

Surface Science Division Room 309 - Session SS2-ThM

Oxide Surface Chemistry

Moderator: S. Joyce, Battelle Pacific Northwest for USDOE

8:20am SS2-ThM1 Coadsorption Studies with Water: a Small Step Toward Understanding the Surface Chemical and Photochemical Properties of TiO₂, M.A. Henderson, Pacific Northwest National Laboratory; **W.S. Epling, C.H.F. Peden,** Pacific Northwest National Laboratory; **U. Diebold,** Tulane University **INVITED**

Perhaps the most prevalent surface species on an oxide surface in any environment or application is water. Depending on the conditions this molecule can be present on oxide surfaces as dissociation fragments (hydroxyls), as molecularly adsorbed species, as a thin physisorbed layer or as a bulk solid/liquid interface. The prevalence of water at oxide surfaces may lead one to think that its role in surface chemistry on oxides, such as TiO₂, is mostly that of a spectator. Although this appears to be the case in the UHV surface chemistry of more strongly bound species such as formate or methanol on TiO₂(110), water has a significant influence on more weakly bound species. This influence leads to interesting chemistry if defect sites are present. After a brief description of the properties of water on TiO₂(110), results will be presented for the formation of bicarbonate from coadsorption of water and carbon dioxide at oxygen vacancies, and for the reaction of molecular oxygen with bridging hydroxyl groups at oxygen vacancies. These results provide insights into photochemical oxidation and reduction processes occurring on titanium dioxide. ^{Footnote 2} ^{FootnoteText} ^{Footnote 1} PNNL is a multiprogram national laboratory operated for the U.S. DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.) 2. This work was funded by the DOE office of Basic Energy Sciences, Materials Sciences, and the DOE Environmental Management Science Program.

9:00am SS2-ThM3 HCl Adsorption and Desorption on a Single-Crystal @alpha-Al@sub 2@O@sub 3@ (0001) Surface, C.E. Nelson, J.W. Elam, S.M. George, University of Colorado, Boulder

The adsorption and desorption of HCl on a single-crystal @alpha-Al@sub 2@O@sub 3@ (0001) surface were examined using laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) techniques. @alpha-Al@sub 2@O@sub 3@ (0001) models Al@sub 2@O@sub 3@ particles generated by solid rocket motors and HCl interactions with these Al@sub 2@O@sub 3@ particles may affect the stratospheric ozone layer. The initial sticking coefficient for HCl on @alpha-Al@sub 2@O@sub 3@ (0001) at 298 K was $S \sim 10^{-3}$. The HCl sticking coefficient decreased nearly exponentially with HCl coverage and the HCl coverage saturated at $\theta_{\text{HCl}} = 0.10 \times 10^{10} \text{ super } 15 @ \text{ molecules/cm}^2 @ \text{ after HCl exposures of } > 10 @ \text{ super } 10 @ \text{ Langmuir}$. HCl desorption from the @alpha-Al@sub 2@O@sub 3@ (0001) surface occurred over a temperature range from 300 K to 650 K. This broad range suggests a distribution of surface sites with different binding energies. HCl desorption results versus HCl coverage prepared by progressively annealing a fully exposed @alpha-Al@sub 2@O@sub 3@ (0001) surface confirmed a wide range of binding energies. Additional HCl desorption results versus HCl coverage prepared by varying the HCl exposure revealed that HCl dissociative adsorption randomly fills adsorption sites independent of their adsorption energy. These results also suggest that surface diffusion between the adsorption sites must be negligible. Modeling of the desorption results was consistent with surface site energies that range from 19 to 36 kcal/mole. These adsorption and desorption results predict that HCl will be stable on @alpha-Al@sub 2@O@sub 3@ rocket exhaust particles at stratospheric temperatures and pressures.

9:20am SS2-ThM4 Dissociative Adsorption and Electron Stimulated Desorption of Cl on TiO₂(110) Studied by STM, AES and ISS, U. Diebold, Tulane University; **G. Leonardelli,** TU Vienna, Austria; **W. Hebenstreit,** Tulane University; **M. Schmid, P. Varga,** TU Vienna, Austria

