

# Thursday Afternoon, November 6, 2003

## Surface Science

### Room 328 - Session SS-ThA

#### Oxide Reactions and Catalysis

Moderator: A. Klust, Tulane University

#### 2:00pm SS-ThA1 Atomic Understanding of Strong Nanometer-Thin Metal/Alumina Interfaces and the Making of Nanoscale Island and Film Catalysts, D.R. Jennison, T.R. Mattsson, Sandia National Laboratories

Chambers, Droubay, Jennison, and Mattsson [Science 297 (2002) 827] recently reported room temperature laminar growth of Co deposited in vacuum from an evaporation source on fully hydroxylated but otherwise clean  $\alpha\text{-Al}_2\text{O}_3$  (0001). We extend this work to a number of metals using density functional (DFT) calculations. The exothermicity of the suggested core reaction,  $2\text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}^{2+}$ , where M represents any metal, is investigated for Cr, Fe, Ni, Cu, Mo, Ru, Rh, Pd, and Al. We find that this reaction is strongly exothermic for most metals. However, while Rh is slightly endothermic, it has a sufficient heat of adsorption to react immediately upon contact. The behavior of Cu cannot be determined within the current accuracy of DFT. Pd is strongly endothermic, suggesting noble metals will not react. By first-principles molecular dynamics simulations of Rh, we confirm a substantial likelihood for direct "hot" reactions driven by the heat of adsorption, as originally proposed. However, Rh has two reaction barriers, indicating more complex kinetics than with Co. Now 1-2 ML films may be made and also nano-islands with steps, both having potential catalysis applications. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### 2:20pm SS-ThA2 Potassium Adsorption on Thin Film Cerium Oxide and Its Effect on Supported Rhodium Activity, D.R. Mullins, Oak Ridge National Laboratory

We have examined the adsorption of K on  $\text{CeO}_2$  thin films and its effect on the adsorption of CO on Rh supported on the  $\text{CeO}_2$ . The K saturation coverage, i.e. the maximum coverage achievable before the onset of multilayer desorption, is ca.  $1 \times 10^{15} \text{ cm}^{-2}$ . This is about twice what has been observed on Rh(111). It is similar to the  $\text{CeO}_2$  (111) surface density of  $0.8 \times 10^{15} \text{ cm}^{-2}$ . The K exhibits three distinct desorption states near 450K, 600 K and 700 K. The K 2p core-level photoemission does not indicate a significant change in binding energy or the presence of multiple K states as a function of annealing temperature and coverage. CO dissociates when adsorbed on Rh on reduced  $\text{CeO}_x$ . It is of interest to determine whether charge transfer from K to  $\text{CeO}_2$  will also cause CO dissociation on Rh supported on  $\text{K/CeO}_2$ . CO desorbs from Rh on fully oxidized  $\text{CeO}_2$  below 500 K and shows little evidence of O exchange with the ceria. The desorption is similar to CO on Rh(111). When K is present, the CO desorption occurs between 600 K and 700 K and shows considerable O exchange with the support. The high temperature desorption is similar to what was observed on  $\text{K/Rh(111)}$  which was ascribed to an interaction between the K and the CO. The high temperature desorption and O exchange are also similar to what has been observed for dissociated CO on Rh supported on reduced  $\text{CeO}_x$ . For the system  $\text{CO/Rh/K/CeO}_2$ , there is no evidence of CO dissociation as indicated by the C 1s photoemission. The C 1s photoemission does indicate the formation of surface carbonates. Carbonates were not observed on either  $\text{K/Rh(111)}$  or  $\text{Rh/CeO}_x$ . @FootnoteText@ @footnote 1@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.

#### 2:40pm SS-ThA3 The Interaction of Methyl Iodide with Surface Defects on $\text{UO}_2$ (100), J. Stultz, S.A. Joyce, M.T. Paffett, Los Alamos National Laboratory

Actinide materials undergo thermal and non-thermal reactions with adsorbed molecules resulting in chemical transformations leading to degradation and gas generation. In most handling and processing scenarios actinide materials readily oxidize forming an actinide oxide interface. Evidence suggests that unique chemistry occurs and may possibly be driven by surface defect sites at these oxide interfaces. To characterize these interactions and possibly quantify surface defect sites, the thermal

reactivity of  $\text{CH}_3\text{I}$  with a well annealed and sputter defected  $\text{UO}_2$  (100) surfaces was investigated. XPS results indicate  $\text{CH}_3\text{I}$  undergoes dissociative adsorption on  $\text{UO}_2$  (100) at 300K in which I reacts and adsorbs selectively at defect sites leaving little or no residual carbon on the surface. Semi-quantification of surface defects was achieved by analysis of the XPS results for moderately high surface defect densities. Low temperature TPD results indicate mono and multilayer  $\text{CH}_3\text{I}$  desorption characteristics similar to that seen for other metal oxide systems. Additionally, low intensity features in the TPD data suggest trace levels of oxidation of residual surface carbon to form formic acid. LA-UR-03-2698.

