Tuesday Morning, October 30, 2012

Surface Science
Room: 21 - Session SS-TuM

Surface Reactivity of Oxides
Moderator: A.L. Utz, Tufts University

8:00am **SS-TuM1 Preparation, Characterization and Catalytic Activity of Model WO₃ Catalysts**, *Z. Dohnalek*, Pacific Northwest National Laboratory **INVITED**
Supported early transition metal oxides have important applications in numerous catalytic reactions. In our studies, conversion of small aliphatic alcohols to alkenes, aldehydes/ketons, and ethers is employed to probe the structure-activity relationships on model WO_3 catalysts. To understand how the structure and binding of WO_3 species affect catalytic properties we prepared a number of well-characterized systems. Direct sublimation of WO_3 solid was used to generate cyclic gas-phase ($WO_3)_3$ clusters. As shown in our matrix isolation experiments, sublimation leads to pure $(WO_3)_3$ clusters. The ($WO_3)_3$ clusters were embedded in alcohol matrices and their support-free chemistry was explored in subsequent temperature programmed reaction experiments. Model supported catalysts were created by depositing $(WO_3)_3$ clusters on $TiO_2(110)$ and $FeO(111)$ and subsequently characterized using scanning tunneling microscopy and surface sensitive spectroscopies. In other studies, epitaxial and nanoporous thin WO_3 films were prepared on $Pt(111)$. The catalytic chemistry of all the systems is compared and contrasted with that observed on unsupported $(WO_3)_3$ clusters. Calculations employing Density Functional Theory provide molecular-level mechanistic insight into the role structure and binding of $(WO_3)_3$ clusters to the support plays in determining their catalytic properties.

8:40am **SS-TuM3 EUV Photon Enhanced Oxidation of Carbonaceous Layer at a TiO₂ Film Surface**, *N.S. Faradzhev, J.T. Yates, Jr.,* University of Virginia, *S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology
We report the photo oxidation of a carbonaceous layer originally grown by 92 eV radiation-induced chemistry. The C film is supported on a surface of a nm thick amorphous TiO_2 film. Photo oxidation is achieved using various oxygen-containing molecules. The TiO_2 film mimics one of the possible protective layers of EUV Lithography optics, and the C film mimics optics contamination produced by 92 eV photons in a EUVL stepper apparatus. The C layer (~4 nm) is deposited by photodecomposition of the linear hydrocarbon molecule, *n*-tetradecane, using the NIST synchrotron ultraviolet facility (SURF III) in an UHV cell. The kinetics of C growth and C removal are monitored in real time using *in situ* single wavelength ellipsometric measurements. After each set of experiments, *ex-situ* XPS is used to detect the residual thickness of the carbonaceous film and the changes in its chemical state. We found that exposure to a vapor beam of several O-containing molecules has little or no effect on the C film in the dark. In the presence of EUV photons, the ability of these molecules to volatilize carbon as either CO or CO_2 increases significantly. The carbon removal rate increases with the partial pressure of the oxidizer. The substrate temperature has little effect on the carbon removal rate and this is in contrast to the rate of radiation-induced C growth that exhibits a very strong temperature dependence. The rate of removal of C depends upon the EUV irradiation and does not occur appreciably in the dark.

Although the studies are not finished yet, our results indicate that processes of C growth and C removal may proceed via different routes. In an earlier study, we found that during C growth, the hydrocarbon molecule arrives at the surface in its ground state and forms a weak bond to the bare or C-covered TiO_2 surface. The molecule is not trapped permanently and will thermally desorb within a characteristic time. It can also be either photo-desorbed or photo-decomposed to produce the carbonaceous film via direct (photo excitation) or indirect (secondary electron excitation, e.g. DEA) processes. For photo oxidation, the first step requires the formation of a strong bond of the oxidizer molecule to the surface. An oxidizer molecule will either arrive at the surface in an electronically excited molecular state or arrive in its ground state and find an EUV-activated long-lived electronically excited state at the surface. In both cases, the oxidizer molecule will stay on the surface for a sufficiently long time to decompose and react to produce a volatile product (e.g. CO).

