

Thursday Morning, October 21, 2010

Surface Science

Room: Picuris - Session SS-ThM

Adsorption and Reactivity on Oxide Surfaces

Moderator: G. Williams, Jefferson Laboratory

8:00am **SS-ThM1 Adsorption and Reaction on Poorly Crystalline γ - Al_2O_3 Surfaces**, *J.H. Kwak, D. Mei, R.J. Rousseau, J. Szanyi, Y. Wang, C.H.F. Peden*, Pacific Northwest National Laboratory **INVITED**

γ -alumina (γ - Al_2O_3), one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for other catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ - Al_2O_3 , and its formation and thermal stability have been and continue to be the subject of a considerable research. However, due to the low crystallinity and very fine particle size of γ - Al_2O_3 , it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ -alumina, relating its surface structure to the origin of Lewis and Brønsted acidity has been of considerable interest and has been studied by solid state NMR and FTIR spectroscopies, and most recently by theoretical calculations. In this presentation, we describe recent studies using ultra-high resolution NMR spectroscopy as an especially useful probe of the γ - Al_2O_3 surface structure, and its relevance to catalytic behavior. In particular, we correlate the NMR spectra with measurements of the adsorption and reaction of light alcohols. In this way, we demonstrate a strong dependence of this chemistry on the presence of specific 5-coordinate Al^{3+} ions. These sites, in turn are a function of the dehydration temperature of the alumina material before use. From these correlations, we are able to explain a considerable number of prior observed phenomena.

8:40am **SS-ThM3 Evolution and Growth of Polar ZnO Nanostructures and their Correlation with Native Point Defects**, *D.R. Doutt, T.A. Merz, Y.F. Dong, L.J. Brillson*, Ohio State University

We have used a complement of depth-resolved cathodoluminescence spectroscopy (DRCLS), Kelvin probe force microscopy (KPFM), atomic force microscopy (AFM), and surface photovoltage spectroscopy (SPS) to measure how polarity, morphology, and nanoscale growth on ZnO surfaces correlate with electrically-active native point defects. Previous DRCLS showed that ZnO nanostructures can grow spontaneously on bare, air-exposed ZnO surfaces and produce electronically-active defects. SPS measures the filling and emptying of these states and thereby their energy level position in the band gap. CLS associates these optical transitions with V_{Zn} and V_{O} -related ($V_{\text{O-R}}$) defects, respectively. Positron annihilation spectroscopy shows that 2.1eV DRCLS emission correlates with V_{Zn} vs. depth, anticorrelating with 2.5 eV $V_{\text{O-R}}$ emission. SPS correlates these emissions with optical unfilling and filling transitions, respectively, within the same near-surface region on a nanometer scale. The SPS V_{Zn} trap state features vary laterally, increasing in nanostructured regions common to ZnO surfaces versus atomically-flat regions. Near both hexagonal pits on (0001) and individual ZnO nano-mounds on both polar faces, 2.1 eV trap densities increase with radial proximity. KPFM maps before and after 2.25 eV illumination show increased potential that reveals large concentrations of V_{Zn} distributed non-uniformly around and extending away from the hexagonal surface pits. These observations all suggest that ZnO nanostructures grow by oxidation of Zn at the free ZnO surface due to mobile Zn atoms extracted from the underlying lattice.

We measured the morphology, potential, and defect distributions of these structures vs. annealing temperature in flowing oxygen over a 400°C range. AFM/KPFM maps of room temperature and annealed (0001) surfaces reveal deep (~150 nm) hexagonal pits with spoke-like *trenches* extending from both the corners and faces of the hexagonal formation and >50 mV positive potentials that increase with temperature. Conversely, (000-1) surfaces initially show few pits with random geometry and *raised* spoke-like ridges extending from pits. After 1 hr at 200 °C, pitting increases with strong (~150 mV) negative potentials and newly formed spoke-like *trenches*. At 300°C, nanoscale mounds grow 5 – 50 nm high and potentials vary further. From AFM increases in nanorod mass vs. temperature, Arrhenius plots yield 130 ± 10 meV (0001) and 150 ± 10 meV(000-1) activation energies, consistent with the low (0.57 eV) activation energy for Zn interstitial diffusion. Overall, this complement of techniques reveals the interplay between ZnO surface nanostructure, polarity, and electronic defects.

