

Surface Science Division

Room 203C - Session SS+HC+MI-TuA

Oxides/Chalcogenides: Structures and Reactions

Moderator: Andrew Teplyakov, University of Delaware

2:20pm SS+HC+MI-TuA1 New Eyes for Nanocatalysis: Atomic Scale Investigations of TiO₂ Chemistry, *Melissa Hines*, Cornell University INVITED

The atomic-scale surface chemistry of nanocatalysis has remained relatively unexplored for two simple reasons. First, nanocatalysts are too small to be studied individually with most surface science techniques. Second, nanocatalysts are typically used at ambient pressure or in solution — conditions where surface contamination is a significant concern. In this talk, I will review our work in developing “new eyes for nanocatalysts” that address both issues.

Addressing the issue of size, I will show that hydrothermal crystal growth techniques can produce anatase nanocrystals suitable for study at the atomic-scale with STM and a panoply of techniques. Despite being synthesized in solution, the nanocrystal surfaces are very clean and passivated by a protecting monolayer. Using these crystals, I will show that the most commonly used functionalization chemistry for oxide nanocatalysts, a carboxylic acid solution, causes the spontaneous reorganization of the nanocatalyst, leading to a five-fold increase in the number of reactive sites.

Addressing the issue of contamination, I will explain the chemical origin of the molecularly ordered interfaces that have been observed by researchers around the world when TiO₂ surfaces are exposed to air or solution. Although these structures have recently been attributed to a new (2 × 1) ordered state of adsorbed H₂O, we show that clean TiO₂ surfaces selectively adsorb atmospheric organic acids that are typically present in parts-per-billion concentrations while effectively repelling other adsorbates, such as alcohols, present in much higher concentrations. This finding may have important implications for TiO₂ photocatalysis, as the self-assembled carboxylate monolayer resists desorption under environmental conditions while effectively blocking the transition metal sites typically implicated in photocatalysis.

As time allows, I will also show that solution-phase techniques can be used to prepare a wide variety near-atomically-perfect, self-assembled monolayers on TiO₂ surfaces.

3:00pm SS+HC+MI-TuA3 Coverage-dependent Water Agglomerates on Fe₃O₄ Surfaces, *Zdenek Jakub*, Vienna University of Technology, Austria; *M. Meier*, University of Vienna, Austria; *J. Hulva*, *J. Pavelec*, *M. Setvin*, *M. Schmid*, *U. Diebold*, Vienna University of Technology, Austria; *C. Franchini*, University of Vienna, Austria; *G.S. Parkinson*, Vienna University of Technology, Austria

The interaction between iron oxides and water plays a key role in many natural and technological processes. Recent water adsorption studies have found significant complexity on metal oxides, with reports of mixed-mode adsorption and hydrogen bonding. Here we present a multi-technique study of water adsorption on Fe₃O₄ surfaces. Utilizing quantitative temperature programmed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS), we identify four partially dissociated phases in the submonolayer regime on the Fe₃O₄(001), corresponding to coverages of 9, 8, 6 and 3 molecules per surface unit cell. These are investigated by non-contact atomic force microscopy (nc-AFM) with tip functionalized by CO molecule, and the observed structures are further interpreted by DFT-based calculations. We clearly demonstrate the existence of partially dissociated dimers and trimers at lower coverage, and a build-up of complex hydrogen-bonded network with increasing coverage. Applying the same approach on the Fe₃O₄(111) we discuss the general trends of water adsorption on Fe₃O₄ surfaces.

3:20pm SS+HC+MI-TuA4 Reversible Structural Evolution and Identification of the Catalytically Active Phase of NiCoO_xH_y During the Oxygen Evolution Reaction (OER), *Bruce E. Koel*, Princeton University