This study is being performed as a part of EUVL Contamination cooperative research at NIST and UVA.

9:00am **SS-TuM4 Reactions of Water with Vacuum Fracture Surfaces of Sodium-Aluminosilicate Glass: Effects of Composition on Reactivity**, *K. Adib, J.E. Dickinson*, Corning Incorporated
We have synthesized different ternary SiO_2:Al_2O_3:Na_2O glasses containing bridging oxygens and non-bridging oxygens (NBO) and fractured them in ultrahigh vacuum to produce pristine surfaces. X-ray photoelectron spectroscopy of oxygen core levels and valence band were used to determine the fraction of non-bridging oxygens (SiONa) to bridging oxygens (SiOSi and SiOAl) on the vacuum fractured surfaces. For those glasses where the NBO fractions of the total oxygen were held constant, a 0.2 eV variance was observed in the binding energies of the NBO O1s core levels consistent with substantial changes, as a function of composition, in the ionicity of the bond between the NBO and sodium. The fracture surfaces were then exposed to partial pressures of H_2O at ambient temperature. It was observed that water reacts primarily with the NBO's to produce SiOH in place of SiONa. Non-bridging oxygens from glass compositions that contained less alumina had lower electron binding energy and were more likely to react with water. Molecular dynamics simulations were used to elucidate the role of H_3O^+ in the reaction of water with the non-bridging oxygens.

9:20am **SS-TuM5 Reactivity of Highly-hydroxylated TiO₂(110) Surface Prepared *via* Carboxylic Acid Adsorption and Photolysis**, *I. Lyubinetsky, Y.G. Du, N.G. Petrik,* Pacific Northwest National Laboratory, *N.A. Deskins,* Worcester Polytechnic Institute, *Z.-T. Wang, M.A. Henderson, G.A. Kimmel*, Pacific Northwest National Laboratory
We present a novel, photochemical approach to prepare a highly-hydroxylated $TiO_2(110)$ and discuss the reactivity of the resulting surface. $TiO_2(110)$ surfaces with an OH_b coverages up to 0.5 ML have been obtained upon trimethyl acetic acid (TMAA) dissociative adsorption and subsequent photolysis at 300 K. The formation and chemistry of such surface have been examined at the atomic level by a combination of scanning tunneling microscopy, temperature-programmed desorption, photo stimulated desorption, and density functional theory methods. Deprotonation of TMAA molecules upon adsorption produces both surface bridging hydroxyls (OH_b) and bidentate trimethyl acetate (TMA) species with saturation coverage of near 0.5 ML. The TMA species can be selectively removed by ultra-violet light irradiation while OH_b's survive photolysis. At high coverages, the OH_b species typically occupy second-nearest neighbor sites along the bridging oxygen row locally forming linear (2´1) structures of different lengths, although the surface is less ordered on a long scale. The annealing of the highly-hydroxylated surface leads to hydroxyl recombination and H_2O desorption with ~100% yield, thus ruling out the diffusion of H into the bulk. In agreement with experimental data, theoretical results show that the recombinative H_2O desorption is preferred over both H bulk diffusion and H_2 desorption processes.

9:40am **SS-TuM6 Infrared Spectroscopy of CO₂ Adsorbed on TiO₂(110)**, *N.G. Petrik, G.A. Kimmel*, Pacific Northwest National Laboratory
We have studied the adsorption of CO_2 on $TiO_2(110)$ using reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). Infrared spectra were obtained for s- and p-polarized light with the plane of incidence parallel and perpendicular to the [001] azimuth of $TiO_2(110)$. As a result, the RAIRS provide detailed information on the adsorption geometry for the CO_2 versus coverage. Initially, CO_2 adsorbs in vacancies in the bridge-bonded oxygen (BBO) rows with the peak for the asymmetric stretch seen at 2346.5 cm^{-1} for both s- and p-polarized light. Hydroxylation or oxidation of the vacancies suppresses this feature. After filling the vacancies, CO_2 adsorbs on Ti_{5c} sites (CO_2(Ti)). The asymmetric stretch for CO_2(Ti) starts at ~2342 cm^{-1} and then red-shifts to 2332 cm^{-1} at 1 ML. CO_2 TPD spectra show that the shift in the RAIRS spectra correlates with a decrease in the CO_2 binding energy from ~47 to ~34 kJ/mol as the coverage increases from 0 to 1 ML. For CO_2(Ti), the absorbances for the s-polarized spectra are similar for both azimuths indicating that the ensemble-average of the adsorbed CO_2 has approximately equal components along both azimuths. The p-polarized RAIRS spectra show that CO_2(Ti) also adsorbs with a component normal to the surface. Between 1 and 1.5 ML, CO_2 adsorbs on BBO sites. These CO_2 absorb only s-polarized light with its plane of incidence parallel to the BBO rows indicating that the molecules are oriented parallel to the surface and

