Monday Morning, November 4, 2002

Surface Science Room: C-112 - Session SS2-MoM

Oxide Structure and Surface Chemistry

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

8:20am SS2-MoM1 TPD Studies of the Chemistry of CCl₄ on Fe₃O₄ (2x2)-(111) Surfaces in the Presence of Adsorbed D₂O, K. Adib, G. Totir, J.P. Fitts, K.T. Rim, G.W. Flynn, R.M. Osgood, Jr., Columbia University Due to their abundance in the crust of the Earth and their high reactivity, the oxides of iron serve as ideal model mineralogical surfaces in environmental catalysis studies. The relevance of the environmental studies is enhanced by considering the effect of water on the reactivity of iron oxide surfaces. Natural single crystals of α -Fe₂O₃ were cut and polished in the (0001) orientation. They were processed in ultrahigh vacuum to produce a surface selvedge of Fe₃O₄ (111)- 2x2 and exposed at ~100 K to D₂O and CCl₄. The TPD studies of adsorbed D₂O indicate a rich surface chemistry with multiple desorption events extending to as high as ~ 800 K consistent with dissociative adsorption of D₂O on the Fe₃O₄ (111) surface. Previous TPD and XPS results indicate that in the absence of D₂O, CCl₄ dissociatively adsorbs on Fe₃O₄ (111) producing chemisorbed Cl and CCl₂ which upon subsequent heating of the surface, abstract lattice iron and oxygen atoms to desorb as FeCl₂ and OCCl₂, respectively. In the presence of adsorbed D₂O, it is observed that the production of FeCl₂ and OCCl₂ are substantially suppressed indicating that the DO fragments block the surface reactive sites. The evolution of the reaction products of CCl₄ with the Fe₃O₄ surface as a function of pre-adsorbed D₂O coverage will be presented.

8:40am SS2-MoM2 Variable Temperature Scanning Tunneling Microscopy Studies of a Natural Single Crystal a -Fe₂O₃(0001) Sample: Termination and Surface Chemistry with CCl₄ and Cl₂, K.T. Rim, T. Müller, J.P. Fitts, K. Adib, Columbia University, N. Camillone III, R.M. Osgood, Jr., Brookhaven National Laboratory, S.A. Joyce, Los Alamos National Laboratory, G.W. Flynn, Columbia University

Variable Temperature Scanning Tunneling Microscopy (VT STM) has been used to study the reactivity of the reduced surface of a natural single crystal $\alpha\text{-}Fe_2O_3(0001)$ sample. STM and LEED measurements reveal that the surface cleaned in ultrahigh vacuum is reduced and composed of a Feterminated Fe₃O₄ (111) region and an O-terminated Fe₃O₄(111) or biphase region. The Fe-terminated Fe₃O₄(111) region exhibits reaction with CCl₄ and Cl_2 , but the O-terminated $Fe_3O_4(111)$ (biphase) region does not undergo reaction. Reaction products (Cl) on the Fe- terminated Fe₃O₄(111) region were observed with STM at room temperature after the reduced surface was exposed to CCl₄ and Cl₂. Chlorines are found to occupy two distinct sites, Fe top sites and O vacancy sites when the surface is exposed to CCl₄ vapor. However Cl occupies only the top sites when Cl₂ is dosed on the surface. The O vacancy sites are created only after surface oxygen atoms are abstracted via reaction with CCl4 to produce phosgene. The reduced surface was exposed to CCl₄ at 238K and the surface temperature changed from 238K to 600K in order to identify reaction products and intermediates (chlorine and dichloro-carbene) and to observe oxygen vacancies following oxygen abstraction from the surface. Related TPD, AES, and XPS results will also be presented to support the VT STM observations.

9:00am SS2-MoM3 Influence of Surface Composition on the Pyrite Mediated Dechlorination Kinetics of Alachlor, *H. Fairbrother*, *D.L. Carlson*, *M.M. McGuire*, *A.L. Roberts*, Johns Hopkins University