Significant improvements in the activity of transition metal oxides (TMOs) for the oxygen evolution reaction (OER) have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, and using conductive supports. However, the complex composition and structure of TMO catalysts have hindered the elucidation of clear structure-activity correlations. We have utilized a range of electrochemical techniques, such as electrical impedance spectroscopy (EIS), and

spectroscopic techniques, including ambient pressure photoelectron spectroscopy (APPEs), for characterization of pure and Ni-modified cobalt (oxy)hydroxide electrocatalysts for OER. In particular, operando Raman spectroscopy and electrochemical techniques were used during the oxygen evolution reaction to identify the composition and local structure of electrodeposited CoO_xH_y and NiCoO_xH_y catalyst films. In these studies, several unique initial catalyst structures and crystallinities were prepared by subjecting the samples to a variety of thermal and electrochemical conditioning procedures before evaluation. During oxygen evolution, Ni-modified CoO_xH_y films with lower initial crystallinity underwent substantial structural evolution that began with an irreversible transformation of a spinel local structure to an amorphous CoO structure at low anodic potentials. Increasing anodic polarization with elevated oxygen evolution rates caused additional structural conversion of the amorphous CoO structure to a complex phase that can be described as an amalgamation of NiOOH and layered CoO₂ motifs (NiOOH-h-CoO₂). The formation of this active structure was correlated with improved OER activity. Formation during oxygen evolution of the same NiOOH-h-CoO₂ structure independent of the initial cobalt oxide structure suggests that this active phase identified in these studies could be the universally active structure for NiCoO_xH_y catalysts.

4:20pm SS+HC+MI-TuA7 Understanding the Growth and Chemical Activity of Titania-Supported MoS_x Clusters, *Donna Chen*, University of South Carolina; *R.P. Galhenage*, University of California at Irvine; *H. Yan*, University of Louisiana Lafayette; *D. Le*, *T.B. Rawal*, *T.S. Rahman*, University of Central Florida

MoS_x clusters have been grown on TiO₂(110) in order to provide a model surface for better understanding adsorbate interactions and chemical activity of supported MoS_x clusters; MoS₂ particles have exhibited excellent catalytic activity for a variety of reactions, particularly for hydrodesulfurization and photocatalysis, and interactions with the support are believed to induce new electronic properties. The MoS_x clusters were grown by deposition of Mo on titania in an atmosphere of H₂S, followed by annealing to 950 K in H₂S. Scanning tunneling microscopy experiments show that clusters with elongated, rectangular shapes and flat tops are formed, and the long axes of the clusters have specific orientations with respect to the [001] direction on TiO₂(110). In contrast, deposition of Mo in the absence of H₂S results in a high density of smaller, round clusters that cover the majority of the surface. The morphologies of MoS_x clusters do not change after exposure to various gases (D₂, CO, O₂, methanol) in ultrahigh vacuum. However, exposure to higher pressures of O₂ (250 mTorr) or air causes the clusters to disintegrate as Mo in the clusters becomes oxidized. Temperature programmed desorption studies with CO on the MoS_x clusters show a distinct desorption peak at 275 K, which is not observed on metallic Mo or titania. Density functional theory calculations demonstrate that the presence of the titania support changes in the favored adsorption site for CO from the (-1010) edge in the pristine MoS₂ to the (10-10) edge for the supported MoS₂. Furthermore, the MoS_x/TiO₂(110) interfacial sites are not favored for CO adsorption.

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4:40pm SS+HC+MI-TuA8 Analyzing Single Atom Catalysts using Low Energy Ion Scattering (LEIS), *Thomas Grehl*, IONTOF GmbH, Germany; *R. ter Veen*, Tascon GmbH, Germany; *D. Kunwar*, *A. Datye*, University of New Mexico; *H.H. Brongersma*, IONTOF GmbH and Tascon GmbH, Germany

An important goal of heterogeneous catalyst synthesis is the dispersion of the active metal uniformly on a catalyst support, ideally achieving atomic dispersion. Isolated atoms dispersed on oxide supports (single-atom catalysts) provide efficient utilization of scarce platinum group metals, and higher reactivity as well as better selectivity for a range of catalytic reactions.

One of the challenges is to achieve high enough loadings and to prevent agglomeration by limiting the synthesis and operation temperature. Consequently, the characterization of these materials is essential to monitor the dispersion.

