

## Surface Science

### Room 203 - Session SS2-MoA

#### Oxide Surfaces Structure and Reactivity

**Moderator:** M.A. Langell, University of Nebraska-Lincoln

2:00pm **SS2-MoA1 Reconstructions of the Polar Oxide Surface MgO(111)**, *S.E. Chamberlain, D.A. Human, X.F. Hu, H.C. Poon, D.K. Saldin, C.J. Hirschmugl*, University of Wisconsin-Milwaukee

Structures of polar oxide surfaces have been of great interest with several models proposed to compensate the "polar surface instability problem," including 1.) adsorption of foreign species, e.g., hydroxylated surface, 2.) surface faceting, 3.) metallization. MgO(111), the polar surface of a prototypical rocksalt structure, has been shown to maintain a 1x1 structure when annealed to low temperatures, and reconstruct when heated to higher temperatures, and thus represents an ideal system for detailed structural analysis. Detailed surface structures for the 1x1 and  $\sqrt{3} \times \sqrt{3} R30^\circ$  reconstructions will be presented, which have recently been obtained with a novel, low-current LEED system. In good agreement with recent photoelectron diffraction and electronic structure calculations, the MgO(111)1x1 surface is mostly terminated with adsorbed OH groups mixed with a small percentage of O terminated patches with significant relaxation, and suggests that the hydroxylated surface is the compensation method of choice for MgO(111)1x1. Results from the  $\sqrt{3} \times \sqrt{3} R30^\circ$  reconstruction will be compared with several structures proposed in the literature. C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000); R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L. D. Marks, M. Gajdardziska-Josifovska, Phys. Rev. Lett. 81 (1998) 4891; V. K. Lazarov, R. Plass, H-C. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, and M. Gajdardziska-Josifovska Phys. Rev. B 71, 115434 (2005); Subramanian A, Marks LD, Warschkow O, Ellis DE, Phys. Rev. Lett. 92 (2004)200411.

2:20pm **SS2-MoA2 Effects of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> on Ultrathin Ordered Alumina Films under Non-UHV conditions: Hydrogen Bonding and Pressure Gaps**, *M. Jain, F. Qin, M. Magtoto, J. Kelber*, University of North Texas

STM, AES and LEED have been used to probe the reactivities of  $\sim 7.5 \text{ \AA}$  thick, ordered Al<sub>2</sub>O<sub>3</sub> films grown on Ni<sub>3</sub>Al(110) and Ni<sub>3</sub>Al(111) substrates for CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> at intermediate pressures (10<sup>-8</sup> Torr - 10<sup>-1</sup> Torr) at room temperature. Results for H<sub>2</sub>O show that at pressures above 10<sup>-4</sup> Torr, 300 K a surface reconstruction is initiated at defect sites which gradually leads to complete loss of long range order without formation of a UHV-stable hydroxide. The effect is pressure, rather than exposure-dependent, indicating a cooperative effect. Similar exposures to CH<sub>3</sub>OH at > 10<sup>-4</sup> Torr, 300 K also induce a reorganization of the oxide film, though less severe than is observed for equivalent exposures of H<sub>2</sub>O. STM constant current imaging at 2.0 V tip/sample bias of an Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) film after a total CH<sub>3</sub>OH exposure of 5.4 x 10<sup>5</sup> L at 10<sup>-4</sup> Torr, 300 K, reveals disordering of the oxide surface. Imaging at 0.1 V, and LEED however, reveals that the oxide/substrate interface still retains long-range order. C coverage remains < 0.05 monolayers at all exposures. Exposures of Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) and Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(110) to pure O<sub>2</sub> at pressures > 10<sup>-4</sup> Torr, 300 K result in no change to the film observable by AES, LEED or STM. No effect is observed for any of these gases at pressures < 10<sup>-7</sup> Torr, even for exposure times > 6 hours. These data indicate that intermolecular hydrogen bonding is important for inducing cooperative reactions at oxide surfaces and intermediate pressures. The data will be discussed with regards to issues of oxide stability and metal particle sintering during catalytic reactions. F. Qin, N.P. Magtoto, J.A. Kelber, Surf. Sci. 565 (2004) L277. This work was supported by the Robert Welch Foundation under grant B-1356.

