Pacific Northwest National Laboratory

By means of postirradiation temperature programmed desorption we have investigated further the states of oxygen adsorbed on rutile TiO@sub 2@. Previous work has shown that annealing the (110) surface in vacuum produces isolated bridging oxygen vacancies, and that these vacancies are intimately connected with molecular and dissociative oxygen adsorption channels. We find that at 120 K illumination of the oxygen exposed surface with photons having energies above the band gap (>3.6 eV) results in depletion of the molecular oxygen state observed at 410 K in TPD, in contrast to the remaining oxygen destined for the dissociative channel. An unusual effect of water overlayers on the O/TiO@sub 2@(110) system is explored. For thick overlayers (> 2 ML), it is possible to generate via UV irradiation a previously unobserved oxygen TPD state. Cross sections for the photoconversion of oxygen into this state are measured, and specific mechanisms for the process are proposed.

## 11:20am SS1+EM-MoM10 Reactions of Acetic Acid, Acetaldehyde and Ethanol on the (111) Surface of Uranium Dioxide Single Crystal, S.V. Chong, H. Idriss, The University of Auckland, New Zealand

The reactions of three C2 molecules having different functional group and polarity, have been investigated on the (111) surface of uranium dioxide single crystal, which has been characterised by LEED and AES. The adsorption of acetic acid, the most polar among the three molecules, indicates a higher sticking probability on the oxygen terminated UO@sub 2@(111) surface, followed by ethanol then acetaldehyde. Temperature Programmed Desorption (TPD) for these molecules displays a rich chemistry. Acetic acid-TPD on a stoichiometric surface yields ketene

(dehydration) as the main product, plus acetaldehyde (reduction) as the minor product. While on an electron beam sputtered surface, two additional products were observed - butene and crotonaldehyde. In the case of acetaldehyde, both sputtered and non-sputtered surfaces yield benzene, with ketene as the additional product on the sputtered surface. The reactions of ethanol on a stoichiometric surface give acetaldehyde and ethylene as the only two products with "equal" amount. The comparison of this latter result with those of other metal oxide single crystals indicates a plausible relationship between the dehydrogenation/dehydration selectivity of primary alcohols and the Madelung potential of the cations. In summary, this investigation has shown the ability of UO@sub 2@(111) single crystal to oxidise, reduce, reductively couple, and trimerise organic molecules.

### 11:40am SS1+EM-MoM11 Surface Reactions on Cr-doped V@sub 2@O@sub 3@, D.S. Toledano, V.E. Henrich, Yale University

Transition-metal oxides are important as gas sensors due to chemisorptioninduced changes in surface conductivity. Conversely, changes in substrate electronic structure may alter surface chemisorption properties. While investigating the effect of metal-insulator transitions in Cr-doped V@sub 2@O@sub 3@ on adsorption, we have observed interesting effects involving surface reduction by CO, as well as differences in adsorption on metallic and insulating substrate phases. (Cr@sub 0.015@V@sub 0.985@)@sub 2@O@sub 3@ exhibits two metal-insulator transitions as a function of temperature; these experiments focus on the insulating phase of single-crystal Cr-V@sub 2@O@sub 3@ using UPS, XPS, LEED and AES. When insulating-phase Cr-V@sub 2@O@sub 3@ (0001) is exposed to CO at 273K, CO appears to adsorb dissociatively up to 10@super 3@ Langmuir. Higher exposures result in a C-containing species, and electron transfer to V cations at energies near E@sub F@; decreased occupation of nonbonding O orbitals is also observed. Heating to 470K desorbs this species, but the surface is further reduced after desorption, with increased charge transfer to V cations. Exposure of a CO-reduced surface to O@sub 2@ does not reoxidize the surface or restore the original electronic structure, but appears to result in adsorbed O@super -@ or (O@sub2@)@super -@ which does not re-enter the lattice unless annealed above 700K. CO adsorption on metallic-phase Cr-V@sub 2@O@sub 3@ differs from that on the insulating phase for intermediate exposures, exhibiting higher initial sticking coefficient and desorption temperature; however, the two phases behave similarly for high CO exposures. Adsorption of H@sub 2@O, SO@sub 2@ and O@sub 2@ on both substrate phases has also been studied. This work was partially funded by NSF grant CTS-96-10140

### **Author Index**

-A-Amrhein, C.: SS1+EM-MoM5, 1 — B — Bargar, J.R.: SS1+EM-MoM3, 1 Brown, Jr., G.E.: SS1+EM-MoM3, 1 - C -Chambers, S.A.: SS1+EM-MoM7, 1 Chong, S.V.: SS1+EM-MoM10, 2 — D — Diebold, U.: SS1+EM-MoM2, 1 — E — El-bjeirami, O.: SS1+EM-MoM8, 2 Eng, P.: SS1+EM-MoM3, 1 Engelhardt, H.: SS1+EM-MoM6, 1 — F — Ferris, F.: SS1+EM-MoM6, 1 Fitts, J.P.: SS1+EM-MoM3, 1 Foster, A.L.: SS1+EM-MoM3, 1 -H-Hebenstreit, E.L.D.: SS1+EM-MoM2, 1 Hebenstreit, W.: SS1+EM-MoM2, 1

### Bold page numbers indicate presenter

Henderson, M.A.: SS1+EM-MoM9, 2 Henrich, V.E.: SS1+EM-MoM11, 2 Herman, G.S.: SS1+EM-MoM7, 1 -1 - 1Idriss, H.: SS1+EM-MoM1, 1; SS1+EM-MoM10, **2** Imaduddin, S.: SS1+EM-MoM8, 2 -K -Kendelewicz, T.: SS1+EM-MoM3, 1 Kim, H.I.: SS1+EM-MoM8, 2 Kim, Y.-J.: SS1+EM-MoM7, 1 - L --Lai, H.-F.: SS1+EM-MoM5, 1 Lee, S.M.: SS1+EM-MoM8, 2 Liu, P.: SS1+EM-MoM3, 1 -M-Merrill, P.B.: SS1+EM-MoM8, 2 -0-Ostergren, J.D.: SS1+EM-MoM3, 1 — P — Parks, G.A.: SS1+EM-MoM3, 1

Peden, C.H.F.: SS1+EM-MoM7, 1 Perkins, C.L.: SS1+EM-MoM9, 2 Perry, S.S.: SS1+EM-MoM8, 2 - Q -Qiu, S.R.: SS1+EM-MoM5, 1 — S — Sutton, S.: SS1+EM-MoM3, 1 -T-Templeton, A.H.: SS1+EM-MoM3, 1 Than, H.T.: SS1+EM-MoM5, 1 Thompson, H.A.: SS1+EM-MoM3, 1 Titheridge, D.J.: SS1+EM-MoM1, 1 Toledano, D.S.: SS1+EM-MoM11, 2 Towle, S.N.: SS1+EM-MoM3, 1 Trainor, T.P.: SS1+EM-MoM3, 1 -w-Wang, L.: SS1+EM-MoM6, 1 Wilson, J.N.: SS1+EM-MoM1, 1 — Y — Yarmoff, J.A.: SS1+EM-MoM5, 1