

Friday Morning, October 22, 2010

Surface Science

Room: Santa Ana - Session SS-FrM

Reactivity of Oxides, Mainly TiO₂

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

8:20am **SS-FrM1 Electronic, Chemical, and Morphological Structure of Ag Nanoclusters Grown on FeO_x/Cu(100)**, *F.N. Womack, R. Singh, Y. Losovy, O. Kizilkaya, R.L. Kurtz, P.T. Sprunger*, Louisiana State University

8:40am **SS-FrM2 Effect of Ti Dopant in Ceria on the Structure of Metal Nanoparticles**, *Y. Zhou, J. Zhou*, University of Wyoming

Ceria plays a major role in the chemistry of supported metal nanoparticles. The nanostructure, redox properties and oxygen storage capacity of ceria can affect the morphology, structure, as well as catalytic reactivity of supported metal nanoparticles. The addition of other metal elements such as Ti can result in structural and electronic modifications of ceria, which not only can enhance the thermal stability of ceria, but also improve its redox properties and oxygen storage capacity. In this paper, we discuss the effect of Ti dopant in the ceria support on the structure of metal particles at the fundamental level. Ti-doped CeO_x(111) thin films were prepared on Ru(0001) as model supports under ultrahigh vacuum conditions. Their structures were examined in detail by LEED, XPS and STM. The nucleation and growth of metal particles including Au and Ni on the doped-ceria surfaces were investigated upon deposition at 300 K as well as after heating to higher temperatures, which is compared to that on the pure ceria supports. The research is sponsored by University of Wyoming start-up fund and Wyoming NASA Space grant.

9:00am **SS-FrM3 Nucleation Behavior of Supported Nanoparticles Fabricated from an Organometallic Precursor under Ultra High Vacuum: A DFT and STM Study**, *H. Khosravian, Z. Liang, A. Uhl, R. Meyer, M. Trenary*, University of Illinois at Chicago

In this combined STM and DFT study, we examine the adsorption of Rh(CO)₂(acac) (acac is acetylacetonate) on a TiO₂(110) single crystal surface, which is aimed at developing an understanding of the relationship between the preferred adsorption sites of the supported organometallic species, and the nucleation behavior of this precursor compound on different surface terminations. The STM images of clean TiO₂(110) show large terraces with the characteristic row pattern that arises from alternating lines of bridging oxygen and uncapped titanium ions. After exposing Rh(CO)₂(acac) to the surface at room temperature the formation of small particles is observed, with diameters of 1 nm or less, and a height of 2.5 Å (i.e., monolayer height). After annealing the sample to 630°C the density and number of the particles is significantly reduced. The particles appear to be monodispersed, with their sizes increased to several nm in lateral directions, and about 5 Å in height (i.e., bilayer height). The findings can be rationalized in terms of deligation of the parent species and agglomeration of the denuded rhodium. The details of the adsorption and deligation Process have been characterized with DFT calculations.

9:20am **SS-FrM4 Oxygen Adatom Formation and Charge Transfer upon O₂ Dissociation on Reduced TiO₂(110)**, *I. Lyubinetsky, Y. Du*, Pacific Northwest National Laboratory, *N.A. Deskins*, Worcester Polytechnic Institute, *Z. Zhang*, Baylor University, *Z. Dohnalek, M. Dupuis*, Pacific Northwest National Laboratory

Combination of the statistical analysis by scanning tunneling microscopy and density functional theory calculations has been used to investigate the initial stages of molecular oxygen dissociation on the reduced TiO₂(110) surface at 300 K. Major O₂ dissociation channel results in the bridging O vacancy (V_O) healing and deposition of a single O adatom (O_a), while minor channel results in formation of O_a pair on regular Ti sites. For latter channel, an intermediate, metastable nearest-neighbor O_a-O_a configuration is observed after O₂ dissociation. This initial configuration is destabilized by Coulomb repulsion of charged O_a's that separate further along the Ti row into energetically more favorable second-nearest neighbor configuration. The potential energy profile calculated for O₂ dissociation on Ti rows and following O_a's separation strongly supports the experimental observations. Our results also suggest that the itinerant electrons associated with the V_O's are being utilized in the O₂ dissociation process at the Ti rows, whereas at least two oxygen vacancies per O₂ molecule are required in order for this process to become viable. Overall, the electrons originating from V_O's provide a larger fraction of charge required for O₂ dissociation, while a smaller fraction can be attributed to Ti interstitials.

