Tuesday Morning, October 3, 2000

Surface Science Room 208 - Session SS1-TuM

Reactions on Oxides and Environmental Chemistry Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

8:20am **SS1-TuM1 Ethylene Polymerization on a CrOx/SiO2 Model Catalyst: XPS, SIMS, RBS and AFM**, *P.C. Thuene, J. Loos,* Eindhoven University of Technology, The Netherlands; *J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Achieving realistic catalytic activity on a model catalyst consisting of Cr on 1 cm2 of planar SiO2 at a loading of 1 Cr per nm2 has proven to be the major challenge in designing a surface science model for the Phillips ethylene polymerization catalyst. Poisons like water or acetylene can deactivate the catalyst within a fraction of a second even if they are present in minute (1ppm) quantities. By using special filters we can now run polymerization reactions at 160ŰC for at least 30 minutes without deactivation of the catalyst. The polymer yield after each polymerization run is measured most conveniently by analyzing scalpel scratches with atomic force microscopy (AFM). The catalyst shows a constant activity with a pseudo turnover frequency of 2.5 C2H4 / Cr s. This corresponds to 250 g PE / gcat h atm if rescaled to the surface area of an industrial catalyst (286 m2/g, Crossfield) which represents a realistic catalytic activity. Owing to the planar geometry, the state of Cr can be determined in detail by using XPS and SIMS, while the polymer morphology can be analyzed with AFM.

8:40am SS1-TuM2 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation, A.G. Sault, J.E. Mudd, J.A. Ruffner, J.E. Miller, Sandia National Laboratories

A fundamental understanding of active sites in mixed metal oxide oxidative dehydrogenation (ODH) catalysts continues to be elusive. In an effort to simplify the complexities inherent in these materials we are growing single phase, oriented mixed metal oxide thin films. Using RF sputter deposition, we have grown 10-2000 Å films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known ODH catalyst. Bulk and surface analysis of films grown on silicon wafers show the desired stoichiometry, but the films are amorphous. Deposition on a 500 Å gold layer grown on oxidized silicon results in films strongly oriented toward the (021) plane of Mg@sub 3@(VO@sub 4@)@sub 2@. This orientation is due to the tendency of gold to grow with (111) planes exposed, which provides an ideal epitaxial substrate for Mg@sub 3@(VO@sub 4@)@sub 2@ (021). This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. By varying oxygen pressure we can deposit films with stoichiometries ranging from fully oxidized Mg@sub 3@(VO@sub 4@)@sub 2@ to partially reduced Mg@sub 3@V@sub 2@O@sub 6@. We will detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films, and report on the catalytic activity of these films for ODH. In general, heating the films above 623 K in vacuum or 100 Torr propane results in at least partial reduction of V(V) to V(III) and segregation of V to the surface. Prolonged reduction at higher temperatures results in complete reduction to Mg@sub 3@V@sub 2@O@sub 6@. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for ODH, which involves participation of lattice oxygen. Catalytic measurements of propane ODH show very low conversions due to the low surface areas of the films. Measurements with more facile ODH reactions (such a 1-butene to butadiene) are underway and will be reported.

9:00am SS1-TuM3 Reactive Scattering Studies of Organophosphorous Compounds on Semiconducting Metal Oxides, J.L. Duncan, S. Ma, R.H. Jackson, B.G. Frederick, University of Maine

Semiconducting metal oxides (SMOs) are promising materials for the development of conductivity-based chemical sensors with a broad range of applications. The reactions of organophosphorous compounds are of interest for detection of pesticides and nerve agents. Improvement of the selectivity of SMO sensors requires an understanding of the steps in the decomposition or reaction mechanism which lead to changes in conductivity. We present results of reactive, molecular beam scattering studies for dimethyl methyl phosphonate (DMMP), and related compounds from tungsten oxide based sensors. The experiments utilize molecular beam doser sources with known flux distributions and a differentially-pumped, calibrated mass spectrometer system allowing the coverage, sticking coefficients, and reactive scattering probabilities to be quantified.

Reactive scattering of methanol, formic acid, trimethyl phosphine oxide, and trimethyl phosphonate, contribute to understanding the decomposition mechanism of DMMP and the associated conductivity changes observed in the SMO films.

