

Wednesday Morning, October 17, 2007

Surface Science

Room: 608 - Session SS1-WeM

Oxide Surface Reactivity

Moderator: V.M. Bermudez, Naval Research Laboratory

8:00am **SS1-WeM1 Influence of Ferroelectric Polarization on Adsorption on BaTiO₃**, *D.B. Li, M. He, J. Garra, D.A. Bonnell, J.M. Vohs*, University of Pennsylvania

Many perovskite oxides such as BaTiO₃ undergo a phase transition from a ferroelectric tetragonal phase to a paraelectric cubic phase at readily accessible temperatures. In the ferroelectric state the material is polar and has a bulk electric dipole whose orientation can be controlled via application of an external electric field. While it has been suggested that the orientation of the ferroelectric dipole on the surface may affect adsorption and reaction of species from the gas phase, examples demonstrating the ferroelectric control of surface reactivity have to date been elusive. In this talk we will present what we believe are the first definitive examples of the influence of ferroelectric polarization on the surface reactivity of BaTiO₃. In the first example, demonstrates the effect of ferroelectric polarization on the adsorption of CO₂ on oxygen vacancies on the surface of a BaTiO₃(001) single crystal. Sub-micron sized out-of-plane domains with the polarization oriented perpendicularly inward (*c*⁻) or outward (*c*⁺) from the surface were produced on the BaTiO₃(001) sample using an AFM tip. Frequency modulation, scanning surface potential microscopy (FM-SSPM) was then employed to measure the potential change of the ferroelectric domains before and after exposure of the poled surface to CO₂. It was observed that CO₂ caused a larger decrease in the surface potential for *c*⁻ domains relative to the *c*⁺ domains, indicating a difference in the amount of CO₂ adsorbing on each domain. In the second example, the amount of methanol that adsorbed on an oriented, BaTiO₃ thin film supported on TiO₂(110) under UHV conditions was found to be dependent on the orientation of the ferroelectric dipole. In this case the sample was poled by heating above T_c and then placing it in contact with an electrode to which a small + or - voltage was applied. For a constant exposure, the amount of CH₃OH that adsorbed at 300 K was found to increase in the following order *c*⁻ > unpoled > *c*⁺. This result has been attributed to a polarization dependent interaction of weakly bound CH₃OH molecules prior to dissociative adsorption at defect sites.

8:20am **SS1-WeM2 Effect of Poling Direction on the Reactivity of Ferroelectric Oxide Surfaces**, *Y. Yun, M. Li*, Yale University, *L. Kampschulte*, Ludwig Maximilians Universität, Germany, *D. Liao, B. Lukanov, E.I. Altman*, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or strongly adsorbing polar molecules. Because opposite charges must be screened on opposite surfaces, different reactivities are expected on positively and negatively poled surfaces. We have studied the surface atomic composition, structure and reactivity of LiNbO₃(0001) surfaces. The surfaces appeared nearly indistinguishable in spectroscopic and diffraction measurements: both surfaces were (1x1) and appeared almost fully oxygen terminated in low energy ion scattering spectra. Despite the structural similarities, differences in reactivity between positively and negatively poled surfaces were observed using TPD. Polar molecules including 2-propanol and acetic acid adsorbed much more strongly on the positive surfaces as evidenced by desorption peak temperatures over 100 K higher. Further, the TPD curves were found to depend unusually strongly on the heating rate. This effect could be attributed to the change in polarization with temperature - the pyroelectric effect- creating a temperature-dependent heat of adsorption. Including this effect, an 11 kJ/mole higher 2-propanol heat of adsorption was estimated for the positive surface. These results will be compared with adsorption of non-polar molecules where the polarization changing with temperature is not expected to affect the strength of the adsorbate-surface interaction. The results for LiNbO₃ will also be compared with PbZr_xTi_{1-x}O₃ thin films to determine the generality of the observed phenomena.