[1] Du, Y.; Dohnalek, Z.; Lyubinetsky, I. *J. Phys. Chem. C* 2008, *112*, 2649.

[2] Du, Y.; Deskins, N. A.; Zhang, Z.; Dohnalek, Z.; Dupuis, M.; Lyubinetsky, I. *Phys. Chem. Chem. Phys.* 2010, DOI: 10.1039/C000250J.

9:40am **SS-FrM5 Chemistry and Physics of Oxide Surfaces: New Insights from Spectroscopic Studies on ZnO and TiO₂ Single Crystals**, *C. Wöll*, Karlsruhe Institute of Technology, Germany **INVITED**

A thorough understanding of microscopic mechanism governing chemical reactions at oxide surfaces requires precise knowledge about the nature of the molecular adsorbates and possible transition states. With regards to the economically very important applications in heterogeneous catalysis, where powder catalysts are being used, an ideal approach would be to first determine vibrational bands of molecular adsorbates on the surface of the powder particles, then to assign them by using a data-basis for the corresponding vibrations measured for single-crystal model substrates and finally relate the remaining bands to e.g. defect-related species using quantum chemistry calculations. Of course, these calculations should be validated by a comparison to the experimental results contained in the model substrates data base. Unlike the case of metal substrates, unfortunately, the corresponding experimental data base for metal oxide single crystal surfaces is very small, mostly a result of the rather severe technical difficulties in applying vibrational spectroscopies to these insulating, often defective surfaces.

In this talk the results of a systematic study carried out for ZnO and TiO₂ single crystals is presented. In particular for ZnO substrates a rather thorough understanding has been reached, both experimentally and theoretically, about atomic and molecular adsorbates (H, CO, H₂O, CO₂, methanol, ...) on ZnO single crystals as well as on powder particles [1]. This progress is largely based on being able to obtain high-quality experimental data using HREELS (high resolution electron energy spectroscopy) and IR-spectroscopy for single crystal surfaces and IR-spectroscopy for powder particles. The last part of the will focus on hydrogen atoms adsorbed on ZnO and TiO₂, some of which are rather surprising [2] and a short glimpse on photochemistry with oxides [3].

[1] Ch. Wöll, *The Chemistry and Physics of Zinc Oxide Surfaces*, Prog.Surf.Sci. 82, 55, 2007

[2] X. Yin, M. Calatayud, H. Qiu, Y. Wang, A. Birkner, C. Minot, C. Wöll, *ChemPhysChem* 9, 253, 2008

[3] Ch. Rohmann, Y. Wang, M. Muhler, J. B. Metson, H. Idriss, and Ch. Wöll, *Chem. Phys. Lett.* 460, 10, 2008

10:20am **SS-FrM7 Imaging Hindered Rotations of Alkoxy Species on TiO₂(110)**, *Z. Zhang, R.J. Rousseau*, Pacific Northwest National Laboratory, *J. Gong*, University of Texas at Austin, *B.D. Kay, Z. Dohnalek*, Pacific Northwest National Laboratory