The catalytic reactivity of a metal oxide can be significantly altered by adsorbed halogen species, but little is known about the adsorption of chlorine on well-characterized model oxide surfaces. We present a combined study of atomically-resolved Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES) and Ion Scattering Spectroscopy (ISS) of chlorine adsorption on TiO₂(110). Chlorine was dosed from a calibrated electrolytic AgCl cell at room temperature. STM reveals a

dissociative adsorption process. For small doses ($\leq 0.01 \text{ Cl atoms/unit cell}$), a large average separation (26 Å) between Cl-Cl pairs indicate that adsorption energy is transformed into kinetic energy of the Cl atoms. The saturation coverage for an annealed surface is 0.3 Cl/unit cell. STM does not show any preferred adsorption at step edges, kink sites or oxygen defect sites. Chlorine atoms can be desorbed from the surface with STM by scanning at sample bias voltages $\geq +4 \text{ V}$. AES measurements are complicated by electron stimulated desorption of the Cl atoms. The desorption cross section is $3 \times 10^{-20} \text{ cm}^2$ for a sputtered surface and $> 2 \times 10^{-17} \text{ cm}^2$ for an annealed surface. ISS (He⁺ ions 1keV, scattering angle 90°) detects Cl only after adsorption on a sputtered surface, while the ISS signal of an annealed surface remains unchanged during adsorption of chlorine.

9:40am SS2-ThM5 Photocatalytic Dehydrogenation of 2-Propanol on TiO₂(110), D. Brinkley, T. Engel, University of Washington

The use of TiO₂ as a photocatalyst is not well understood at a fundamental level in environmental remediation. We have investigated the thermal and photocatalytic oxidation of small oxygen containing molecules on TiO₂ single crystal surfaces using modulated molecular beam techniques. The role of specific surface orientations, defect sites and densities, oxygen sources, surface temperature, and reaction mechanisms on the reaction probability of incident molecules are essential issues that must be understood in order to maximize the efficiency of TiO₂ as a photocatalyst. For the specific case of 2-propanol on TiO₂(110), we found that the total probability for a thermal reaction is less than 0.03 for a single collision of an incident molecule with the surface. The major and minor products in the thermal reaction are propene and acetone respectively. The reaction probability can be increased to 0.15 in the presences of bandgap radiation and molecular oxygen on a sample which has been preannealed in vacuum to create oxygen vacancies. The increase in reactivity is due entirely to the dehydrogenation channel of the reaction. Even a fully oxidized TiO₂(110) surface has a reaction probability of 0.08 under the same conditions. The steady state reaction yield for this system is maximized at a temperature of 350 K, with an appreciable reaction rate between 250 K and 600 K. The yield is limited by desorption of acetone below 300 K and by the decrease in the surface coverage of the reactants above 400 K. The low thermal reactivity and the significant photochemical reactivity is attributed to free radical reactions initiated through electron trapping by adsorbed molecular oxygen. Our results suggest that the reaction proceeds primarily through a mechanism in which holes are trapped by undissociated 2-propanol molecules. Studies on TiO₂(100) are currently underway and a comparison of the reactivity of this orientation with that of the (110) surface will be presented.

10:00am SS2-ThM6 Photo-stimulated NO Adsorption on Metal Oxides, E.R. Blomiley, E.G. Seebauer, University of Illinois, Urbana

Coal combustors generate large quantities of NO_x compounds that face increasingly stringent regulation. Current NO removal technologies depend in part on selective catalytic reduction (SCR) processes that react NO with reductants like CO or NH₃ at high temperature. The high costs of reheating the flue gas over the catalyst and problems with slip of the reductant past the reactor have stimulated searches for alternative technologies. Here we examine the surface photochemistry underlying one particularly novel alternative: injection of an inexpensive semiconducting metal oxide (like Fe₂O₃) in an illuminated flue geometry in order to stimulate photoadsorption. The NO-laden particulates are then removed in an electrostatic precipitator. We have shown in high and low-pressure experiments that while pure iron and titanium oxides are inactive for NO removal, iron oxides supporting adsorbed Cl display significant activity even at room temperature. The presence of such activity is surprising, and appears to result from a complex interaction between the underlying semiconductor, the adsorbed Cl, weakly adsorbed water, and the photogenerated charge carriers. The activity remains surprisingly robust even in the presence of active gaseous species like SO₂. Temperature-programmed desorption reveals that some of the NO desorbs essentially reversibly, some forms NO₂, and the remainder desorbs intact while the substrate decomposes by volatilization of iron chlorides. The potential for such reactions to influence tropospheric NO_x chemistry in urban areas will be discussed.