9:20am SS1-TuM4 Chemistry of SO@sub 2@ and NO@sub 2@ on ZnO(0001)-Zn and ZnO Powders: Changes in Reactivity with Surface Structure and Composition, J.A. Rodriguez, T. Jirsak, J. Dvorak, J. Hrbek, Brookhaven National Laboratory

Synchrotron-based photoemission and x-ray absorption spectroscopy have been used to study the interaction of SO@sub 2@ and NO@sub 2@ with ZnO(0001)-Zn and polycrystalline surfaces of zinc oxide (films and powders). Important differences are observed when comparing the behavior of the adsorbates on these oxide surfaces. These differences are in a part a result of changes in structural properties (flat vs rough surfaces), but in some cases they clearly originate in variations in surface composition (Zn-adsorbate vs O-adsorbate interactions). For example, the Znterminated (0001) face of ZnO interacts weakly with SO@sub 2@ (desorption temperature of adsorbate < 200 K). In contrast, the SO@sub 2@ molecules interact readily with O sites of Ar@super +@ sputtered ZnO(0001)-Zn or polycrystalline ZnO forming very stable SO@sub 3@ species. Due to its radical nature, adsorbed NO@sub 2@ is more chemically active than SO@sub 2@. After dosing nitrogen dioxide to ZnO(0001) at 100 K, chemisorbed NO@sub 2@ and NO@sub 3@ coexists on the surface. Partial transformation of NO@sub 2@ into NO@sub 3@ is observed from 150 to 300 K. The data for the NO@sub 2@/ZnO(0001)-Zn system clearly prove that large quantities of NO@sub 3@ can be formed on metal sites of an oxide surface as a consequence of partial decomposition or disproportionation of NO@sub 2@.

9:40am SS1-TuM5 Adsorption of S and Cl on TiO@sub 2@(110) Studied by Ultra-violet Photoelectron Spectroscopy, E.L.D. Hebenstreit, W. Hebenstreit, U. Diebold, Tulane University; H. Geisler, Xavier University; D.A. Hite, P.T. Sprunger, Louisiana State University; S.N. Thornburg, C.A. Ventrice, Jr., University of New Orleans

One of the most severe poisonings of metal and metal oxide catalytic systems is induced by sulfur contamination. In order to obtain a better knowledge of the mechanism for contamination of catalysts at a microscopic level, an ultra-violet photoelectron spectroscopy (UPS) study of the adsorption of elemental S and Cl on reduced TiO@sub 2@(110) surfaces has been performed. A previous study of the adsorption of S on TiO@sub 2@(110) has shown that a variety of overlayer structures can be obtained, depending on the temperature of adsorption.@footnote 1@ Below ~120 °C, S adsorbs preferentially on the exposed Ti rows and forms a weakly ordered overlayer. Above ~120 °C, there is a change in the S adsorption site from on top of the Ti rows to a replacement of the surface O. UPS measurements show that the surface defect state of the reduced TiO@sub 2@ substrate is quenched upon adsorption of S at RT. In addition, there is a shift of 0.4 eV in the valence emission to lower binding energy that results from an "un-bending" of the valence band. Adsorption of S at ~350 °C results in an enhancement of the surface defect state and the appearance of new emission features within the band gap of the TiO@sub 2@. Both the defect state and the emission features within the band gap resonate at the Ti 3p to 3d absorption threshold. A shift in the Ti 3p core emission of ~0.5 eV to lower binding energy and a reduction in the O 2s emission are also observed. These results indicate that there is an increase in the population of Ti 3d states from a loss of surface O. Cl adsorption at RT behaves similarly to S with a quenching of the surface defect state and a 0.4 eV shift of the valence band. Although adsorption of Cl at 200 °C results in an enhancement of the surface defect state, no new emission features are observed within the band gap of the TiO@sub 2@. @FootnoteText@ @footnote 1@ E. L. D. Hebenstreit, W. Hebenstreit, and U. Diebold, Surf. Sci. (in press).

10:00am SS1-TuM6 Thermal Production of Phosgene from Carbon Tetrachloride Reactions on Natural Single Crystal @alpha@-Fe@sub 2@O@sub 3@ Surfaces in Ultrahigh Vacuum, K. Adib, N. Camillone III, J.P. Fitts, D. Mocuta, K.T. Rim, G.W. Flynn, R.M. Osgood, Jr., Columbia University; S.A. Joyce, Pacific Northwest National Laboratory

Oxides of iron have important applications as catalysts and reactive sites for various classes of chemical reactions. They have a significant environmental role in the speciation of toxic metal cations and the dehalogenation of halocarbons. This environmental role is important due to the abundance of iron oxides in the Earth's crust and due to their higher reactivity compared to other metal oxides. We use ultrahigh vacuum for a detailed study of the chemistry of a well-characterized surface of