9:00am **SS-ThM4 Atomic Structure and Site Specific Reactivity at Ferroelectric Oxide Surfaces**, *L. Kraya, D.A. Bonnell*, The University of Pennsylvania

The functionality of ferroelectric compounds are inspiring new approaches for catalysis, water splitting, information storage, and nanofabrication. The atomic details of interactions at ferroelectric surfaces are as important as those on other oxides but have been less amenable to examination. Recently we have determined the thermodynamic stability of a wide range of reconstructions on BaTiO_3 (100) and also demonstrated that surface reactions depend on the orientation of the ferroelectric polarization. Here we examine the 3×1 and $R5 \times R5$ reconstruction in atomic detail. Reaction of the $R5 \times R5$ structure with CO_2 is imaged by scanning tunneling microscopy as a function of exposure and the site occupation quantified. In addition, the effect of locally reorienting the ferroelectric polarization with an STM tip is determined by scanning tunneling spectroscopy. Offsets in local I/V curves are related to energy level shifts due to the local field induced by the polarization.

These results will be contrasted with those on non ferroelectric oxides.

9:20am **SS-ThM5 Selective Oxidation of Ammonia on $\text{RuO}_2(110)$: a Combined DFT and KMC Study**, *T.S. Rahman, S. Hong*, University of Central Florida, *A. Karim*, Brookhaven National Laboratory

We have used a combination of density functional theory (DFT) and kinetic Monte Carlo (KMC) simulations to calculate the reaction rates for the selective oxidation of ammonia on the $\text{RuO}_2(110)$ surface. We find that the overall energy barrier for $\text{NH}_3 + \text{O} \rightarrow \text{NH} + \text{H}_2\text{O}$ is 0.56 eV, while that for $\text{N} + \text{N} \rightarrow \text{N}_2$, and $\text{N} + \text{O} \rightarrow \text{NO}$ to be 0.27 and 0.14 eV, respectively. In accompanying KMC simulations, in which we include in addition to the above key processes, several intermediates and their reactions (18 processes), we find selectivity towards NO and N_2 formation, as a function of O_2 pressure range, in excellent qualitative and quantitative agreement with experiment [1]. As for the high reactivity of $\text{RuO}_2(110)$ we concur that hydrogen bonding between ammonia, and its intermediates, with adsorbed and substrate oxygen play a critical role by making H abstraction facile such that NH decomposition is a spontaneous, non-activated process. As for the high selectivity of $\text{RuO}_2(110)$ for ammonia oxidation, the significantly-restricted N diffusion caused by reaction intermediates present on the $\text{RuO}_2(110)$ surface severely affects the recombination rate for $\text{N} + \text{N} \rightarrow \text{N}_2$ while $\text{N} + \text{O} \rightarrow \text{NO}$ is much less affected by such reduced N diffusion due to dissociatively-adsorbing O_2 species on $\text{RuO}_2(110)$. As a result, NO production is remarkably favored than N_2 production even at low O_2 pressure. These results highlight the important role of the chains of undercoordinated Ru atoms on this surface.

[1] Y. Wang, K. Jacobi, W.-D. Schoene, and G. Ertl, J. Phys. Chem. B 109, 7883 (2005).

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9:40am **SS-ThM6 Electron Paramagnetic Resonance Evidence for the Formation of O_2^- on the Surface of Ultra Thin MgO/Mo Films**, *A. Gonchar, T. Risse, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Theoretical calculations [1, 2] have predicted novel catalytic properties of ultra thin MgO films for CO oxidation. In particular, molecular oxygen is thought to be activated on ultra thin MgO films due to a charge transfer from the metal substrate resulting in the formation of paramagnetic O_2^- .

We have investigated the adsorption of O_2 on ultra thin MgO(001) films grown on Mo(001) single crystals using in situ Electron Paramagnetic Resonance (EPR) spectroscopy. Adsorption of oxygen on 4 ML thick MgO(001) films creates an EPR signal associated with the formation of O_2^- radicals. The orientation of these radicals on the MgO surface is deduced from angular dependent EPR measurements. The properties of O_2^- radicals with respect to thermal stability and external parameters such as the film thickness will be discussed.