2:40pm **SS2-MoA3 Structural Characterisation and Reactivity of V<sub>2</sub>O<sub>5</sub>(001) Thin Films**, *S. Guimond, M.A. Haija, A. Uhl, H. Kühlenbeck, H.J. Freund*, Fritz Haber Institute of the Max Planck Society, Germany

Vanadium oxides are used as catalysts for several oxidation reactions, including the selective oxidation of hydrocarbons and the oxidative dehydrogenation of alkanes to olefins. In spite of their importance, many

questions about the molecular structure and the reaction mechanisms at their surfaces remain unanswered. For instance, a range of vanadium oxidation states exists (from 2+ to 5+) and it is often argued that lower oxidation states like V<sub>2</sub>O<sub>3</sub> could take part in some of the reactions taking place at the surface of the V<sub>2</sub>O<sub>5</sub>-based catalysts. In the present work, we prepared well ordered V<sub>2</sub>O<sub>5</sub>(001) thin films and studied their interaction with different molecules. The films were grown on Au(111) by evaporation of vanadium in a partial pressure of oxygen. Under typical UHV conditions, the films are terminated by vanadyl groups which are not part of the V<sub>2</sub>O<sub>5</sub> bulk structure. As indicated by XPS and vibrational spectroscopy, the oxygen atoms contained in the V=O groups can be removed by electron irradiation, resulting in a surface terminated by metal atoms. This reduction process was followed with STM. The chemical activity of the two surfaces with respect to the adsorption of O<sub>2</sub>, H<sub>2</sub>O, CO and propane was investigated with XPS, IRAS and TDS. While the surface terminated by vanadyl groups was found to be chemically not very active, a rather high activity was observed for the V-terminated surface: O<sub>2</sub> adsorption re-establishes the V=O groups via a charged precursor at low temperature, similar to the case of oxygen on Cr<sub>2</sub>O<sub>3</sub>(001). After thermal desorption of an adsorbed CO layer, the surface is partially re-oxidized, meaning that part of the CO oxygen remains on the surface and forms vanadyl groups. Water dissociates on the surface, forming a layer of hydroxyl groups which is stable up to 500 K. Propane is partially transformed into propene, possibly via an oxygen-containing intermediate.

3:00pm **SS2-MoA4 The Multiple Roles of Oxygen in Organic Photo-oxidation on TiO<sub>2</sub>: Insights from Studies on a Model Photocatalyst Surface**, *M.A. Henderson*, Pacific Northwest National Laboratory; *J.M. White, M.D. Robbins*, University of Texas at Austin; *H. Uetsuka*, Kanagawa Academy of Science and Technology, Japan; *H. Onishi*, Kobe University, Japan

The primary role that molecular oxygen has been viewed to play in organic photo-oxidation processes on high surface area TiO<sub>2</sub> photocatalysts has traditionally been restricted to that of an electron scavenger. However, some groups have proposed more direct involvement of O<sub>2</sub> in reactions with organics. Typical photocatalytic studies employ high surface area powders which are often difficult to characterize on the molecular scale. Results presented in this talk on a model TiO<sub>2</sub> photocatalyst, rutile TiO<sub>2</sub>(110), provide more detailed information on the roles of O<sub>2</sub> and show that O<sub>2</sub> not only acts as an electron scavenger but also: is involved in thermal reactions with organics and OH groups, blocks organic adsorption sites, and competes with adsorbed organics for photo-generated holes. Results on the photo-oxidation of trimethyl acetate, isobutene and acetone will be used to illustrate these functions of O<sub>2</sub> during photocatalysis on TiO<sub>2</sub>. Additionally, it will be shown that the function of oxygen oscillates through these different roles as a typical C<sub>n</sub> hydrocarbon is oxidized to completion (i.e., to CO<sub>2</sub> and water) by sequential removal of C<sub>1</sub> units.

3:20pm **SS2-MoA5 Iron Oxide Thin Films as Supports for Model Catalytic Systems**, *S. Shaikhutdinov*, Fritz-Haber Institute, Germany