#### 3:00pm SS-ThA4 Thermal and Radiation-Induced Chemistry of Water on Uranium Dioxide Surfaces, J. Stultz, M.T. Paffett, S.A. Joyce, Los Alamos National Laboratory

Most plans for the disposition of surplus nuclear materials involve storage in sealed containers where the evolution of gases from reactions of adsorbed water could present both pressure and flammability hazards. In order to better understand the relative importance of the thermal- and radiation-induced chemistry, we have studied the interactions of water on single crystals of uranium dioxide. Temperature programmed desorption and electron stimulated reaction/desorption are used to examine the chemistry. In the absence of radiation, water adsorbs/desorbs molecularly on nominally pristine oxide surfaces with a binding energy of only a few kcal/mole greater than water with itself. The strength of this interaction is large enough to indicate that  $\text{UO}_2$  surfaces handled outside the driest of environments will be covered with water. External low energy electron irradiation is used to simulate the effects of radiolytic chemistry induced by decay particles. The principle neutral gaseous radiolytic products are  $\text{H}_2$ ,  $\text{O}_2$ , and water. The relative yields are strongly dependent on temperature and coverage. Ion desorption, which is often sensitive to minority species, indicates that surface hydroxyls, presumably formed at defect sites, are stable up to high temperatures (~600K).

#### 3:20pm SS-ThA5 Gas Sensing Mechanism of $\text{SnO}_2$ , M. Batzill, B. Katsiev, Tulane University; A. Chaka, National Institute of Standards and Technology; U. Diebold, Tulane University

Stannic oxide is widely used as a gas sensing material for reducing and oxidizing gases. Variations in the surface oxygen concentration of metal-oxide gas sensors play an important role for explaining their response to a change in the surrounding gas phase. Here we show for different low index  $\text{SnO}_2$  surfaces that non-stoichiometric surface terminations are favored at a low oxidation potential of the environment (e.g. UHV conditions). Under such conditions the low-energy (110) surface forms complex surface reconstructions in order to accommodate the loss of surface oxygen. The (101) and (001) surfaces, on the other hand, retain bulk terminations for both stoichiometric and reduced surfaces. The stability of these surfaces is explained on ground of the dual valency of Sn (SnII and SnIV) and the rutile-structure of  $\text{SnO}_2$  that allow the (001) and (101) surfaces to attain a  $\text{Sn}^{2+}\text{O}^{2-}$  stoichiometry by removal of bridging oxygen atoms. The surface structures have been determined by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). For reduced surfaces, angle resolved UPS was employed to characterize the dispersion of the surface electronic states. The variation of the surface composition has been measured by temperature programmed ion scattering spectroscopy. The experimental results are verified by density functional theory calculations that show the stability of different surface phases as a function the oxygen chemical potential. This variable surface composition accompanied by a change in the electronic structure is proposed to be the fundamental process of the gas sensing mechanism for  $\text{SnO}_2$ .

#### 3:40pm SS-ThA6 Photoinduced Reaction Dynamics of Halocarbon Adlayers on the $\text{Fe}_3\text{O}_4$ (111)-(2x2) Selvege of $\text{Fe}_2\text{O}_3$ (0001), G.G. Totir, Y. Le, R.M. Osgood, Jr., Columbia University

Electron transfer reactions on surfaces play a key role in electrocatalysis and in photoinduced processes in surface-adsorbate systems. More recently, interest in understanding the reactivity of iron oxides toward halogenated hydrocarbons has been stimulated by applications in catalysis and environmental decontamination procedures. We used time-of-flight (TOF) and temperature programmed desorption (TPD) to study the electron transfer reaction dynamics and photochemistry of halocarbons on surface reconstructed single crystal hematite,  $\text{Fe}_2\text{O}_3$  (0001). For example, TPD spectra recorded at various coverages of methyl iodide adsorbed at 100 K on the magnetite,  $\text{Fe}_3\text{O}_4$ , termination of single crystal hematite,

# Thursday Afternoon, November 6, 2003

indicate a rich surface chemistry, with multiple desorption events, similar to results previously obtained for other adsorbates on the same surface. Furthermore, angle-resolved TOF results for monolayer coverage of methyl iodide on Fe<sub>3</sub>O<sub>4</sub> (111)-(2x2) indicated that the methyl fragments produced from dissociative electron attachment were ejected at an angle of ~ 0° with respect to the surface normal. Post-irradiation desorption spectra for methyl iodide and carbon tetrachloride on the magnetite surface, and results discussing adsorbate orientation and coverage dependence will be presented.