The effects of different pyrite surface compositions on the dechlorination kinetics of the herbicide alachlor were investigated. Chloroacetamides, including alachlor, are an important class of herbicides, which are encountered as ubiquitous contaminants in surface and groundwater. Currently, the understanding of the processes controlling the environmental fate and transformations of alachlor is somewhat fragmented. Alachlor can be dechlorinated by Fe(0). Because several iron sulfide minerals have been shown to dechlorinate low molecular weight alkyl and vinyl halides, we investigated the reactivity of alachlor with pyrite (FeS₂), a common minor constituent of sediments and aquifers. We found that the primary product is deschloroalachlor, the result of reductive dechlorination. This process may be important in natural systems, as previous work has identified deschloroalachlor in groundwater. In this study, we have employed a liquid cell directly coupled to a surface analysis chamber to examine the effect of surface defect sites on the pyrite mediated dechlorination kinetics of alachlor. The influence of surface chemical composition on the

dechlorination of the organohalide alachlor (a herbicide) by pyrite was studied by XPS in conjunction with GC-MS. On natural pyrite surfaces, the dechlorination process exhibited first-order kinetics, indicative of a limited number of surface sites that were consumed during reaction. In contrast, pyrite surfaces modified by ion bombardment, which are dominated by sulfur vacancies, exhibited markedly different reaction kinetics characterized by an initial induction period of low reactivity during which time the surface is oxidized by water. These results indicate that monosulfide species are not responsible for alachlor reduction on pyrite. In a broader sense this study illustrates the intimate relationship that exists between surface chemical composition and reactivity at the liquid-solid interface.

9:20am SS2-MoM4 Adsorption and Desorption of Methanol on WO₃ (100) Surfaces, S. Ma, F.G. Amar, B.G. Frederick, University of Maine

We have investigated the role of intermolecular interactions, surface site heterogeneity, and surface diffusion during the desorption of methanol from the oxidized and reduced surfaces of (100) oriented, epitaxially grown WO₃ films on Al₂O₃(1-102) substrates. Ultra-violet photoelectron spectroscopy (UPS) showed that methanol adsorbed molecularly on the oxidized WO₃ surface but dissociatively on the reduced surface. On both surfaces, calibrated thermal desorption spectroscopy (CTDS) showed desorption of methanol in an asymmetric peak which shifts to lower temperature with increasing coverage, typical of water and alcohols on other oxide surfaces. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface by monitoring the W4f and valence band region, while separate STM studies indicate that the surface is heavily stepped. Monte Carlo simulations indicate that surface heterogeneity and rapid diffusion are consistent with the observed desorption spectra. By contrast, simulations on a homogeneous surface require repulsive intermolecular interactions, which is inconsistent with hydrogen bonding.

9:40am **SS2-MoM5 Interaction of Co₃O₄ Single-Crystal Surfaces with Water**, *M.A. Langell*, *D.A. Pugmire*, University of Nebraska-Lincoln, *W.H. McCarroll*, Rider University

Vacuum-annealed and vacuum-cleaved Co3 O4 single-crystal substrates have been characterized using the UHV surface analytical techniques of Auger electron spectroscopy, x-ray photoelectron spectroscopy, low energy electron diffraction and high resolution electron energy loss spectroscopy. Particular emphasis in this study has been placed on the characterization of surface oxygen, which often shows complex photoemission structure from core oxygen states, and of the tetrahedral/octahedral site occupancy of cobalt surface cations as it relates to the defect character of the spinel surface. These well-defined surfaces are subsequently probed by adsorption of H₂O, both at low ($\leq 10^{-6}$ Torr) and high (1-10 Torr) water vapor pressures. Dissociative adsorption to produce surface hydroxyls is an important process for air-exposed oxides and this mechanism was found to occur upon water exposure for the Co₃O₄ surface under UHV conditions. However, hydroxylation was most readily observed for stoichiometric surfaces upon electron or thermal activation of the water adsorbate. These surface species will be compared to hydroxyls generated under high vacuum and atmospheric conditions.

10:00am SS2-MoM6 Surface Chemistry of Calcined UO₂ Powders, A.J. Nelson, T.C. Meier, C.K. Saw, L.V. Griffith, Lawrence Livermore National Laboratory

High resolution X-ray photoemission spectroscopy (XPS) was used to examine the surface composition and chemical bonding of calcined UO₂ powders as a function of process parameters. It is believed that the surface composition of the powder grains ult imately affects packing density. XPS quantitative analysis revealed O/U ratios indicative of mixed uranium valences. In addition, high resolution U 4f7/2,5/2 core-level spectra revealed reoxidation of U^{4+} to U^{6+} for the lower temperatures, and a reduction of U^{6+} to $U^{4\ast}$ for the higher temperatures using $4 \ddot{\%}~H_2/Ar.$ Reoxidation can also be affected by the presence of water or OH, and the powder samples calcined at the lower temperatures have the highest OH?/O2? peak area ratio. Also, electrons in the 6d, 5f, and 7s orbitals near the valence band maximum can participate in bond formation so long as adjacent atoms are capable of donating their electrons to these unfilled orbitals. The valence band electronic structure for the higher temperature calcinations clearly shows a stronger 5f emission peak near the Fermi edge, a feature that is indicative of a highly localized state. Results were correlated with bulk structural analysis using x-ray diffraction. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

