

Monday Afternoon, October 30, 2017

Surface Science Division

Room: 25 - Session SS+AS+HC-MoA

Surface Science for Energy and the Environment

Moderators: Steven Bernasek, Yale-National University of Singapore, Bruce Koel, Princeton University

2:20pm **SS+AS+HC-MoA3 Photochemistry of CO, Acetone and O₂ on Reduced Rutile TiO₂(110)**, *Greg Kimmel, N.G. Petrik, M.A. Henderson*, Pacific Northwest National Laboratory **INVITED**

TiO₂ is an important photocatalyst with many practical applications. However, a fundamental understanding of the thermal and non-thermal reactions on TiO₂ surfaces is still lacking. We use ultrahigh vacuum (UHV) surface science techniques to investigate in detail representative reactions on single crystal rutile TiO₂(110). For this talk, I will focus on the ultraviolet (UV) photon-stimulated reactions of CO, acetone and oxygen adsorbed on TiO₂(110). For CO co-adsorbed with O₂, CO₂ is produced during UV irradiation. The CO₂ preferentially desorbs in the plane perpendicular to the bridge-bonded oxygen (BBO) rows at an angle of 45°. Furthermore, the production rate of CO₂ is zero when the UV irradiation starts and reaches a maximum value at intermediate times before decaying at longer times. The results demonstrate that the photooxidation of CO is a multi-step reaction that proceeds through a metastable intermediate state that is oriented perpendicular to the BBO rows. This state is consistent with an O-O-C-O state found via density functional theory. For acetone co-adsorbed with oxygen, previous research suggests that a thermal reaction between acetone and adsorbed oxygen to form an acetone diolate precedes the photochemistry. During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy (IRAS), we have identified the acetone diolate. We have also measured the angular distribution of the photodesorbing methyl radicals. Consistent with its ejection from acetone diolate, we observe a peak in the distribution at ~45° in the plane perpendicular to the BBO rows. However, a second photodesorption peak normal to the surface indicates that a second, previously unidentified, reaction channel is available. We attribute this second channel to the photo-induced formation of an enolate intermediate. When only O₂ is adsorbed on TiO₂(110), its photochemistry depends on the coverage. For small coverages, only ~14% desorbs while the rest either dissociates during UV irradiation, or remains molecularly adsorbed on the surface. For the maximum coverage of chemisorbed oxygen, the fraction of O₂ that photodesorbs is ~45%. While photo-generated holes are responsible for the O₂ photodesorption, photo-generated electrons are responsible for the photo-induced O₂ dissociation. In general, these studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO₂.

3:00pm **SS+AS+HC-MoA5 The Role of Band Alignment in Ketone Photooxidation on TiO₂(110)**, *Amanda Muraca*, Stony Brook University, *M.G. White*, Brookhaven National Lab and Stony Brook University

Organic photooxidation processes on the TiO₂(110) surface often show enhanced photoproduct yields in the presence of oxygen. For a series of simple ketones, it has widely been established that the photoactive surface species is a ketone-oxygen complex (η_2 -ketone diolate) formed by interaction with O-adatoms, whereas the η_1 -bound ketone is mostly photo-inactive.¹ The question remains, however, why the ketone-oxygen complexes are more photoactive than the adsorbed ketone alone. One possible explanation is that the diolate species have higher densities of molecular states near the valence band maximum (VBM) of TiO₂ where resonant electron transfer to thermalized holes is expected to occur. To test this hypothesis, a series of methyl photoyield measurements, with and without co-adsorbed oxygen, were compared for a number of substituted ketone molecules (R(CH₃)CO; R = H, methyl, ethyl, butyl, propyl, phenyl, and trifluoromethyl) with varying ionization potentials (IPs). Experimentally, we observe a near linear correlation between the methyl photoproduct enhancement yields (diolate vs ketone) and the IPs of the bare ketone. These results suggest that as the ketone IP moves to higher energies, its hybridized orbitals move further (deeper) from the VBM and thereby exhibit a larger photoproduct enhancement when forming the ketone-diolate. This explanation points to orbital band alignment as the key factor determining ketone photooxidation activity, but this conclusion is largely based on the gas-phase properties and well established ideas of substituent effects. To gain more insight on our experimental results, we are currently using electronic structure calculations, both cluster models and periodic DFT, that could potentially provide more detail on band alignments for these molecules bound on the TiO₂(110) surface.

1. M. A. Henderson, N. A. Deskins, R. T. Zehr, M. Dupuis, *J. Catal.* **2011**, 279, 205; N. G. Petrik, M. A. Henderson, G. A. Kimmel, *J. Phys. Chem. C* **2015**, 119, 12262.

3:20pm **SS+AS+HC-MoA6 Storing Gases in Nanoporous Metal organic Frameworks Materials with a Surface Barrier Layer**, *Kui Tan*, the University of Texas at Dallas, *S. Jensen, S. Zuluaga*, Wake Forest University, *E. Fuentes, E. Mattson, J.-F. Veyan*, University of Texas at Dallas, *H. Wang, J. Li*, Rutgers University, *T. Thonhauser*, Wake Forest University, *Y.J. Chabal*, University of Texas at Dallas

