Wednesday Afternoon, November 2, 2011

Surface Science Division
Room: 107 - Session SS-WeA

Adsorption & Reactions on Oxide Surfaces
Moderator: S.L. Scott, University of California, Santa Barbara

2:00pm SS-WeA1 Direct Observation of O$_2$ Molecular Chemisorption at Two Distinctive Sites of TiO$_2$(110), *Z.T. Wang, Y.G. Du, Z. Dohnálek, I. Lyubinetsky*, Pacific Northwest National Laboratory
The chemistry of oxygen on TiO$_2$ surfaces is an important component in many catalytic and photocatalytic processes, such as water splitting and waste remediation, and has been extensively studied. So far, the majority of fundamental research has been carried out on the model transition-metal oxide surface of the rutile TiO$_2$(110). The investigation of molecular adsorption of O$_2$ can be considered as a natural first step providing information about possible O$_2$ surface chemistry on TiO$_2$(110). Both experiment and theory have demonstrated that O$_2$ dissociatively adsorbs at bridging oxygen vacancies (V$_O$) sites and five-fold coordinated terminal titanium atoms (Ti$_{5c}$) at elevated temperatures. At sufficiently low temperatures, the majority of the ensemble-averaging technique studies suggested that O$_2$ molecularly chemisorbs at V$_O$ sites on reduced surfaces (at T < 150 K). However, recent STM studies reported a contradict result that the O$_2$ dissociation at V$_O$ sites has been observed at temperatures as low as ~ 110 K.

In this work, we investigated the initial stages of oxygen adsorption on reduced TiO$_2$(110) with high-resolution scanning tunneling microscopy (STM) at 50 K. Molecularly chemisorbed O$_2$ species, not directly observed until now on TiO$_2$(110), have been imaged at two distinctive adsorption sites (V$_O$ and Ti$_{5c}$) using "extremely mild" tunneling conditions. While O$_2$ species at Ti$_{5c}$ site appears as a single protrusion centered on the Ti$_{5c}$ row, the O$_2$ at V$_O$ manifests itself by a disappearance of the V$_O$ feature. The dissociation of chemisorbed O$_2$ can be readily induced by tunneling conditions that are normally used for TiO$_2$(110) imaging, and the dissociation details strongly depend on the scanning parameters and the type of the O$_2$ adsorption site. The O$_2$ molecules chemisorbed at low temperatures at these two distinct sites are the most likely precursors for the two O$_2$ dissociation channels, observed at temperatures above 150 and 230 K at the V$_O$ and Ti$_{5c}$ sites, respectively. In general, our results provide a molecular level insight into the thermal chemistry of O$_2$ on reduced TiO$_2$, and assist in understanding of the surface reactivity of transition-metal oxides.

2:20pm SS-WeA2 The Interaction of Carboxylic Acids with Rutile TiO$_2$ (110) Single Crystal Surfaces: Results from IR-Spectroscopy, *M. Buchholz,* Karlsruhe Institute of Technology (KIT), Germany, *M.C. Xu, Y.M. Wang,* Ruhr-University Bochum, Germany, *A. Nefedov, C. Wöll*, Karlsruhe Institute of Technology (KIT), Germany
The role of oxides is central in many technological areas such as gas sensing, catalysis and thin film growth. Zinc oxide and titanium oxide are also important for photocatalysis and photooxidation, e.g. of CO to CO$_2$[1]. In the Graetzel-cell, organic molecules bound to TiO$_2$-substrates via carboxylate bonds effectively convert photons into electric energy. In last decades numerous IR investigations of oxide powders, including the different modifications of TiO$_2$, have been reported. An unambiguous assignment of the features in the complex IR spectra recorded for molecules bound to the oxide powder particle surfaces, however, is only possible on the basis of data recorded for well-defined reference systems, e.g. surfaces of single crystals. Unfortunately, studies on oxide single crystals are extremely scarce due to the fact that the sensitivity of reflection IR-spectroscopy for molecular adsorbates is two orders of magnitude lower for oxides than for metal single crystals. Only recently was is possible to overcome these technical problems by employing a novel, optimized spectrometer.[2] Here, we will demonstrate the performance of this highly sensitive IRRAS-setup by presenting high-quality IR-spectra obtained for two molecules, benzoic acid and terephthalic acid, adsorbed on rutile TiO$_2$ (110). Owing to the fact that many Dye Sensitized Solar Cells (DSSCs) consist of dyes grafted to the oxide support via carboxylate groups determining and controlling the adsorption of carboxylic acids on oxidic substrates is fundamental to understanding the energy transfer from the molecule to the substrate. For the present experiments, monolayers of terephthalic acid (TPA) and benzoic acid (BA) were first deposited under UHV-conditions on a rutile TiO$_2$ (110) surface at room temperature. Subsequently the sample was transferred in the main chamber and subjected to an analysis in a highly sensitive UHV IRRAS system. While for BA the