10:20am SS2-MoM7 Examination of the Redox Chemistry of Water with the Oxidized and Reduced Surfaces of CeO₂(111), M.A. Henderson, M.H. Engelhard, C.H.F. Peden, C.L. Perkins, S. Thevuthasan, Pacific Northwest National Laboratory

Ceria is important in automotive three-way catalysts because of its ability to store and release oxygen as reaction conditions oscillate between oxidizing and reducing conditions. The effect of such redox oscillations on adsorbate chemistry is not well understood, although the chemistry of water on oxide surfaces is known to depend on the surface's redox state.¹ Two groups have recently reported conflicting results for the interaction of water with reduced $\text{CeO}_2(111)$ films, with one group reporting $\text{Ce}^{3\scriptscriptstyle+}$ oxidation² and the other reporting Ce^{4+} reduction.³ In both cases, the $CeO_2(111)$ films were thin (≤ 50 Å) and were grown on metal substrates (Ru(0001)² and Pt(111)³). We have studied the interaction of water with a 500 Å CeO₂(111) film grown on Y-stabilized ZrO₂(111). TPD measurements for varying coverages of water on either oxidized (800 K in O2) or vacuum reduced (at 850 K) CeO₂(111) are suggestive of predominately molecularly adsorbed water, and show no evidence for irreversible decomposition either in terms of water consumption or H₂/O₂ desorption. Complimentary core and valence band photoemission results show that adsorbed water does not increase or decrease the level of Ce^{3+} in the reduced $CeO_2(111)$ surface, although water exposure at 600 K shows a slight increase in Ce³⁺ over that seen from annealing in UHV at the same temperature. Comparison of our results for the $CeO_2/ZrO_2(111)$ system with those from thin CeO_2 films grown on metal substrates suggests that metal substrates may participate in water redox chemistry on ceria.

¹ M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1.

² Lj. Kundakovic et al., Surf. Sci. 457 (2000) 51.

³ U. Berner et al., Surf. Sci. 467 (2000) 201.

10:40am SS2-MoM8 Interface Mediated Defect Formation in Ultrathin Cerium Oxide Films, C. Castellarin-Cudia, S. Surnev, S. Eck, M.G. Ramsey, F.P. Netzer, Karl-Franzens-Universität Graz, Austria

The oxygen storage and release capabilities of cerium oxide are important factors for its use as an additive in the three-way catalyst for automotive emission control. The ceria can act as an oxygen pump, which under fuelrich conditions gives up oxygen, whereas under fuel-lean conditions it can take in oxygen. A key step in this process is the formation and destruction of oxygen vacancy defects at the ceria surface. Here we report the observation of defect formation, at the atomic level using STM, in ultrathin cerium oxide layers on a Rh(111) substrate surface. The ceria overlayers have been fabricated in situ by reactive evaporation of Ce metal onto the heated substrate (250°C) in an oxygen atmosphere, and reducing ambient conditions have been simulated by annealing in vacuum. Ceria overlayers on Rh(111) grow in a CeO₂(111)-type structure and annealing of submonolayer coverages to ~500°C produces thin, well-ordered Ce-oxide island nanostructures. The island surfaces display atomic resolution in the STM and reveal a Moiré superstructure, as a result of the lattice mismatch between the oxide overlayer and the Rh substrate. Further annealing to ~600°C leads to partial reduction and an ordered array of oxygen vacancies, which form a defect superlattice of the same dimensions as the Moiré structure. Several defect signatures can be distinguished in the atomically resolved STM images. We propose that the defect superlattice is mediated by the metal-oxide interface, via a lattice-mismatch induced strain effect. This creates catalytically active sites for the preferential reduction of the ceria, i.e. the formation of oxygen vacancy defects, and constitutes a novel mechanism for the formation of interface-stimulated active centers. ^{*}Supported by the Austrian Science Foundation.