**4:00pm SS-ThA7 Photo-oxidation of Trimethyl Acetic Acid on the Surface of TiO<sub>2</sub>(110), M.A. Henderson, J. Szanyi,** Pacific Northwest National Laboratory; *J.M. White*, University of Texas, Austin

TiO<sub>2</sub> has received considerable attention for its use as a photocatalyst in the destruction of organics. Complexities associated with microcrystalline TiO<sub>2</sub> (e.g., identification of surface active sites and intermediates) often hamper mechanistic study of the step-by-step conversion of organics into CO<sub>2</sub>. In an attempt to address mechanistically the photo-oxidation of organics on TiO<sub>2</sub>, we employ rutile TiO<sub>2</sub>(110) as a model photocatalyst and trimethyl acetic acid (TMAA) as a model organic. A saturation exposure of TMAA at 300 K results in dissociation of the acid O-H bond to form bidentate trimethyl acetate (TMA) and OH groups at the bridging anion sites. In TPD, recombination of TMA and OH to form parent occurs between 300 and 550 K, along with water from OH combination and some TMA decomposition to isobutane and isobutene. However, the majority of the TMA adlayer decomposes to CO and isobutane/isobutene at 650 K. UV exposure was performed at 110 K in order to capture intermediates during photolysis, subsequently analyzed in TPD. UV exposure in the absence of O<sub>2</sub> results in rapid conversion of the species responsible for the 300-550 K TPD states into acetate groups. In contrast, the TMA species responsible for the 650 K TPD states are converted into isobutene/isobutene and CO<sub>2</sub> by cleavage of the C-COO bond. Inclusion of O<sub>2</sub> does not affect the rate of acetate formation, but accelerates the conversion of the 650 K TMA into isobutene/isobutane. Evidence has been found for the continued photo-oxidation of the C<sub>4</sub> daughter products into C<sub>3</sub> species. These reactions do not appear to be wavelength dependent for photons with energies in excess of the TiO<sub>2</sub> bandgap. Based on these results, we propose that products of hole trapping on TMA depend on the structural environment of the adlayer, and that a limited amount of electron trapping permits some degree of photochemistry in the absence of O<sub>2</sub>.

**4:20pm SS-ThA8 The Origin of Photo-induced Hydrophilicity on TiO<sub>2</sub> Surfaces: Photo-generation of Surface Oxygen Vacancies or Photo-oxidation of Adsorbed Organics?, J. Szanyi, M.A. Henderson,** Pacific Northwest National Laboratory; *J.M. White*, University of Texas, Austin

Since the discovery of the photocatalytic nature of TiO<sub>2</sub> in the 1970s, significant efforts have been made to understand both the properties of the oxide material itself and the catalytic processes that occur on its surfaces. In recent years the photo-induced hydrophilic nature of TiO<sub>2</sub> has been discovered and studied. The hydrophilic behavior continues after removal of the light, but gradually degrades to the pre-irradiation conditions. Most of the original work from Japan suggests that hydrophilicity and photo-oxidation of surface organic contaminants are unrelated properties of TiO<sub>2</sub>. They propose UV generated oxygen defect sites on the TiO<sub>2</sub> surface as the origin of hydrophilicity. In turn, the oxidation of oxygen vacancies by O<sub>2</sub> in the air has been proposed as the mechanism for the slow degradation of hydrophilicity of a TiO<sub>2</sub> surface. In order to understand the origin of photo-induced hydrophilicity of TiO<sub>2</sub>, we have studied the adsorption of water on a clean and trimethyl acetic acid covered TiO<sub>2</sub>(110) surface under carefully controlled experimental conditions. TPD of H<sub>2</sub>O suggests that irrespective of the presence or absence of vacancies, water wets the TiO<sub>2</sub> surface as evidenced by the sequential filling of monolayer, second layer and multilayer states as a function of increasing coverage. On the other hand, the monolayer water TPD state is absent for water adsorbed on a TiO<sub>2</sub>(110) surface pre-saturated with trimethyl acetate (TMA) species, formed from decomposition of the acid. Exposure of the TMA adlayer to UV light in 5x10<sup>-6</sup> torr O<sub>2</sub> results in nearly complete photo-oxidation of the organic and restoration of the ability of the surface to directly bind water. In this presentation, based on these molecular-level UHV studies, we propose that the origin of photo-induced hydrophilicity on TiO<sub>2</sub> surfaces is likely due to photo-oxidation of adsorbed organics that create a hydrophobic monolayer.