8:40am **SS1-WeM3 The Interaction of NO₂ with MgO(100) Studied with Photoemission Spectroscopy**, *D.E. Starr, Ch.D. Weiss*, Lawrence Berkeley National Laboratory, *S. Yamamoto, A. Nilsson*, Stanford Synchrotron Radiation Laboratory, *M. Salmeron, H. Bluhm*, Lawrence Berkeley National Laboratory

NO_x compounds are very harmful environmental contaminants commonly formed in combustion processes. Their adsorption onto the surfaces of alkaline-earth metal-oxides has recently received a great deal of attention due to the use of alkaline-earth metal-oxides as NO_x storage compounds for controlling emissions during combustion under fuel-lean conditions. In this work we have studied the adsorption of NO₂ on MgO(100) films grown on Ag(100) using photoemission spectroscopy. Many of the previous experimental studies of this system were performed at low temperatures with subsequent thermal heating under Ultra-High Vacuum conditions. In this study we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption and reaction of NO₂ onto MgO(100) at 300 K and 10⁻⁶ torr NO₂ pressures for exposures ranging from a few Langmuir up to twenty thousand Langmuir. At these conditions, we find that the NO₂ initially adsorbs as NO₂ with low coverage (~0.05 ML). Upon increasing exposure, we observe a reduction in the coverage of NO₂ and the presence of adsorbed NO₃. Further, at high exposure we find increasing coverage of NO₃ (~0.30 ML) without the presence of NO₂ on the surface. This indicates that the production of NO₃ on the surface likely occurs via initial NO₂ dissociation which produces adsorbed O which then oxidizes NO₂ to form NO₃.

9:00am **SS1-WeM4 The Interaction of NO₂ with BaO: From Cooperative Adsorption to Ba(NO₃)₂ Formation**, *J. Szanyi, C.-W. Yi, J.H. Kwak*, Pacific Northwest National Laboratory

The adsorption and reaction of NO₂ on a thick (> 30 ML), pure BaO film deposited onto an Al₂O₃/NiAl(110) substrate at 90 K and the higher temperatures were investigated with surface science techniques such as temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS) techniques. For the first time, it was clearly demonstrated that BaO readily reacts with NO₂ to initially form nitrite-nitrate ion pairs by the cooperative adsorption mechanism predicted by theoretical calculation. These nitrite/nitrate pairs readily form even at 90 K. In the decomposition process of these pairs first the nitrite species release an NO molecule, and nitrate species decompose in two steps: at lower temperature as NO₂ only, then, at higher temperature, as NO + O₂. The results of NO₂ adsorption/reaction on this model system are identical to those we have found on a high surface area 20 wt.% BaO/γ-Al₂O₃ sample with the exception of surface nitrates that were only observed on the high surface area material.

9:20am **SS1-WeM5 Reactivity of Low-dimensional Oxide Nanostructures***, *F.P. Netzer*, Karl-Franzens University Graz, Austria
INVITED

Oxide materials in nanostructured layers exhibit physical and chemical properties that are significantly different from their respective properties in macroscopic bulk phases. This novel behaviour forms the basis for many potential applications of oxide nanostructures in diverse areas of the emerging nanotechnologies. Here we discuss the physico-chemical properties of ultrathin oxide overlayers (nanolayers = thickness ≤ 10 ML), grown on metal single crystal surfaces, in terms of their novel structural concepts, their modified electronic behaviour and their sensitivity to changes in the chemical environment. A multitude of experimental techniques (STM, SPA-LEED, XPS, NEXAFS, UPS, HREELS) in conjunction with ab initio DFT model calculations has been applied to characterise the oxide nanolayers deposited on Pd and Rh substrate surfaces. The oxide materials considered comprise nickel, manganese and cobalt oxide phases. Specifically, we will discuss chemical and structural aspects of phase transformations of Mn-oxide overlayers in the 1-10 ML range on Pd(100). Emphasis will be put on the structural transition from the MnO(100) to the MnO(111) orientation as a function of the chemical potential of oxygen and on the oxidation of MnO to Mn₃O₄ surface phases. The chemical interaction of NiO(100) surfaces, epitaxially grown on Pd(100), with metallic cobalt and Co-oxide overlayers is addressed from the viewpoint of generating sharp antiferromagnetic-(anti)ferromagnetic interfaces. It is shown that CoO(100) can be grown epitaxially on NiO(100) and that a 1-2 ML CoO buffer layer can inhibit the oxidation reaction of Co metal overlayers, thus forming a sharp AFM-FM interface. The oxidation of metallic quasi-one-dimensional (1-D) Ni nanowires, formed on the stepped Rh(15 15 13) surface, to 1-D Ni-oxide phases is illustrated. The latter are compared to the 2-D Ni-oxide phases that develop by reactive physical

vapour deposition on the same stepped Rh surface, in order to assess the dimensionality aspects in the formation of oxide nanostructures.