Metal particles deposited on thin oxide films have been shown to be suitable model systems for studying structure-reactivity relationships of metal catalysts. A detailed understanding of the surface structure of the oxide films is a crucial prerequisite. It has been previously shown that well-ordered FeO(111), Fe<sub>3</sub>O<sub>4</sub>(111) and alpha-Fe<sub>2</sub>O<sub>3</sub>(001) films can be prepared on a Pt(111) substrate in a controllable manner. In this presentation, we report on the determination of the surface structure of these iron oxide films using scanning tunneling microscopy, temperature programmed desorption and vibrational spectroscopy of CO as a probe molecule. In particular, we have found that the Fe<sub>3</sub>O<sub>4</sub>(111) surface is terminated by 1/2 monolayer (ML) of iron, with an outermost 1/4 ML consisting of octahedral Fe<sup>2+</sup> cations situated above a 1/4 ML of tetrahedral Fe<sup>3+</sup> ions. The most strongly bound CO, which desorbs at 230 K, is assigned to adsorption to Fe<sup>3+</sup> cations present at the step edges, whose geometry is predicted on the basis of coordinative unsaturation and excess surface charge concepts. For the alpha-Fe<sub>2</sub>O<sub>3</sub>(001) surface, experimental and theoretical evidence is presented which shows that the hematite may be terminated with ferryl (Fe=O) groups, which has never been considered for iron oxide surfaces. In addition, the structure and adsorption properties of metals (Pd, Au) deposited on these films are studied. For example, CO is found to react with lattice oxygen of Fe<sub>3</sub>O<sub>4</sub> at the Pd/oxide periphery. Oxygen desorption at elevated temperatures

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resulted in structural changes of the system. The results for the model catalytic systems supported on the iron oxides are compared with data previously obtained for other (non-reducible) oxide films.

**3:40pm SS2-MoA6 Role of Dichlorocarbene in the Surface Chemistry of Halomethanes on Fe@sub 3@O@sub 4@(111)-(2X2) ; a Comparative Thermal Desorption Study, Y. Le, G.G. Totir, G.W. Flynn, R.M. Osgood, Columbia University**

Iron-oxide surface chemistry plays an important role in understanding chemical routes for the environmental degradation of chlorinated halocarbons. An earlier study had shown the importance of dichlorocarbene in controlling the thermal reaction products for CCl@sub 4@ chemisorbed on magnetite-terminated hematite surfaces. In this talk, we report on an investigation of the surface chemistry of CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on a UHV-prepared Fe@sub 3@O@sub 4@(111)-(2X2) seldge of single-crystal @alpha@-Fe@sub 2@O@sub 3@ (0001). Our experiments use UHV, temperature programmed reaction and desorption (TPR/D) measurements of dosed surfaces, along with LEED and Auger probes. The TPR/D spectra show that dissociative formation of dichlorocarbene, followed by its reaction with lattice oxygen and other adsorbed surface species, is central to the surface chemistry of halocarbons in general, and of halomethanes in particular on the (2X2) reconstructed surface of hematite. The specific branching ratios of the various desorbed products including metal-halides are compared for adsorbed CCl@sub 4@, CBr@sub 2@Cl@sub 2@, and CH@sub 2@Cl@sub 2@ on the (2X2) surface. Our experiments show clearly the importance of CCl@sub 2@ intermediates in these surface reactions.

**4:00pm SS2-MoA7 Methyl Radical Chemistry on Clean and UO@sub 3@-Covered Single Crystal Hematite Surfaces, L. Liu, Columbia University; P.C. Stair, Northwestern University**

The partial oxidation of methane over oxide catalysts is controlled by the surface reaction of methyl radicals. Methyl radical chemistry was studied on two model surfaces in UHV: Clean, (0001) orientation single crystal hematite and UO@sub 3@ supported on a crystalline hematite thin film. Temperature Programmed Desorption (TPD) showed that methyl radicals adsorb on the Fe@sub 3@O@sub 4@ (111)-terminated hematite (0001) surface at 300 K and desorb intact at higher temperatures. At saturation coverage, the XPS C(1s) line position is consistent with methoxide ions on the surface, and the carbon-surface bond energy determined by threshold TPD analysis is similar to the C-O bond energy of surface methoxide ions. In contrast, methyl radicals produce only very small desorption features on the biphasic-terminated hematite (0001) surface. The coverage of adsorbed methyl was obtained by quantification of the TPD data. Saturation coverage was  $1 \times 10^{14}$ /cm<sup>2</sup> on the Fe@sub 3@O@sub 4@ (111)-terminated surface but only  $3.7 \times 10^{12}$ /cm<sup>2</sup> on the biphasic-terminated surface, consistent with adsorption on regular surface sites and defect sites, respectively. Since the two surfaces both contain Fe@sub 2+@, Fe@sub 3+@, and O the differences in methyl radical adsorption must be due to differences in surface structure. Based on an analysis of the structures reported in the literature it is proposed that methyl radicals adsorb on surface oxygen atoms with a dangling bond perpendicular to the surface plane on the Fe@sub 3@O@sub 4@ (111)-terminated surface. On the hematite-supported UO@sub 3@ surface, partial oxidation products, such as methanol, formaldehyde, and CO were identified by TPD. XPS quantification indicates that UO@sub 3@ forms a monolayer structure on the hematite support. The increased reducibility of UO@sub 3@ compared to hematite is responsible for the change in surface chemistry. A surface methoxide ion is the proposed reaction intermediate.