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@alpha@-Fe@sub 2@O@sub 3@ (hematite). Natural single crystal samples of hematite were cut and polished in the (0001) orientation. They were processed in-situ to produce a surface selvedge of Fe@sub 3@O@sub 4@ 2x2 reconstruction, as verified by LEED, and dosed at ~100K with CCl@sub 4@. The surface reactions were studied by temperatureprogrammed desorption (TPD). The multiplicity of desorption waves observed indicates a complex chemistry involving molecular adsorption and dissociative adsorption on at least two distinct kinds of surface site. The TPD results indicate the formation of COCl@sub 2@ (phosgene) as well as C@sub 2@Cl@sub 4@ and high temperature desorption of iron chlorides. We observe significant differences in the TPD spectrum following the first dosing of the surface as compared to those measured following subsequent dosings indicating a marked change in the surface upon initial exposure. This change is commensurate with the titration of surface defects during the initial reaction stages. Preliminary measurements of the UV photochemistry of the adsorbed CCl@sub 4@ on this surface will be presented.

10:20am **SS1-TuM7 Multiplet Splitting and Crystal Field Strengths at Iron Oxide Surfaces**, *T. Droubay*, *S.A. Chambers*, Pacific Northwest National Laboratory; *B.P. Tonner*, University of Central Florida

The metal core-level spectra of 3d-transition metal oxides exhibit complex lineshapes due to multiplet splitting in the final state. The crystal field splitting largely determines the degree of multiplet structure. We have measured surface and bulk-sensitive Fe 2p core-level spectra at high energy resolution for several MBE-grown iron oxide epitaxial films. Line shape differences are observed between surface and bulk sensitive photoemission spectra, indirectly revealing differences in crystal field strength. In order to determine the surface crystal field strength, we have utilized XAS L-edge spectra of bulk iron oxides, and have calculated these spectra from first principles using an atomic multiplet theory. Agreement of ultra-high resolution experimental absorption spectra and theoretical models is excellent. We then used the theoretical multiplet model to simulate the bulk-sensitive XPS core-level spectra by broadening to account for the increased lifetime and adjusting peak heights to optimize agreement between theory and experiment. This step produced an accurate value for the bulk crystal field strength. The metal ion site symmetry was then reduced in the calculation and agreement re-optimized between theory and surface sensitive XPS spectra to obtain the equivalent surface crystal field strength. Determination of the crystal field strength at the surface may provide an insight into oxide surface reactivity.

10:40am SS1-TuM8 Scanning Electron Microscopy Studies of the Hydration of Alkali Halides, *S.A. Joyce*, *J.P. Cowin*, Pacific Northwest National Laboratory

Morphological and phase changes of several salts which are important constituents of sea-salt aerosols were examined in an environmental scanning electron microcospe as function of both water vapor pressure (from ~2 to 18 Torr) and temperature. For highly soluble materials, dissolution can occur by incorporation of water from the gas phase. The dissolution of NaCl and NaBr samples upon exposure to water vapor have been imaged and the observed temperature dependence of the deliquescence pressures agree well with previous studies. The deliquescence is initially observed as the surface of a crystal becomes featureless, followed by a rounding and spreading of the solution droplet on the sample holder. NaBr converts to the dihydrate (NaBr*2H@sub 2@O) at water pressures roughly half the deliquescence pressure. The formation of the hydrate can be readily observed in the SEM. Unlike the case of deliquescence, no significant changes in the microtopography are initially observed, rather hydration results in a change in the contrast. Dark regions on the surface nucleate and grow as the hydration proceeds. The rate of hydration/dehydration is a strong function of the pressure (i.e. the saturation ratio). Prolonged hydration results in an increase in the roughness of the surface presumably due to microcrystallite formation as a stress-relief mechanism. Cycling hydration/dehydration results in higher roughness. Delamination and spalling have been observed upon rapid dehydration. Both effects increase the net surface area. Such cycling is very common in the atmosphere versus changes in altitude, time, and the day/night cycle, and should have a strong impact on water-soluble aerosol morphology. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

11:00am **SS1-TuM9 Reactivity of Water toward NaCl(100),** *A.J. Leavitt, R.D. Huffstetler, Jr., J.W. Russell, J.I. Brauer, J.K. Cutchins, C.D. Lane, M.B. Reddy, F.A. Khan,* State University of West Georgia