expected bidentate carboxylate bonding is observed, for TPA the presence of two carboxylic acid groups leads to interesting complications. The IR-spectra allow, in particular, answering the question whether for the flat-lying TPA species observed in scanning probe techniques[3] the carboxylic acid group is still protonated, a question which could not be answered by the results from x-ray absorption spectroscopy[3].

[1] M. C. Xu, Y. K. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. M. Wang, H. Idriss, C. Wöll, *Phys. Rev. Lett.* **2011**, *106*, 138302.

[2] Y. M. Wang, A. Glenz, M. Muhler, C. Wöll, *Rev. Sci. Instrum.* **2009**, *80*, 113108.

[3] P. Rahe, M. Nimmrich, A. Nefedov, M. Naboka, C. Wöll, A. Kühnle, *Journal of Physical Chemistry C* **2009**, *113*, 17471.

2:40pm SS-WeA3 The Adsorption Dynamics and Interfacial Charge Trapping Behavior for Acetic Acid on Rutile TiO$_2$ Surfaces, *J. Tao, T. Luttrell, M. Batzill*, University of South Florida
Using temperature programmed desorption (TPD), scanning tunneling microscopy (STM) and ultraviolet photoemission spectroscopy (UPS), we have observed very different adsorption dynamics for acetic acid on rutile TiO$_2$(110) and (011)-2×1 surfaces at room temperature. While the bidentate adsorption of carboxylic acids on the (110) surface is well-established, we find a monodentate adsorption on the (011)-2×1 surface as the most likely adsorption geometry. On the (011)-2×1 surface, the initial sticking of adsorbed acetic acid is low. It appears that initial adsorption occurs at defects. These adsorbed acetates then act as nucleation sites for further adsorption. This adsorption mechanism results in the formation of quasi-1D acetate clusters running along direction. The role of acetate adsorption in the formation or annihilation of excess charges in TiO$_2$ is also found to be different on these two surfaces. We find that bidentate adsorption of acetate on the (110) surface results in extraction of excess charges from the substrate, while mono-dentate adsorption on the (011)-2×1 surface causes net-charge donation to the substrate. More interestingly, a difference in the binding energy of excess charges, or Ti-3d band gap states, has been observed. On the TiO$_2$(011)-2×1 surface the binding energy is ~0.3 eV higher than on the (110) surface. This difference is explained by the different crystal fields on the reconstructed (011) surface compared to the bulk-truncated (110) surface. At the rutile TiO$_2$(011)-2×1 surface, Ti-ions are located in a distorted square pyramidal coordination environment, which we propose causes the shift in binding energy of excess electrons at the Ti-site. The differences in binding energy of electrons trapped at the surface for the two surfaces may contribute to the face dependent photocatalytic activity of rutile TiO$_2$.