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10:40am SS1-WeM9 Adsorption Energetics of Ag on CeO₂(111), J.H. Baricuatro, J. Farmer, C.T. Campbell, University of Washington

The energetics of Ag deposition on well-defined films of CeO₂(111) were investigated using adsorption microcalorimetry. Thin films of CeO₂(111) were grown on Pt(111) at 700 °C by thermal evaporation of Ce under a reactive atmosphere of O₂. Ag was evaporated from an effusive vapor source and the resultant surface structures were probed using a combination of low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and low-energy He⁺ ion scattering spectroscopy (LEIS). The adsorption of Ag exhibited a sticking coefficient that is close to unity (0.98), independent of coverage. The enthalpy of adsorption of Ag was initially low (ca. 200 kJ/mol) but increased with Ag coverage up to the sublimation enthalpy of bulk Ag. The effect of surface oxygen vacancies on the adsorption energy of Ag was also investigated.

11:00am SS1-WeM10 Redox Properties of HCOOH over CeO₂ Surfaces: Pathways to Surface Oxidation and Reduction, S.D. Senanayake, D.R. Mullins, Oak Ridge National Laboratory

This study undertakes a close scrutiny of the reaction of HCOOH, the simplest C-1 carboxylic acid, with the surfaces of CeO₂, a well defined (111) oriented lanthanide oxide system. HCOOH is an important precursor to the formation of CO₂ and H₂ in the water-gas-shift (WGS) reaction, in which ceria (in combination with noble metal particles) is also used as a stable support rich in oxygen storage capacity. The HCOOH is observed to adsorb by way of a formate intermediate species (HCOO⁻) through the dissociation of the acidic H over both CeO₂ (Ce⁺⁴) and CeO_x (Ce⁺⁴/Ce⁺³) surfaces. This species will be compared to other C1 adsorbates observed such as methanol¹ and formaldehyde² reacting over ceria, which yield methoxy (CH₃O) and dioxyethylene (CH₂O₂) species, respectively. The dissociated H species recombines with surface O and desorbs as H₂O <300K. At 300K polarization dependent C K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) data suggest that the formate is adsorbed in a bi-dentate structure with the O-C-O plane oriented normal to the surface. In addition to water, Temperature Programmed Desorption (TPD) spectra indicate the evolution of CO₂ (m/z 44) and H₂ (m/z 2) around 350-400K followed by only CO desorption in two regimes at 450 and 525K. The net result is a slight reduction of the ceria substrate. In a reversal of roles, formic acid oxidizes the reduced CeO_x surface. No H₂O or CO₂ desorbs at lower temperatures but is replaced with desorption of only CO and H₂ between 450-600K. Soft X-ray Photoelectron Spectroscopy (sXPS) indicates that formate is again the only surface intermediate. With the introduction of Rh nanoparticles to the reduced and oxidized Ceria surfaces the formate decomposition is observed over ceria. Furthermore, sXPS also shows CO adsorption on Rh (C1s ~286eV) that decomposes further to give Rh-C species (284.5eV) which can be compared to CO reaction over Rh / CeO_x surfaces.³

¹J. Phys. Chem. B., 110 (32) 15994 (2006).

²Surf. Sci., 600 1540 (2006).

³J. Catal., 188 340 (1999).

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11:20am SS1-WeM11 Hydrogen Diffusion on TiO₂(110) at Elevated Temperatures, S.-C. Li, J.M. White, University of Texas at Austin, Z. Zhang, B.D. Kay, Z. Dohnálek, Pacific Northwest National Laboratory

The TiO₂ chemistry has been widely investigated in both fundamental science and technical applications, due to its intriguing chemical properties. One of the important applications is the photochemical hydrogen production from H₂O. On a prototypical TiO₂(110) surface, the bridge-bonded oxygen (BBO) vacancies have been shown to be the primary reactive sites for H₂O dissociation yielding geminate pairs of OH groups. In this study we use variable temperature Scanning Tunneling Microscopy (STM) to investigate intrinsic hydrogen diffusion along the BBO rows as a function of temperature. The hopping rates deduced from the consecutively collected STM images at temperatures ranging from 320K to 420K are analyzed. The prefactors and activation barriers are extracted as a function of OH-OH separation using the Arrhenius analysis. A comparison of the hopping rates for hydrogen and deuterium shows a strong isotope effect.