**4:40pm SS-ThA9 The Adsorption and Reaction of NO on Single Crystal Titanate (TiO<sub>2</sub> and SrTiO<sub>3</sub>) Surfaces, C.H.F. Peden, S. Azad, M.H. Engelhard, M.A. Henderson, J. Szanyi, L.-Q. Wang,** Pacific Northwest National Laboratory

The control of NO<sub>x</sub> (NO and NO<sub>2</sub>) emissions from combustion processes, including vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion), where the need is to selectively reduce NO<sub>x</sub> with a reductant in a large background of the competing oxidizing species, O<sub>2</sub>. A wide variety of oxide materials, including zeolites, are known to be effective for selective catalytic reduction of NO<sub>x</sub> from the exhaust of 'lean-burn' engines. As such, there has been much interest for some time in determining the kinetics of adsorption and surface reactions of NO and NO<sub>2</sub>, as well as identifying the composition and structure of the mechanistically important adsorbed NO<sub>x</sub> species on this class of catalytic materials. In this presentation, we will discuss selected results from our ongoing studies aimed at addressing some of the considerable remaining uncertainties about these processes. In particular, we will compare and contrast the results of our temperature programmed desorption (TPD) and x-ray photoemission spectroscopy (XPS) studies of NO adsorption on single crystal TiO<sub>2</sub> and SrTiO<sub>3</sub> surfaces. Both weakly adsorbed NO and the reaction product, N<sub>2</sub>O, were observed in TPD from TiO<sub>2</sub>(110). The N<sub>2</sub>O is formed from an 'NO-like' species identified with XPS. However, NO is the only desorption product from a SrTiO<sub>3</sub>(100) surface. @FootnoteText@ @footnote 1@M. Shelef and R.W. McCabe, Catal. Today 62 (2000) 35. @footnote 2@The work was carried out at Pacific Northwest National Laboratory (PNNL) and funded by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Divisions of Chemical Sciences and Materials Sciences. Experiments were performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility located at PNNL and supported by the DOE's Office of Biological and Environmental Research.

**5:00pm SS-ThA10 An FTIR Study of Methanol, Water and Acetic Acid on MgO(100) Under Ambient Conditions, M.C. Foster,** University of Massachusetts

We have investigated the interactions occurring between the MgO(100) surface and a series of small molecules, namely water, methanol and acetic acid. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. The adsorbate of interest is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. Photometry then allows for the quantitative determination of adlayer coverages from absorbance measurements using a modified Beer-Lambert Law. The substrates have also been inspected with atomic force microscopy (AFM) both before and after each series of experiments. The interactions of these adsorbates with MgO(100) under room temperature conditions and pressures on the order of 10 Torr vary from physisorbed, as is the case with methanol all the way up to dissociatively chemisorbed, as is the case with acetic acid resulting in the formation of magnesium acetate under these experimental conditions.

## Author Index

### Bold page numbers indicate presenter

— A —

Azad, S.: SS-ThA9, 2

— B —

Batzill, M.: SS-ThA5, **1**

— C —

Chaka, A.: SS-ThA5, 1

— D —

Diebold, U.: SS-ThA5, 1

— E —

Engelhard, M.H.: SS-ThA9, 2

— F —

Foster, M.C.: SS-ThA10, **2**

— H —

Henderson, M.A.: SS-ThA7, **2**; SS-ThA8, 2; SS-

ThA9, 2

— J —

Jennison, D.R.: SS-ThA1, **1**

Joyce, S.A.: SS-ThA3, 1; SS-ThA4, **1**

— K —

Katsiev, B.: SS-ThA5, 1

— L —

Le, Y.: SS-ThA6, 1

— M —

Mattsson, T.R.: SS-ThA1, 1

Mullins, D.R.: SS-ThA2, **1**

— O —

Osgood, Jr., R.M.: SS-ThA6, 1

— P —

Paffett, M.T.: SS-ThA3, 1; SS-ThA4, 1

Peden, C.H.F.: SS-ThA9, **2**

— S —

Stultz, J.: SS-ThA3, **1**; SS-ThA4, 1

Szanyi, J.: SS-ThA7, 2; SS-ThA8, **2**; SS-ThA9, 2

— T —

Totir, G.G.: SS-ThA6, **1**

— W —

Wang, L.-Q.: SS-ThA9, 2

White, J.M.: SS-ThA7, 2; SS-ThA8, 2