Low Energy Ion Scattering (LEIS) is a surface analytical technique that quantitatively determines the elemental composition of the outer atoms with ultimate surface sensitivity. LEIS is compatible with non-conducting supports and insensitive to topography, making it an ideal tool to analyze both model and industrial catalysts. Due to its unique surface sensitivity the results of the analysis usually correlate directly with the properties of the catalyst.

This contribution demonstrates the analysis of Pt/CeO₂ single atom catalysts using LEIS. During synthesis (atom trapping) the Pt precursor is

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heated in air at 800 C to form mobile Pt species that deposit on the support and are strongly bound. On high surface area ceria, metal loadings of 3 wt. % can be achieved while maintaining almost exclusively single atoms. We will describe how LEIS was essential to demonstrating the single atom nature of the catalyst. In conjunction with X-ray absorption spectroscopy (XAS), Aberration-Corrected Scanning TEM (AC-STEM) and Diffuse Reflectance Infrared Absorption Spectroscopy (DRIFTS) we were able to develop an accurate picture of the sites that bind Pt ions on the support. The atomistic model for the single atom Pt catalyst was corroborated by Density Functional Theory (DFT).

The LEIS results revealed that with increasing metal loading, the fraction of Pt visible to LEIS decreased by 20%. However XAS, DRIFTS and AC-STEM confirmed that the Pt was present in single atom form even at the highest metal loadings. Further analysis led to the realization that the Pt atoms are present in close proximity at high loadings, causing some of the Pt to be rendered invisible to LEIS. The loss in LEIS signal could be correlated with the differences in reactivity for CO oxidation, which otherwise could not be easily explained. This application demonstrates the extreme sensitivity of LEIS which makes this analytical approach essential for study of heterogeneous catalysts used in industry.

Part of this work was supported by DOE grant DE-FG02-05ER15712 and NSF grant EEC-1647722.

5:00pm SS+HC+MI-TuA9 Synthesis and Characterization of Metals Supported on ZnO Nanoparticles, Amanda Haines, D.F. Ferrah, J.C. Hemminger, University of California at Irvine

Various metals on transition metal oxide supports, such as Cu/ZnO, have been widely studied to understand their role in CO₂ hydrogenation. However, there still remains a dispute as to the role of the oxide supports and the surface oxidation state of the active metal and its efficacy in the reduction of CO₂, namely on the nature of CO₂ adsorption and activation. Here, we have designed and characterized a model catalytic system that will enable us to explore the chemistry of various metals (M: i=Pt,Cu) on ZnO supports. ZnO nanoparticles (NPs) have been deposited on an inert highly oriented pyrolytic graphite (HOPG) substrate by physical vapor deposition (PVD). From scanning electron microscopy (SEM), we have seen that hexagonal shaped ZnO nanoparticles are formed on a defect-free HOPG substrate. Different surface plasma treatments have been explored to create defect sites on the HOPG substrate to better control the density of the ZnO NPs and various substrate temperatures have been studied to investigate its effect on the size, morphology, structure and chemistry of the NP growth process. Different metals, Pt and Cu, are photodeposited on the ZnO NPs and fully characterized using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature programmed desorption (TPD) to gain fundamental information about the oxidation states and active sites of these M_i/ZnO NPs. Future work will involve reactivity studies on the fully characterized M_i/ZnO NPs using ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) to investigate the surface chemistry, intermediates and products of this catalyst to gain insight into the reaction mechanism of CO₂ hydrogenation.

5:20pm SS+HC+MI-TuA10 Molecular Water Adsorption and Reactions on α -Al₂O₃(0001) and α -Alumina Particles, Greg Kimmel, N.G. Petrik, Pacific Northwest National Laboratory; P.L. Huestis, J.A. LaVerne, University of Notre Dame; A.B. Aleksandrov, T.M. Orlando, Georgia Institute of Technology