The first scanning tunneling microscopy (STM) study of the rotational dynamics of organic species on oxides is presented. Variable-temperature STM and dispersion-corrected density functional theory (DFT-D) are used to study the alkyl chain conformational disorder and dynamics of 1-, 2-, 3- and 4-octoxy species on rutile TiO₂(110). Initially, the geminate pairs of the octoxy and bridging hydroxyl species are created via octanol dissociation on bridging-oxygen (O_b) vacancy defects. The STM images provide time averaged snapshots of octoxy species rotating among multiple energetically nearly-degenerate configurations accessible at a given temperature. The calculations show that the underlying corrugated potential energy surface is a result of the interplay between attractive van der Waals dispersion forces leading to weak attractive C··Ti and repulsive C··O_b interactions which lead to large barriers of 50-70kJmol⁻¹ for the rotation of the octoxy alkyl chains across the O_b rows. The relative populations of various conformations as well as the rotational barriers are found to be perturbed as a result of additional C··hydroxyl repulsions when the geminate hydroxyl groups are present.

This research 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.

10:40am **SS-FrM8 Hydrogen Bonding Controls the Dynamics of Catechol Adsorbed on a TiO₂(110) Surface**, *S.-C. Li*, Tulane University, *L.-N. Chu, X.-Q. Gong*, East China University of Science and Technology, China, *U. Diebold*, Tulane University and Vienna University of Technology, Austria

Direct studies of how organic molecules diffuse on metal oxide surfaces can provide insights into catalysis and molecular assembly processes. We studied individual catechol molecules, C₆H₄(OH)₂, on a rutile TiO₂(110) surface with scanning tunneling microscopy (STM). Surface hydroxyls enhanced the diffusivity of adsorbed catechol molecules. The capture and release of a proton caused individual molecules to switch between 'mobile' and 'immobile' states within a measurement period of minutes. Density functional theory (DFT) calculations show that the transfer of H from surface hydroxyls to the molecule and its interaction with surface hydroxyls substantially lowered the activation barrier for rotational motion across the surface. Hydrogen bonding can play an essential role in the initial stages of the dynamics of molecular assembly.

11:00am **SS-FrM9 Design of Highly Stable Molecular Interfaces to TiO₂ Surfaces**, *R.A. Franking*, University of Wisconsin-Madison, *S.A. Chambers*, Pacific Northwest National Laboratory, *R.J. Hamers*, University of Wisconsin-Madison

The integration of molecular systems with TiO₂ is of interest in a wide range of emerging applications. Previously we developed a photochemical reaction which highly stably and covalently binds terminal alkenes to nanocrystalline and single crystal TiO₂. Here we further develop the reaction to allow the controlled binding of short chain molecules with highly flexible, modular functionalities. Using XPS, FTIR and AFM, we demonstrate that by adding methyl substitutions around the alkene double bond, uniform grafting of the molecules can be controlled from the monolayer to the multilayer regime. Through secondary reactions, click chemistries can be used to attach photo sensitizers and biologically active molecules with the stable linker to the surface. These highly functional molecules grafted to TiO₂ facilitate the study of charge transfer and photo catalysis for wide range of applications involving organic semiconductor oxide interfaces.

11:20am **SS-FrM10 CO Photooxidation on Reduced TiO₂(110) Surface**, *N. Petrik, G.A. Kimmel*, Pacific Northwest National Laboratory

Photo-induced reactions between O₂ and CO on reduced rutile TiO₂(110) surface are studied at low temperature (~30K). Photon stimulated desorption (PSD) of O₂, CO₂ and CO (not reported earlier) are observed with comparable yields. Results indicate that CO₂ is produced from the chemisorbed O₂ molecule residing in the oxygen vacancy and CO molecule physisorbed on the Ti site next to it. The PSD angular distribution for CO₂ is non-cosine, narrow and off-normal: it peaks at ~ 40 degrees to the surface normal in the (001) plane (across the Ti and O rows on the surface). The results are consistent with CO₂ produced from the (Ti)-O-C-O-O-(V_O) transition state complex predicted theoretically. CO PSD from the TiO₂(110) surface is enhanced dramatically by the presence of chemisorbed O₂ molecules, where photo-desorbing CO may be a by-product of the CO photooxidation process.

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