perpendicular to the BBO rows. The CO_2 RAIRS spectra are compared with STM results and DFT theory to provide detailed insight into its molecular orientation and coverage-dependent mobility.

10:40am SS-TuM9 Low-temperature Dissociation of CO_2 on Ni/CeO$_2$/Ru(0001) Model Catalyst, *D.D. Kong*, University of Science and Technology of China, *K.-H. Ernst*, EMPA, Switzerland, *J.F. Zhu*, University of Science and Technology of China

Model Ni/CeO$_2$ (111) catalysts were prepared by depositing nickel atoms onto well-ordered cerium oxide films grown on Ru(0001) and were investigated using photoelectron spectroscopy (XPS) and reflection absorption infrared spectroscopy (RAIRS). It is found that the fully oxidized CeO_2 thin films are slightly reduced to $CeO_{1.97}$ after 0.2 ML Ni deposition. When CO_2 is exposed to the surface of clean CeO_2(111) film at 97 K, the physisorbed linear molecular CO_2 and carboxylate species are observed. However, on the CeO_2(111) surface covered with 0.6 ML Ni, CO_2 immediately dissociates upon adsorption at 97 K, leading to the formation of Ni-CO adsorbates and partial oxidation of Ni nanoparticles. This dissociation activation of CO_2 is inhibited when Ni nanoparticles on CeO_2 are pre-oxidized. In contrast to the results reported for CO_2 adsorption on Ni single-crystals where the dissociation temperature was found to be higher than 240 K, the much lower dissociation temperature (~97 K) for CO_2 on Ni nanoparticles supported on CeO_2(111) suggests that the Ni/CeO$_2$ catalyst exhibits high activity toward CO_2 activation.

11:00am SS-TuM10 Adsorption and Diffusion of Acetone on Rutile TiO$_2$ (110), *B. Zhang, Y. Xia*, Baylor University, *J. Ye, Q. Ge*, Southern Illinois University Carbondale, *Z. Zhang*, Baylor University

Understanding the surface reaction processes of acetone on metal oxide surfaces is important for photo-oxidation of toxic organic molecules. We have studied the adsorption and the diffusion of acetone on reduced rutile TiO$_2$(110) surfaces using variable temperature scanning tunneling microscopy (STM). At room temperature (RT) acetone molecules prefer to adsorb on bridging-bonded oxygen vacancy sites. The sequential isothermal STM images show that acetone molecules are mobile at RT. They hop between unoccupied vacancy sites via both apparent along-row diffusion and apparent cross-row diffusion processes. Images obtained at temperatures below RT show that there are two barriers involved in these diffusion processes: (1) the diffusion barrier along the Ti row, and (2) the barrier from the vacancy site to the neighboring Ti row. The latter is the rate limiting step. DFT calculations agree with experimental results.