Thursday Morning, November 5, 1998

10:20am **SS2-ThM7 The Reaction of H@sub 2@S, S@sub 2@ and SO@sub 2@ with ZnO and Cu/ZnO Surfaces**, *S. Chaturvedi, J.A. Rodriguez, T. Jirsak, J. Hrbek, M. Kuhn*, Brookhaven National Laboratory

The surface chemistry of H@sub 2@S, S@sub 2@ and SO@sub 2@ on polycrystalline ZnO and Cu/ZnO surfaces was investigated using synchrotron-based photoemission and ab initio SCF calculations. At 100 K, polycrystalline ZnO dissociates H@sub 2@S into HS, and the adsorbed HS species decompose at temperatures between 300 and 400 K leaving S atoms that are bonded to zinc sites of the oxide. By dosing S@sub 2@ to zinc oxide, one can generate a sulfur saturation coverage (0.7 ML) that is larger than that obtained after dosing H@sub 2@S (0.5 ML) and induce the formation of small amounts of SO@sub 3@ species on the surface. Possible reaction pathways for the dissociation of S@sub 2@ on ZnO(0001) and ZnO(1010) terraces were studied using ab initio SCF calculations. At low sulfur coverages, an adsorption complex in which S@sub 2@ is bridge bonded to two adjacent Zn atoms (Zn-S-S-Zn) is probably the precursor state for the dissociation of the molecule. H@sub 2@S and S@sub 2@ mainly react with the zinc sites of the oxide. In contrast, SO@sub 2@ preferentially bonds to oxygen forming a mixture of SO@sub 3@ and SO@sub 4@ at 100 K and pure SO@sub 4@ at 300 K. Results from ab initio SCF calculations indicate that SO@sub 2@ adsorbs on an oxygen site to form SO@sub 3@ which then extracts an oxygen from the ZnO lattice to form SO@sub 4@. The last step in this process has a substantial activation energy, and after dosing SO@sub 2@ to ZnO at 100 K a mixture of SO@sub 3@ and SO@sub 4@ is produced on the surface. Cu two-dimensional islands supported on ZnO show a band structure that is substantially different from that of pure metallic copper. The Cu/ZnO surfaces exhibit a reactivity towards H@sub 2@S and S@sub 2@ that is larger than that of ZnO but smaller than that of metallic copper.

10:40am **SS2-ThM8 Methanol Adsorption and Reactivity at U and UO@sub 2@ Surfaces**, *M.T. Paffett, J.A. Lloyd*, Los Alamos National Laboratory

In specific actinide materials storage situations it has been often observed that deleterious hydrocarbon interactions at actinide oxide surfaces have lead to a buildup of potentially explosive gases (usually H@sub 2@) arising from predominately radiolytic effects. Much less emphasis however, has been given to the deleterious consequences of unforeseen catalytic or reactive chemical events, arising from the storage of actinides and actinide oxides in mixed waste (actinides with organic solvents). In this vein we are seeking to unravel some of the fundamental details of reactive surface chemistry at model actinide oxide surfaces. In this study, the interaction of methanol-d (CH@sub 3@OD) with U and UO@sub 2@ surfaces has been studied using x-ray photoelectron spectroscopy (XPS), thermal desorption-mass spectrometry (TDMS), and secondary ion mass spectrometry (SIMS) over the temperature range of 90-500K. Low temperature (90 K) adsorption on uranium resulted in formation of methoxy species along with condensed phase adsorbed methanol. Room temperature (300K) adsorption on uranium produces only methoxy species, uranium carbide and uranium oxide. Heating to 400K completely decomposes the adsorbed methoxy species: 25% desorbing as methane and the remaining methoxide irreversibly converting to uranium oxycarbide (UO@sub 0.7@C@sub 0.3@). Concomitant with these C fragment conversion processes, desorption of hydrogen and deuterium is also seen over a wide temperature regime. Methanol-d adsorption on UO@sub 2@ also produces a methoxy surface species at surface temperatures < 150K and submonolayer exposure. Adsorbate decomposition following thermal desorption releases gaseous CH@sub 4@, H@sub 2@, HD, and D@sub 2@. Oxygen derived from the methanol molecule was incorporated into the UO@sub 2@ layer. The reactive adsorption and thermal decomposition of methanol at U and UO@sub 2@ surfaces is compared with that observed at other metal and metal oxide surfaces.