The research described in this presentation was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

11:40am SS1-WeM12 The Adsorption of Cysteine and Co-Adsorption of Cysteine and Gold on TiO₂(110), E. Ataman, C. Isvoranu, J.N. Andersen, J. Schnadt, Lund University, Sweden

The bonding of organic molecules to transition metal oxide surfaces such as TiO₂ is a concern central to the construction and optimization of molecule-based devices. Organic-inorganic interfaces are presently receiving increasing attention due to both fundamental and application interests. Interest also derives from the role of TiO₂ as a support for metal catalyst particles such as Au nanoclusters, which act as an excellent catalyst for, e.g., the low temperature CO oxidation reaction. The cluster size of the Au particles has to remain within an optimum range for the catalyst to preserve its activity. However, the Au clusters are prone to coalescence as a function of temperature and gas exposure. In order to retain the catalytic activity it is important to hinder this growth process. The idea developed here is to use L-cysteine as a spacer between the clusters, since it strongly binds to the TiO₂ surface via its carboxylic group. It is well-known that the thiol group of cysteine interacts with gold, which then might establish the missing link between the gold clusters and the spacer molecules. We have investigated the adsorption of L-cysteine as well as the co-adsorption of L-cysteine and gold on rutile TiO₂(110) by means of x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and scanning tunneling microscopy (STM). The spectroscopy results clearly show that the notion of a molecule-TiO₂ substrate bond via the carboxylic group of the molecule is correct. This finding receives further support from the STM measurements. The basic geometry characterized by the oxide-carboxylate bond is retained even for the co-deposition case; however, the S 2p spectra indicate an additional interaction between the gold clusters and molecules. An interesting additional feature of the spectroscopy experiments was the observation of very rapid beam damage, which we attribute to a facile change in the protonation status of the amino and thiol functional groups.

12:00pm SS1-WeM13 Density Functional Theory Study of Hydrogen Cyanide and Formamide over Rutile TiO₂ (110) and (011) Surfaces, P.R. McGill, H. Idriss, The University of Auckland, New Zealand

Formamide is a compound of considerable interest, owing to its ability to yield nucleobases during photoreaction over TiO₂ in both aqueous¹ and ultrahigh vacuum conditions.² The mechanisms for this synthesis have been postulated to involve the generation and subsequent decomposition of HCN polymers on the surface. While a number of experimental studies have investigated formamide and HCN adsorption to the surfaces of TiO₂,^{2,3,4} computational work has focused on their interaction with metal surfaces.⁵ In this study, a series of periodic DFT calculations are conducted on formamide and HCN adsorption to the (110) and (011) bulk terminated surfaces of rutile TiO₂, employing plane wave basis sets and the PBE exchange correlation functional. Dissociative adsorption appears favoured for formamide on both investigated surfaces; the formamide molecule binding in a bridging manner across two surface Ti sites analogous to that of formic acid on the rutile TiO₂ (110) surface. Molecular adsorption through the carbonyl oxygen's interaction with the surface Ti is also found to be energetically favourable, though to a lesser extent. No stable interaction mode is observed for molecular adsorption through the N atom to the surface Ti species, in agreement with IR studies³ conducted on formamide over polycrystalline TiO₂. HCN was found to strongly prefer to adsorb on the surface in an orientation perpendicular to the surface, with the nitrogen binding to a surface Ti. Dissociative adsorption is found to be less favourable than molecular adsorption, with dissociative adsorption through the C atom yielding a greater stability than through the N atom. Adsorption modes parallel to the surface (which are reported on metal surfaces³) do not appear to represent energy minima, and convert back to perpendicular configurations on geometry optimisation.

¹Saladino, R., Cresti, C., Costanzo, G. DiMauro, E. (2004) Curr.Org.Chem. 8, 1425.

²Senanayake, S.D., Idriss, H. (2006) Pro. Nat. Acad. Sci. USA. 103, 1194.

³Wu, W.C., Liao, L.F., Chuang, C.C., Lin, J.L. (2000) J.Catal. 195, 416.

⁴Raskó, J., Bánsági, T., Solymosi, F. (2002) Phys.Chem.Chem.Phys. 4, 3509.

⁵Oliva, C., van den Berg, C., Niemantsverdriet, J.W.H., Curulla-Ferre, D. (2007) J. Catal. 245, 436.

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