11:00am SS2-MoM9 Identification of Defect Sites on Oxide Surfaces, Y.D. Kim, J. Stultz, T. Wei, A.K. Santra, D.W. Goodman, Texas A&M University

Defect sites on oxide surfaces play an important role in various catalytic reactions, as well as in adhesion and in nucleation of metal clusters. Thus, identification and quantification of defect sites on oxide surfaces are important steps in the understanding of many catalytic reactions. Recently we have used several techniques to identify various defect sites on oxide surfaces including metastable impact electron spectroscopy (MIES), water and CO-temperature programmed desorption (TPD), MIES of adsorbed Xe (MAX), and electron energy loss spectroscopy (EELS). MIES data for MgO(100) and SiO2 thin films are very sensitive to extended defect sites as well as point defect. Point defects result in the appearance of band gap states, whereas extended defects cause broadening of the O(2P) band. MAX data change significantly with increasing defect densities for various oxide surfaces. The adsorption of D2O and CO also has been used to identify various defect sites since their TPD spectra change significantly in the presence of defect sites. Recent EELS data acquired for low and highly defective oxide surfaces will also be discussed.

11:20am SS2-MoM10 Polar ZnO(0001)-Zn and ZnO(000-1)-O Surfaces: Geometric and Electronic Structure, Stabilization Mechanisms, O. Dulub*, U. Diebold, Tulane University

The geometric and electronic structure of the (0001)-Zn and (000-1)-O polar surfaces of ZnO were studied with Scanning Tunneling Microscopy (STM) and Spectroscopy (STS), as well as Low Energy Electron Diffraction (LEED). Sharp (1x1) LEED patterns were recorded for both surfaces. The STM images of the ZnO(0001)-Zn surface reveal flat triangular terraces of single step height (~2.6 Å), exhibiting two domains rotated by 180 degrees with respect to each other. STM shows a high density of triangular pits of various sizes and slightly rounded small holes. Triangular islands of different sizes were also observed on the terraces, and the smaller ones exhibit size-dependent special shapes. STM images from the O-terminated (000-1) surface reveal a quite different morphology. The surface is composed of flat, well ordered terraces without pits or added small islands. The terraces are separated mainly by double-layer high step edges (~5.2 Å) that include an angle of 120 degrees. STS indicates a slightly (but reproducibly) different electronic structure of the two polar surfaces. The filled states on the O-terminated face are shifted toward the Fermi level. Based upon the STM and STS results, two stabilization mechanisms are proposed for (0001)-Zn and (000-1)-O surfaces. A charge transfer from the O to the Zn-terminated surface makes the latter more metallic. Since metallic Zn is known to have an extremely high vapor pressure even at low temperatures, it possibly evaporates off the surface. Depleting the Zn-terminated surface of 1/4 of zinc atoms removes the infinite dipole moment and therefore stabilizes the crystal. The special shapes of the smallest ('magic') islands observed in STM images of the (0001)-Zn surface are consistent with the proposed model.

11:40am SS2-MoM11 The Polar O-ZnO(000-1) Surface: Stability and Interaction with Hydrogen, *M. Kunat*, *St. Gil Girol*, *U. Burghaus*, *Ch. Wöll*, Ruhr-University Bochum, Germany

The question about the stability of the polar surfaces of zinc oxide has been the topic of many experimental and theoretical investigations. Here we report on an investigation using the highly surface sensitive method of Heatom scattering (HAS). The clean, H-free surface shows (1x3) superlattice spots in He-atom diffraction scans. This finding is in contrast to previous work¹ where the presence of a (1x1) overlayer was found, but is in agreement with Taskers rule,² which predicts instabilities for polar oxide surfaces. After optimizing the preparation conditions for the O-ZnO(000-1) surface, in particular by employing annealing in an oxygen atmosphere, we were able to observe weak (1x3) spots not only with HAS but also in low energy electron diffraction (LEED). Exposure to hydrogen atoms leads to the disappearance of the (1x3) overlayer spots and the formation of a welldefined (1x1) diffraction pattern in both HAS and LEED, similar to the case of the Zn-ZnO(0001) surface previously studied in our laboratory.³ The formation of the H-atom overlayer is accompanied by a shoulder in the O1s XPS data, indicating the formation of OH-species. In addition first results of sticking coefficients of carbon monoxide as a function of hydrogen preexposure will be discussed.

¹ A. Wander, F. Schedin, P. Steadman, A. Norris, R. MCGrath, T.S. Turner, G. Thornton, and N.M. Harrison, Phys. Rev. Lett. 86 (2001) 3811.

² P.W. Tasker, J. Phys. C: Solid State Phys. 12 (1979) 4977.

³ Th. Becker, St. Hövel, M. Kunat, Ch. Boas, U. Burghaus, and Ch. Wöll, Surf. Sci. 486 (2001) L502.

* Morton S. Traum Award Finalist

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