References

[1] A. Hellman, S. Klacar, and H. Grönbeck, JACS 2009, 131, 16636–16637

[2] P. Frondelius, H. Häkkinen, and K. Honkala, PCCP 2010, 12, 1483–1492

10:40am **SS-ThM9 Franck-Condon Broadening of the XPS of Ionic Materials**, *P.S. Bagus*, University of North Texas, *C.J. Nelin*, Maury's Trail, *E.S. Ilton*, Pacific Northwest National Laboratory

We present an analysis of the width of X-Ray photoelectron spectroscopy, XPS, features that relates the broadening of these features to the chemical activity and reactivity of oxide surfaces. The use of synchrotron radiation allows high resolution measurements of core-level XPS with instrumental resolutions of ~250 meV, or even higher. However, the XPS spectra of many materials, especially oxides and other ionic systems, have features that are much broader than would be expected from instrumental and lifetime broadenings. For example, there are four levels that contribute to the main Mn 2p_{3/2} XPS peak of MnO that are not fully resolved with high resolution synchrotron measurements [1] even though the levels are separated from each other by ~1.5 eV. [2] In another example for the XPS of CeO₂, [3] broadenings of the theoretical results of ~2.5 eV FWHM are required to have the theory match experiment. While surface effects or other inhomogeneities might, in principle, account for large broadenings, we investigate here the contribution to XPS broadening due to vibrational excitations in the final ionic states. Large Franck-Condon broadenings are known for photoemission from molecules [4] but have not been studied in connection with the broad features in the XPS of ionic crystals. We investigate changes in the metal-oxygen bond length for ionic states of MnO and CeO₂, where a metal core-level has been ionized, using wavefunctions and energies for embedded cluster models of these materials. Initial and final state potential energy surfaces are determined for breathing motions of the nearest oxygen neighbors of the ionized metal cation. These surfaces allow us to determine the Franck-Condon envelope for transition from the $\nu=0$ initial, ionized state to vibrationally excited levels of the final, ionized state and show the broadenings that arise from these excitations. Furthermore, we make correlations between the changes in the metal-oxygen bond distances in the ionic states with changes, increases, in the final state covalent metal-oxygen bonding over the initial state covalent character. This correlation may provide a new and novel way to use high resolution photoemission to obtain information about the nature and strength of the bonding in ionic materials.

(1) V Bayer, R Podlucky, C Franchini, F Allegretti, X Bo, G Parteder, MG Ramsey, S Surnev, FP Netzer: *Phys. Rev. B* **76**, 165428 (2007).

(2) PS Bagus, ES Ilton: *Phys. Rev. B* **73**, 155110 (2006).

(3) PS Bagus, CJ Nelin, ES Ilton, M Baron, H Abbott, E Primorac, H Kuhlbeck, S Shaikhutdinov, HJ Freund: *Chem. Phys. Lett.* **487**, 237 (2010).

(4) PS Bagus, EK Viinikka: *Phys. Rev. A* **15**, 1486 (1977).

11:00am **SS-ThM10 Ethylene Glycol Adsorption and Decomposition over CeO₂ (111) Surfaces**, *T.-L. Chen*, *F.C. Calaza*, *S.H. Overbury*, *D.R. Mullins*, Oak Ridge National Laboratory

Hydrogen production from the reforming of oxygenated hydrocarbons is highly dependent on the heterogeneous reactions provided by its catalysts. Cerium oxide supported metal catalysts can offer a means of reducing precious metal loading and achieving higher selectivity. Thus studying the direct contribution from the metal oxide surface to the decomposition of the molecules can give insight into the catalytic reforming process.

In light of our previous characterization on C₁-C₃ oxygenate reactions on well-defined cerium oxide thin films, we further examine ethylene glycol as a model system for bio-mass derived hydrocarbons. As the simplest diol, ethylene glycol has two symmetric hydroxyl groups which are available to interact with the surface. The adsorbates can bond to the surface through either one or both of these oxygens, which may lead to a different decomposition pathways.

On the surface of the fully oxidized ceria ethylene glycol appears to initially bond to the surface through only one of the C-O groups. As the temperature is increased both ends interact with the surface and one C-O group is converted into a carboxylate group (COO). The primary reaction products are acetaldehyde, ethylene, acetylene, water and H₂. CO desorption was also observed indicating some of the oxygenates experienced C-C bond breaking. On a reduced surface one end of the molecules undergoes C-O cleavage resulting in a C-Ce bond rather than an additional C-O bond. The surface intermediate is a carbanion, similar to what was observed for acetaldehyde. More acetylene is observed from a reduced surface.