Alumina and its interactions with water are important in areas ranging from electronics and catalysis to environmental science. However, a basic understanding of the adsorption and reactions of water on even the simplest alumina surface, the (0001) surface of α -alumina, remains elusive. We have investigated the adsorption and reaction of water on single crystal, α -Al₂O₃(0001) in ultrahigh vacuum, and α -alumina particles in ambient conditions, using temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and other surface science techniques. For a water coverages of 1 and 2 H₂O/(surface Al³⁺) on α -Al₂O₃(0001), no evidence for the surface hydroxyls expected from dissociative adsorption was observed, while the ν_2 vibration of molecular water was observed. Electron-stimulated desorption of molecular water at low coverages also indicated molecular or mixed (molecular plus dissociative) adsorption. In contrast with the single crystal results, IR spectra of water adsorption on alumina particles indicated the presence of surface hydroxyls that persist even after annealing to high temperatures in oxygen. The results, which are consistent with at most a small amount of water dissociation on the Al-terminated (0001) surface, are difficult to

reconcile with calculations suggesting that the barrier to dissociation is small. However, the results are consistent with recent vibrational sum frequency experiments showing that the hydroxylation of the Al-terminated (0001) surface takes many days even at ambient pressures and temperatures.

5:40pm SS+HC+MI-TuA11 Applying Low Temperature Titration for Determination of Metallic Sites on Active Oxide Supported Catalysts, Jerry Pui Ho Li, Z. Liu, Y. Yang, ShanghaiTech University, China

Catalysts are used in a variety of applications from the production of fuels or consumer chemicals, and the environment. Characterization of such catalysts is critical, since it allows for an accurate representation of its effectiveness. For optimum design and efficient utilization of catalysts, it is important to be able to connect model catalyst and industrial catalyst turnover frequencies (TOF) based on the same benchmark for active sites, such as metallic sites, for catalyst evaluation and further kinetics studies. Characterization of the active sites with chemisorption is ideally performed with high time resolution and sensitivity; particularly for catalysts with low loading of the active particles.

Chemisorption study is the common method for active site determination, but has limitations for active heterogeneous catalysts; particularly industrial catalysts because the method often cannot distinguish the redox on metallic sites and catalyst support. An online micro reactor combined with online mass spectroscopy was developed for kinetics studies within wide temperature (as low as liquid nitrogen) and pressure ranges. Pt and Cu based catalysts are used as demonstration of this technique for metallic sites quantitative calibration in this study. Pt catalysts were characterized using CO oxidation and Cu catalysts were characterized using N₂O decomposition. By comparing titration products curves (CO₂ for Pt catalysts, and N₂ for Cu catalysts) versus temperature for both supported samples, narrow subzero temperature windows are found for each catalyst, demonstrating that the titration products are only related with metallic sites. Pure metallic powder was analyzed for confirmation. Specialized chemisorption procedure was established for each sample. This procedure shows a reliable direct titration measurement recipe for the characterization of supported catalysts, quantifying only the metallic sites for catalysts while being selective against surfaces that contribute secondary reactions often found with more complex supports.

We also present a specialized chemisorption technique applied for metallic sites determination of Au nanoparticles on TiO₂ support through CO at low temperature by comparing IR assignment.

6:00pm SS+HC+MI-TuA12 Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures, Shanyuan Niu, University of Southern California; G. Joe, University of Wisconsin - Madison; H. Zhao, M. Mecklenburg, University of Southern California; T. Tiwald, J.A. Woollam Co. Inc; K. Mahalingam, Air Force Research Laboratory; H. Wang, University of Southern California; M. Kats, University of Wisconsin - Madison; J. Ravichandran, University of Southern California

Optical anisotropy is a crucial building block to engineer the polarization of light in polarizing optics, light modulators, imaging and communication systems. While metamaterial architectures with form birefringence can overcome the limited optical anisotropy available in widely used natural anisotropic crystals, their deployment is limited by the demanding fabrication. We demonstrate the realization of giant optical anisotropy via chemically engineering the polarizability tensor in a natural material, BaTiS₃, which has a highly anisotropic quasi-1D structure and features easily accessible in-plane anisotropy. Large single crystals were grown with the chemical vapor transport method. We report the observation of a large, broadband infrared birefringence and linear dichroism. As-grown crystals demonstrate strong dichroism with two distinct optical absorption edges for light with polarizations along two principal axes. To our knowledge, the unprecedented birefringence in the transparent region is more than twice as large as that in any other bulk crystal.

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