11:00am **SS2-ThM9 The Chemistry of CeO@sub 2@(001) and Ce@sub 1-x@Zr@sub x@O@sub 2@(001) Studied by Mass-Spectroscopy of Recoiled Ions**, *G.S. Herman, Y. Gao, C.H.F. Peden*, Pacific Northwest National Laboratory

Ceria has found considerable use in automotive catalytic converters due to its oxygen storage properties. Ceria can provide oxygen under fuel-rich conditions, to reduce CO and hydrocarbon emissions, and remove oxygen under fuel-lean conditions, to reduce NOx emissions. The addition of zirconium to ceria has been found to improve the oxygen storage properties and increase the stability of the ceria particles. We have used the technique of mass-spectroscopy of recoiled ions (MSRI) to investigate the interaction of O@sub 2@, D@sub 2@, and D@sub 2@O with CeO@sub 2@(001) and Ce@sub 1-x@Zr@sub x@O@sub 2@(001) (x<0.20)

films grown by plasma-assisted molecular beam epitaxy. The MSRI technique is extremely surface sensitive, probing the composition in the very topmost atomic layers. By using the temperature programmed mode of MSRI we were able to measure the corresponding signals for @super 18@O@sub 2@, D@sub 2@, and D@sub 2@O to monitor the adsorption, desorption and dissolution of these species. In the temperature range from 300-1000 K, we have found that the O signal increases linearly with temperature for all three molecules. The Ce signal, however, varies considerably over this temperature range depending on the molecular species. The results for the pure ceria and mixed ceria/zirconia films will be compared.

11:20am **SS2-ThM10 Reduction of Trace Element Contaminants in Aqueous Solution by Iron and Iron Oxides**, *S.R. Qiu, H.-F. Lai, J.A. Yarmoff, C. Amrhein, M.J. Roberson, M. Hunt*, University of California, Riverside

Irrigation drainage and wastewater often contain elevated levels of trace oxyanions and oxyanions, such as selenate, chromate and uranyl, which can be detrimental to humans and wildlife. A potential remediation method is to reduce the contaminants to less mobile forms by reacting the water with zero-valent iron. In this reaction, the iron serves as both an electron source and a catalyst. Most previous studies of this system were limited to the simulation of field work on a macroscopic scale. Consequently, little is known about the basic chemical interactions of these toxic ions at the water-metal interface. Our objective is to determine the microscopic reaction mechanisms by combining surface science methods and bulk chemical studies. Our bulk studies have indicated that the reactions are first-order. For surface studies, iron foil is first prepared in a UHV chamber by sputtering, or iron oxides are prepared by exposure of a hot Fe foil to O2 in UHV. The sample is then transferred to an aqueous solution containing the relevant ions. The pH and amount of dissolved oxygen in the solution are carefully controlled. The reacted surfaces are then characterized in UHV by surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) or scanning tunneling microscopy (STM). We find that films of partially reduced Se, Cr and U are formed by the reaction. The reduction of U is very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. The details of the surface reduction reaction mechanisms will be presented, and the implications of our results on the practical deployment of this remediation method will be discussed.

11:40am **SS2-ThM11 Formation of Nitro-PAH on Flyash Particle Surfaces: The Significance of Particle Substrate on PAH Nitration**, *G.S. Strossman, T.F. Fister, R.W. Odom*, Charles Evans & Associates; *R.W. Linton*, University of North Carolina, Chapel Hill

Polycyclic aromatic hydrocarbons (PAH) are present in the atmosphere in both the gas phase and condensed onto particle surfaces. Coal flyash particles are an important source of condensed PAH since both are byproducts of coal combustion. Many PAHs are hazardous in their own right due to their carcinogenic or mutagenic nature; however another factor to be considered is the transformation of PAH into potentially more harmful analogues during their exposure to the atmosphere. One example is the formation of nitro-PAH after exposure of the parent PAH to atmospheric NO@sub 2@. A full understanding of these reactions requires determining how the near surface composition of flyash particles can affect the rate of nitration of adsorbed PAH. The PAH studied in this work was benzo[a]pyrene (BaP). BaP was chosen for its reactivity and because its size (5 rings) makes it likely to exist in the atmosphere primarily in the condensed phase. Submonolayer coverages of BaP on four different flyashes were exposed to NO@sub 2@ in both dry air and with different levels of relative humidity. The samples were analyzed by TOF-SIMS, a technique that can both obtain surface elemental information and detect low levels of organic molecular species on single particles in the 3-10 @micron@ range. The results show a distinct relationship between the particle compositions and the formation of nitro-BaP, both macroscopically and among individual particles within a single flyash sample. Furthermore, for two Class C (calcium-rich) flyashes, the role played by the substrate is distinctly different between dry air and humid air exposures, while for a class F flyash (high Al, Si and Fe, low Ca) no such difference is observed.

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