11:20am SS-TuM11 Variations in Reactivity for Acetaldehyde and Acetic Acid with the Crystallographic Orientation of Cerium Oxide Thin Films, *P.M. Albrecht, D.R. Mullins*, Oak Ridge National Laboratory

Cerium oxide is a vital component in many heterogeneous catalytic processes. The various crystallographic faces of ceria present significantly different surface structures and compositions, which may result in an orientation-dependent catalytic reactivity. The structure and composition determine the availability of adsorption sites, the spacing between those adsorption sites, and the ability of surface O to participate in a reaction. The adsorption and reaction of various oxygenated hydrocarbons on cerium oxide surfaces are of interest from the standpoint of understanding the catalytic properties of the material. Studies on the interactions of alcohols, aldehydes, ketones, and carboxylic acids on well-defined CeO_2 surfaces have been motivated predominantly by the rich chemistry produced by the variation in the Ce oxidation state and the associated O vacancies. Alcohols, carbonyls, and carboxylic acids vary significantly in their strength of interaction with the surface and consequently in their reaction products. Here, we report a study of the adsorption and dissociation of acetaldehyde (CH_3CHO) on CeO_2(100). CeO_2(100) films were grown by pulsed laser deposition on Nb-doped $SrTiO_3$(100). In addition to the fully oxidized CeO_2(100) surface, experiments were conducted on reduced surfaces containing ~60% Ce^{3+} ($CeO_{1.7}$) prepared by methanol exposure at 660 K. Reaction products were monitored by temperature programmed desorption (TPD), and surface intermediates were determined by soft x-ray photoelectron spectroscopy (sXPS) and near-edge x-ray absorption fine structure (NEXAFS). The key result is that acetaldehyde reacts with oxidized CeO_2(100), whereas it does not react with oxidized CeO_2(111). The most intense products are CO, CO_2, and water, with trace amounts of crotonaldehyde and acetylene. On reduced $CeO_{1.7}$(100), the oxygenated products are largely eliminated and ethylene and H_2 are produced. Residual C is also left on the surface. Recent results indicate that the chemistry of acetic acid (CH_3COOH) is also significantly different on CeO_2(100) compared to CeO_2(111). Acetone is a major product on CeO_2(100) whereas only a trace amount of ketonization occurs on CeO_2(111). Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

11:40am SS-TuM12 The Entropies of Adsorbed Molecules, *C.T. Campbell, J.R.V. Sellers*, University of Washington

Adsorbed molecules are involved in many reactions on solid surface that are of great technological importance. As such, there has been tremendous effort worldwide to learn how to predict reaction rates and equilibrium constants for reactions involving adsorbed molecules. Theoretical calculation of both the rate constant and equilibrium constant for such reactions require knowing the standard entropy and enthalpy of the adsorbed molecule. While much effort has been devoted to measuring and calculating the enthalpies of well-defined adsorbates, few measurements of the entropies of adsorbates have been reported. We present here a new way to determine the standard entropies of adsorbed molecules (S_{ad}^0) on single crystal surfaces from temperature programmed desorption data, prove its accuracy by comparison to entropies directly measured using equilibrium adsorption isotherms on MgO(100), and apply it to published data to extract new entropies. Most importantly, when combined with reported entropies, we find that at high coverage they linearly track the entropy of the gas-phase molecule at the same temperature (T) as:

$$S_{ad}^0(T) = 0.70\ S_{gas}^0(T) - 3.29R,$$

with a standard deviation of only 2R from 0 to 60R, where R is the gas constant. These entropies, which are ~2/3 of that for the gas, are huge compared to most theoretical predictions (e.g. the harmonic approximation commonly employed in combination with DFT estimates of reaction barriers). This relationship applies at temperatures where desorption rates are fast enough to perform EAI and TPD measurements (~10^{-3} to 100 monolayers/s). It provides an important tool to aid in estimating equilibrium constants and rate constants for reactions where these adsorbates are involved, as proven here for prefactors in the Arrhenius rate constant for desorption. The prefactor can be estimated as :

$$\nu = (k_BT/h)\ \exp\{0.30\ S_{gas}^0(T)/R + 3.29 - 9.31\ \ln[(m/m_{Ar})(T/298K)]\},$$

where m/m_{Ar} is the mass of the adsorbate relative to Ar. For longer adsorbed molecules where $S_{gas}^0(T)$ exceeds 60 K (e.g. linear alkanes with >11 carbons), their entropies remain a constant 20.7R below gas entropies, and ~10.4R below Trouton's Rule for liquid entropies.

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