The dependence of the reaction pathways on the coverage of ethylene glycol was also examined on the oxidized and reduced surfaces. At larger coverage, the formation of carboxylates or carbanions is hindered which suggests that the formation of these species may be sterically limited.

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supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

11:20am **SS-ThM11 Synthesis and Characterization of Cerium Oxide Nanoparticles with Well-defined Crystallographic Terminations**, *S.H. Overbury*, *M. Li*, *Z. Wu*, *D.R. Mullins*, *J. Howe*, Oak Ridge National Laboratory

Through hydrothermal synthesis techniques it is possible to create oxide nanoparticles with highly uniform dimensions and shapes and therefore with crystallographically well-defined terminations. These mono-faceted nanocrystals provide an opportunity to examine structure dependence in surface chemistry with the advantage of using methods appropriate to high surface area materials. We have synthesized cubic, octahedral and rod-shaped nanoparticles of CeO₂ that are terminated exclusively in (100), (111) or a mixture of (100) + (110) crystallographic terminations, respectively. These have been used to compare reducibility, stability and adsorption of water, oxygen and alcohol with the goal of characterizing and understanding the effect of surface structure upon the reaction of these molecules with the surface or with other adsorbates. Multi-wavelength Raman and FTIR in the DRIFTS mode are performed in controlled ambient pressure gas streams, and are combined with pulsed / switched chemisorption and temperature programmed techniques. UV Raman reveals that the CeO₂ nanocrystals contain stable bulk-like Frenkel defects, identified by a characteristic Raman feature, and these are more prevalent in the rod-like particles with (110) + (100) termination. Reduction of the nanoparticles in hydrogen at 673 K leads to oxygen vacancies that are identified by a Raman feature near 560 cm⁻¹ and the rods are more easily reduced while the octahedral are the least. Oxygen vacancies are immediately removed by O₂ at room temperature on all ceria polymorphs. Upon adsorption of isotopically labeled O₂ at 80 K on reduced surfaces, peroxide and superoxide species are observed and these dissociate or desorb as the temperature is increased. Clustered and isolated peroxides are distinguished by their Raman frequency and their relative ratio depends upon degree of reduction and surface structure. Adsorption of D₂O and H₂O on each of the surfaces was probed by DRIFTS at room temperature following dehydroxylation at 673 K. Following a pulse of water, OD (OH) features are observed with characteristic IR frequencies. These results are compared to "single crystal" RAIRS studies on CeO₂(111) oriented films and with previously published IR studies of highly dispersed, polycrystalline CeO₂ crystals of undefined structure terminations. The features observed agree with previous work but their prevalence differ between the faceted nanocrystals and the differences allow structural assignments of the IR features. The results lead to a re-assignment of the IR features.

11:40am **SS-ThM12 Surface Analysis of Selected Metal-Doped Adsorbent Materials for Logistics Fuels Desulfurization**, *R.A. Quinlan*, NSWC, Carderock Division, *J.M. Heinzel*, NSWC, *A.N. Mansour*, NSWC, Carderock Division

Transportation fuels, i.e., gasoline, diesel and jet fuels have been identified as a potential hydrogen source for fuel cell applications due to their high energy densities, ease of storage and availability. However, these liquids, especially the diesel and jet fuels, can contain extremely high concentrations of sulfur. If hydrogen or reformat syngas is to be produced from these high sulfur content fuels, catalyst degradation of the reformer system can occur. Additionally, sulfur compounds such as H₂S and COS are capable of poisoning follow-on processing operations and the electrode catalyst of the fuel cell. Therefore, desulfurization is paramount for the development of logistics fuels as a hydrogen production source. Recently titania and silica supported silver have shown high performance as regenerable desulfurization sorbents. A variety of techniques have been employed to specifically investigate the active form of the material, and the nature of the adsorptive sites and their interactions with the support, as well as the adsorbed species. Specifically, x-ray photoelectron spectroscopy (XPS) to study the surface chemistry and x-ray absorption spectroscopy (XAS) to study the bulk structure of composite materials were utilized. This provides insight into how the Ag/support system enables such high adsorptive capacities.

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