References:

1. J. Tao, T. Luttrell, J. Bylsma, and M. Batzill, *J. Phys. Chem. C* 2011, 115, 3434

2. J. Tao and M. Batzill, *J. Phys. Chem. Lett.* 2010, 1, 3200.

3:00pm SS-WeA4 Effect of the Adsorption Geometry of Zinc-Tetraphenylporphyrin Derivatives on ZnO and TiO$_2$, on the Exciton Delocalization Pathways, *S. Rangan, S. Coh, R.A. Bartynski, K. Chitre, J. Rochford, E. Galoppini*, Rutgers University, *C. Jaye, D.A. Fischer*, National Synchrotron Light Source
ZnTPP derivatives are attractive candidates for photoinduced electron-transfer mediators in dye sensitized solar cells (DSSCs). Many fundamental properties of the dye/metal oxide interface are not known and need careful consideration. In particular, the influence on solar cells efficiency, of the energy alignment and of the molecular packing at the surface, remains unclear. In this work, using x-ray, UV and inverse photoemission spectroscopies in conjunction with density functional theory (DFT) calculations, we have determined the energy alignment of molecular levels with respect to the substrate band edges for several ZnTPP derivatives adsorbed on ZnO(11-20) and TiO$_2$(110) surfaces. The ZnTPP derivatives were functionalized with COOH anchoring groups, to allow a priori either upright or flat adsorption on the surfaces. While the energy alignment, a critical parameter to allow charge separation at the dye/semiconductor interface, is found similar for all of these systems, large differences in solar cells efficiencies are observed. We have thus explored the adsorption geometry of the same ZnTPPs at the surface of ZnO and TiO$_2$ using UV-visible absorption and NEXAFS spectroscopies and scanning tunnel microscopy. It is found that that dye/dye interactions is an important factor, for electron transfer to the substrate. For ZnTPPs, upright adsorption opens deleterious exciton delocalization pathways, due to dipole/dipole interactions competing with electron transfer to the substrate. Choosing the adsorption geometry is thus critical for the electronic pathway control.

4:00pm SS-WeA7 Adsorption of Trimethylacetic Acid on Stoichiometric and Reduced CeO$_2$(111) Surfaces, *S.P. Sanghavi, A.S. Karakoti, M.I. Nandasiri, W. Wang, P. Nachimuthu, P. Yang, S.V.N.T. Kuchibhatla, S. Thevuthasan*, Pacific Northwest National Laboratory

The use of nanoparticles in energy, environmental and medical applications has been growing significantly in recent years. In most of these applications, the nanoparticles are being used in as-synthesized form and/or functionalized through ligand conjugation. When particle size decreases to nanometer scale, a large percentage of the atoms are at or near the surface which makes the surface highly dynamic and reactive in nature. Consequently, these particles exhibit unique properties that make their characterization more difficult by conventional spectroscopic methods. Furthermore, knowledge on how the ligand molecules bind to the surface of nanoparticles is very limited. To better understand the interactions between ligand molecules and the surface of nanoparticles, we used a model system approach to study the interaction between the carboxylate anchoring group from trimethylacetic acid (TMAA) and CeO$_2$(111) surfaces as a function of oxygen stoichiometry. The epitaxial CeO$_2$(111) thin films 50nm in thickness were grown on YSZ(111) by oxygen plasma-assisted molecular beam epitaxy at 650°C under 2.5x10^{-5} Torr of oxygen plasma. The sample films from MBE system were transferred to X-ray photoelectron spectroscopy (XPS) system and sputter cleaned to remove any surface contamination during the transfer. Following sputtering, stoichiometric CeO$_2$(111) surface was obtained by annealing the thin film under 2.0x10^{-5} Torr of oxygen at ~550°C for 30 min. In order to reduce the CeO$_2$(111) surface, the thin film was annealed in ~5.0x10^{-10} Torr vacuum at 550°C, 650°C, 750°C and 850°C for 30 min to progressively increase the oxygen defect concentration on the surface. XPS was used to characterize these surfaces prior to and following dissociative adsorption of TMAA on these surfaces using a molecular doser. The saturated TMAA coverage and the oxygen defect concentration were determined from XPS elemental composition. The saturated TMAA coverage on CeO$_2$(111) surface is found to increase with increasing oxygen defect concentration. This is attributed to increase in under coordinated cerium sites on the surface with increase in the oxygen defect concentrations. In parallel, we studied the interactions of TMAA adsorbed at various sites on the stoichiometric CeO$_2$(111) surface using periodic density functional theory (DFT) calculations. Both energetics and electronic properties of the surface and TMAA will be presented and correlated with experimental observations.