**4:20pm SS2-MoA8 Characterization of the Co@sub 3@O@sub 4@(111) Single Crystal Surface, E.M. Marsh, M.A. Langell, University of Nebraska-Lincoln**

The (111) face of the Co@sub 3@O@sub 4@ single crystal has been characterized using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED) to establish the cleanliness, composition, and order of the (111) surface. The vibrational modes of the Co@sub 3@O@sub 4@(111) face were then investigated by high-resolution electron energy loss spectroscopy (HREELS) and the Fuchs-Kliewer phonon spectrum was obtained with an incident electron energy of 3.77 eV. Data taken on the (111) surface has been compared to previously reported values taken from the (110) surface of the Co@sub 3@O@sub 4@ single crystal. HREELS was also used to study the vibrational modes of H@sub 2@O as an adsorbate on the surface to test the accuracy of the log-deconvolution algorithm in removing the multiple scattering modes of the phonon spectrum.

**4:40pm SS2-MoA9 The Interaction of Carbonyls with Oxide Surfaces: The Adsorption of Formaldehyde on CeO@sub X@(111), J. Zhou, D.R. Mullins, Oak Ridge National Laboratory**

Formaldehyde, CH@sub 2@O, chemisorbs on both oxidized and reduced cerium oxide surfaces. Near-edge X-ray Absorption Fine Structure (NEXAFS) and synchrotron-excited Soft X-ray Photoelectron Spectroscopy (SXPS) indicate that chemisorption occurs through the formation of a dioxymethylene, CH@sub 2@O@sub 2@, intermediate. On the fully oxidized surface this intermediate is weakly bound and results in molecular formaldehyde desorption between 200 K and 300 K. On a reduced cerium oxide surface the intermediate is more strongly adsorbed and desorbs as formaldehyde near 460 K. Some of the dioxymethylene disproportionates producing formate and methoxy intermediates above 450 K. These intermediates dissociate to form H@sub 2@ and CO products above 550 K. At large formaldehyde exposures polymerization occurs on both the oxidized and reduced ceria surfaces. The polymer decomposes to produce formaldehyde between 300 K and 400 K. The adsorption of formaldehyde, which occurs through the conversion of the carbonyl to carbondioxy on the oxide surface, is contrasted with the adsorption of methanol in which the hydroxyl bond is broken and methoxy is formed on the ceria. The methoxy group is more stable than dioxymethylene on the ceria surface and leads to decomposition products above 560 K rather than the recombinative desorption of methanol. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

**5:00pm SS2-MoA10 Structure and Reactivity of the Positively and Negatively Poled Surfaces of LiNbO@sub 3@(0001), M. Li, D. Liao, E.I. Altman, Yale University**

The effect of ferroelectric poling direction on the structure and reactivity of the LiNbO@sub 3@(0001) surface was studied using reflection high energy and low energy electron diffraction, x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy, and temperature programmed desorption (TPD). The surfaces were prepared by annealing at 1175 K in air at atmospheric pressure and then cleaned by exposure to oxygen plasmas in UHV. Following this procedure, both the positive and negative surfaces gave (1x1) diffraction patterns. No evidence of reconstructions was observed suggesting that both surfaces are bulk terminated with the negatively poled surface exposing Li ions and the positive surface Nb ions, in contrast to prior work that suggested an oxygen termination for both surfaces that would require a reconstruction to maintain the proper stoichiometry. Photoelectron spectra also showed little difference between the positive and negative surfaces with both showing Nb only in the 5+ oxidation state, and valence level spectra with nearly identical emission due to O 2p derived states and no emission in the bandgap due to reduction. These results are also in contrast to a prior study that suggested reduction of the Nb ions near the negatively poled surface. Differences in reactivity of the two surfaces towards CO@sub 2@, water, and 2-propanol is being characterized using TPD along with XPS and UPS.

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