The role of water-mediated reactions that occur on particulate NaCl surfaces is relevant to atmospheric chemistry. A temperature-programmed desorption (TPD) study of water adsorbed onto NaCl(100) was performed. Water was adsorbed onto the surface held at a temperature of 130 K at a variety of water fluences, then thermally desorbed into a quadrupole mass spectrometer in an ultrahigh vacuum chamber. Water molecularly adsorbs onto the surface and desorbs in a first-order process at ~143 K for fluences corresponding to 10% of a monolayer. As the water fluence is increased, the temperatures of maximum desorption shifts higher suggesting stabilization of the water layer through hydrogen bonding. Further increases in water fluences lead to a constant area under the desorbing peak suggesting the buildup of a condensed layer of the water on the NaCl surface. This desorption feature does not appear to saturate at very high fluences of water. These results are consistent with previous work by Falsch and Henzler (UPS study) and Peters and Ewing (IR study). This work was supported by Research Corporation.

11:20am SS1-TuM10 Surface Segregation of Bromine in Bromide Doped NaCl: Implications for the Seasonal Variations in Arctic Ozone, S. Ghosal, J.C. Hemminger, University of California, Irvine

Episodes of ozone depletion attributed to chemistry of gas phase bromine compounds in marine regions of the Arctic boundary layer have been reported at polar sunrise. Models for the source of brominated compounds in the marine Arctic troposphere have focussed on surface chemistry of sea salt ice and aerosols even though the molar ratio of Cl@super-@ to Br@super-@ in sea salt is expected to be ~660 to 1. X-ray photoelectron spectroscopy (XPS) studies described here show, for the first time, substantial segregation of Br@super-@ to the surface of NaCl samples with low level Br@super-@ dopant. Water exposure plays an important role as it provides enhanced ionic mobility in such systems allowing the surface segregation as the system approaches thermodynamic equilibrium. Our XPS results are confirmed by scanning electron microscopy (SEM) imaging of the salt sample surface after water vapor exposure, which shows NaBr crystallites that form at the surface. Our experiments provide the first experimental evidence of surface segregation in mixed alkali halide solids.@footnote 1@ The segregation phenomenon displayed here is likely to play an important role in a wide range of atmospheric phenomena that involve surface reactions of sea salt particles and aerosols. @FootnoteText@ @footnote 1@ This work was supported by the NSF Grant ATM-9707285.

11:40am SS1-TuM11 Isothermal Desorption Kinetics of H@sub 2@O from @super 1@H@sub 2@@super 16@O, @super 1@H@sub 2@@super 18@O and @super 2@H@sub 2@@super 16@O Ice Multilayers, J.A. Smith, F.E. Livingston, S.M. George, University of Colorado at Boulder

The mechanism of H@sub 2@O desorption from ice can be explored by examining the H@sub 2@O desorption kinetics from ice composed of the various H@sub 2@O isotopomers. The isothermal desorption kinetics of H@sub 2@O from @super 1@H@sub 2@@super 16@O, @super 1@H@sub 2@@super 18@O and @super 2@H@sub 2@@super 16@O ice multilayers were measured using optical interferometry. These experiments were performed at temperatures between 175-195 K using ice multilayers grown epitaxially on a Ru(001) surface. The desorption rates of @super 1@H@sub 2@@super 16@O and @super 1@H@sub 2@@super 18@O were very similar. The desorption kinetics for @super 1@H@sub 2@@super 16@O were E@sub d@ = 13.9 +/- 0.2 kcal/mol and @nu@@sub d@ = 10@super 32.6 +/- 0.3@ molecules/cm@super 2@ s. In contrast to the expectation that the H@sub 2@O desorption rate should scale with the square root of molecular mass, the desorption rate of @super 2@H@sub 2@@super 16@O was approximately a factor of two slower over the measured temperature range. The desorption kinetics for @super 2@H@sub 2@@super 16@O were E@sub d@ = 14.8 +/- 0.4 and @nu@@sub d@ = 10@super 33.4 +/- 0.5@ molecules/cm@super 2@ s. The desorption kinetics for the three H@sub 2@O isotopomers are explained using transition state theory. The rotational degrees of freedom yield the main differences. The differences in the activation energies are related to the zero-point energies of frustrated rotations on the ice surface. The differences in pre-exponentials are associated with the moments of inertia of the desorbing molecules.

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