4:20pm SS-WeA8 Reactivity Differences between CeO$_2$(100) and CeO$_2$(111) Thin Films, *D.R. Mullins, F.C. Calaza, S.H. Overbury, M.D. Biegalski, H.M. Christen*, Oak Ridge National Laboratory

Cerium oxide is a principal component in many heterogeneous catalytic processes. One of its key characteristics is the ability to provide or remove oxygen in chemical reactions. The different crystallographic faces of ceria present significantly different surface structures and compositions that may alter the catalytic reactivity. The structure and composition determine the availability of adsorption sites, the spacing between adsorption sites and the ability to remove O from the surface.

To investigate the role of surface orientation on reactivity, CeO2 films were grown with two different orientations. CeO2(100) films were grown *ex situ* by pulsed laser deposition on Nd-doped SrTiO3(100). The structure was characterized by RHEED, XRD and reflectometry. CeO2(111) films were grown *in situ* by thermal deposition of Ce metal onto Ru(0001) in an oxygen atmosphere. The structure of these films has been studied by LEED and STM. Attempts to grow CeO2(100) *in situ* by physical vapor deposition on Pt(100) and Pd(100) failed due to preferential growth of CeO2(111) on these supports.

The chemical reactivity was characterized by the adsorption and decomposition of various molecules such as methanol, water and acetaldehyde. Reaction products were monitored by TPD and surface intermediates were determined by soft x-ray photoelectron spectroscopy. In general the CeO2(100) surface was found to be more active, i.e. molecules adsorbed more readily and reacted to form new products, especially on a fully oxidized substrate. However the CeO2(100) surface was less selective with a greater propensity to produce CO, CO2 and water as products. The differences in chemical reactivity are discussed in light of possible structural terminations of the two surfaces.

4:40pm SS-WeA9 Adsorption and Photo-Reactivity of CO on TiO$_2$(110), *N.G. Petrik, G.A. Kimmel*, Pacific Northwest National Laboratory

We have studied the low-temperature adsorption and reactions of CO on reduced, oxidized, hydroxylated, and electron-irradiated TiO$_2$(110) using temperature programmed desorption, photon-stimulated desorption (PSD) and reflection-absorption infrared spectroscopy (RAIRS). Changing the condition of the crystal surface and the adsorbate coverage provides insight into the interactions of adsorbed CO with 5-fold coordinated Ti sites, (Ti$_{5c}$), bridge-bonded oxygen (BBO) sites, and defect sites (oxygen vacancies, bridging hydroxyls and radiation-induced surface defects). Infrared spectra were obtained for light with the plane of incidence parallel and perpendicular to the [001] azimuths of TiO$_2$(110). For adsorption on Ti$_{5c}$ sites, the RAIRS spectra are consistent with CO adsorbed nearly perpendicular to the surface. For adsorption on BBO sites, the molecules adsorb parallel to the surface and perpendicular to the rows of BBO atoms. The reactivity of various molecular adsorption forms of CO is probed using PSD. In CO photo-oxidation, the PSD yields of CO and CO$_2$ change dramatically with initial CO coverage, indicating the importance of the relative position and orientation of O$_2$ and CO molecules for the photochemical reaction.

5:00pm SS-WeA10 Adsorption of Carbon Dioxide on Rutile TiO$_2$(110): A Scanning Tunneling Microscopy Study, *X. Lin, B.D. Kay, Z.T. Wang, I. Lyubinetsky, Z. Dohnalek*, Pacific Northwest National Laboratory

Understanding the fundamental aspects of CO$_2$ adsorption and reaction on well-characterized oxide surfaces is critical in providing fundamental understanding on how to control catalytic carbon sequestration and CO$_2$ conversion to fuels. A model oxide surface, rutile TiO$_2$(110) is used to investigate the adsorption properties of CO$_2$ using scanning tunneling microscopy (STM). STM images obtained before and after *in-situ* doses of CO$_2$ at 50 K reveal that the CO$_2$ molecules preferentially bind in bridge-bonded oxygen vacancy (V$_O$) defect sites. We show that electron injection from the STM tip can induce CO$_2$ reduction to CO and V$_O$ annihilation. After the saturation of V$_O$'s, CO$_2$ molecules preferentially adsorb on five-fold coordinated Ti sites, where they remain mobile even at 50 K. The mobile CO$_2$ molecules may be corralled by other immobile species such as CO. The contrast observed in the STM images suggests that the distribution of mobile CO$_2$ molecules tracks the distribution of the subsurface charge as demonstrated by the CO$_2$ induced standing wave patterns along the Ti rows. The adsorption behavior of CO$_2$ on hydroxylated TiO$_2$ surfaces will also be presented.

5:20pm SS-WeA11 Interaction of ZnO-supported Cu Oxides with CO and CO$_2$, *Z. Zhang, F. Wang, M. Le, M. Ren, J. Flake, P. Sprunger, R. Kurtz*, Louisiana State University

Cu and Cu-oxide nanoclusters supported on ZnO are prototypical catalysts for the electrochemical reduction of CO and CO$_2$ to methanol. In this report we describe the interaction of CO and CO$_2$ with Cu oxide nanoclusters on ZnO(10$\underline{1}$0) with a combination of surface sensitive tools including STM for structural information, EELS for electronic and vibrational studies as well as synchrotron-based photoemission for electronic properties. Cu is deposited onto ZnO and oxidized with a combination of O-exposure and annealing procedures to result in two distinct Cu-oxide (CuI and CuII) clusters, which preferentially nucleate and grow at step edges. Photoemission shows a large charge transfer between the oxide cluster and the substrate surface as well as significant band bending. It is believed that the CO$_2$ adsorption, forming a carbonate species, and consequent reduction, is coupled to the induced defects and electronic perturbation of the CuO$_x$/ZnO nanoclusters, absent in the case of Cu/ZnO nanoclusters. In addition to vibrational EELS and TDS to characterize the adsorption of the CO and CO$_2$ adsorption species, similar results from Au on ZnO(10$\underline{1}$0), which shows a lack of cluster formation growth, will be compared and contrasted.

5:40pm SS-WeA12 Microfabricated Nitrogen-Phosphorus Detectors: Surface Work Function and Thermionic Emission, *M.T. Brumbach, R.F. Hess, R.J. Simonson, M.W. Moorman, T.J. Boyle*, Sandia National Laboratories

Chemically selective sensors are required for detection of chemical warfare agents with ever increasing demands on the selectivity, sensitivity, lifetime, speed, and reduced power consumption of these devices. Strategies for reducing the scale of these sensors have been explored to produce microfabricated Nitrogen-Phosphorus Detectors (NPDs) to accommodate these many requirements. The device incorporates sol-gel derived alkali

metal silicate thin films on low thermal mass silicon substrates for field portable gas chromatography applications. In spite of the long history of NPDs, the details of the chemically-mediated emission related to their selectivity are not well understood. The NPD signal current ultimately depends on the transfer of electrons across the surface potential barrier of the thermionic cathode emitter. Two classes of competing mechanisms have been described in the literature to account for the chemically-selective ionization observed in NPDs: (a) gas-phase ionization models and (b) surface mediated electron emission. The latter mechanism has been the focus of our measurements of the surface work function of candidate emitter materials as a function of composition, structure, temperature, and ambient atmosphere. Specifically, both the local work function variations by scanning probe measurements and effective average work function by measuring total emission will be discussed.

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