Enhancing gas adsorption in porous materials such as metal organic frameworks (MOFs) is critical to many technologies such as energy storage and gas capture and separation. In contrast to the previous efforts focusing on chemically modifying the entire MOFs structure to increase the affinity to gas molecules, in our recent work [Nature Communications, 2016, 7, 13871], we demonstrated an entirely new approach to trap small molecules by depositing a layer of ethylenediamine (EDA) on the external surface without penetrating inside the bulk of crystals in the gas loading process, and forms a monolayer cap that can effectively trap weakly adsorbed molecules (CO, CO₂, SO₂, C₂H₄, NO) or prevent their penetration. A combination of surface sensitive techniques *in-situ* infrared spectroscopy, X-ray photoelectron spectroscopy with gas cluster sputtering, low energy ion spectroscopy, and *ab initio* calculations demonstrate that the EDA layer is less than 1nm thick and arranges in a manner that increases CO diffusion barrier by ~24 times. Motivated by this finding, we further explore other capping media to store molecules inside MOFs. The latest experimental results suggest at least two ways: one is the deposition of a thin layer of aluminum oxide exclusively onto the external surface of certain MOFs with a narrower pore size (< 1.2 nm) by using common atomic layer deposition (ALD) precursor trimethylaluminum (TMA). Aluminum oxide is not able to grow inside MOFs since the reactivity of TMA with adsorbed H₂O is significantly reduced due to nano-confinement effects; another convenient way is post-exposure of gas-loaded MOF-74 to NH₃. NH₃ is preferentially adsorbed on the outer layer of MOFs crystals during the controlled exposure time (<10 min), as a result of which, the diffusion barrier of small gas molecules such as CO, CO₂, SO₂ in NH₃ decorated MOFs channels dramatically increases by the hydrogen bonding interaction. The ability to create surface barrier layers on MOFs external surfaces constitutes a new paradigm for trapping small gas molecules within nanoporous materials in general, and in MOFs in particular.

4:00pm **SS+AS+HC-MoA8 Active Species and Structures of Modified Oxide Catalysts for the Oxygen Evolution Reaction (OER)**, *Z. Chen*, Princeton University, *L. Cai*, Xi'an Jiaotong University, China, *Bruce Koel*, Princeton University

Transition metal oxides (TMOs) are promising catalysts for oxygen evolution with the potential to replace precious metal-based catalysts (e.g. IrO_x and RuO_x). Significant improvements to the OER activity of TMOs have been made by tailoring the morphology and crystal structure of the catalysts, incorporating dopants, as well as using conductive supports. However, clear structure-activity correlations remain elusive because of the complex composition and structure of TMO catalysts. In this contribution, we utilizing a range of spectroscopic techniques for characterization of Ce-modified copper oxide (CuO_x) and Ni-modified cobalt (oxy)hydroxides to reveal the OER active species and structures of these catalysts. In the case of Ce-modified CuO_x, Ce incorporation (6.9 at%) into CuO_x led to 3.3 times greater OER activity compared to pure CuO_x, and this is coincident with significant structural changes due to an increasing amount of disorder. By combining X-ray photoelectron and Raman spectroscopy techniques, a strong correlation between OER performance with tetravalent Ce (Ce⁴⁺) ions was observed up to a concentration corresponding to CeO₂ phase segregation. We propose a strong promoting effect of Ce⁴⁺ for OER in this system. In the case of Ni-modified CoO_xH_y, operando Raman spectroscopy was used to reveal a drastic transformation of a spinel Co₃O₄-like structure into a more active (oxy)hydroxide structure under applied potential. Such a transformation was only observed in the presence of uniformly distributed Ni ions. These two examples, i.e. the promoting effect of Ce⁴⁺ and the formation of active OER structures in Ni-modified CoO_xH_y, reveal the importance of chemical state and local structure considerations for the rational design of OER oxide-based OER catalysts.

4:40pm **SS+AS+HC-MoA10 Cactus Based-Mucilage as an Alternative Natural Dispersant for Oil Spill Applications**, *Fei Guo*, *D. Steebins*, *S. Thomas*, *R. Toomey*, *N. Alcantar*, University of South Florida

Functional surfactants from natural materials have the advantage of being biodegradable and can be obtained through sustainable agriculture. The functional natural surfactants was extracted from the *Opuntia ficus indica* cactus plant. The properties of the cactus plant-based mucilage were studied

on the surface tension change, droplet size, and stability of Oil in Water (O/W) emulsions, toxicity, and dispersion effectiveness. Surface tension test was used to quantify the variation of surface tension of the Oil/Water (O/W) emulsion with the application of cactus mucilage and conventional dispersants (COREXIT 9500). The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:50, and 1:20), Volume ratio of oil (3 and 6% v/v). It is observed that the application of NE reduced the surface tensions of the O/W emulsions. It also can be seen that the surface tensions of the O/W emulsion displayed a distinction among the different DORs at a lower volume ratio of oil. The results of the dispersion obtained using mucilage extracts were compared with using COREXIT 9500. The surface tensions of emulsions with cactus mucilage were similar as that with COREXIT 9500. The average droplet size in the systems with cactus mucilage were smaller when compared with the systems using the COREXIT 9500. Smaller droplet size implies higher emulsion stability, and may improve the biodegradation of oil. The baffled flask test was conducted to determine the influence of three environmental factors with cactus mucilage on oil dispersion. The percentage effectiveness of the dispersion was the response variable for this experiment. The factors and the levels of each factor were as follows: DOR (mg/mg) (control, 1:200, 1:100, 1:75, 1:50, 1:35, and 1:20), salinity of the synthetic seawater (10 and 35 PSU), and mixing speed (150, 200, and 250 rpm). The results showed that the dispersion effectiveness increased as DOR increased. There was also a good distinction among the different DORs. The increasing of the amount of cactus mucilage caused a reduction of the interfacial tension of O/W emulsion which made it easier to form the oil droplets. The cactus mucilage performed better at a lower salinity. The toxicity of the mucilage and COREXIT 9500 were evaluated by a standard EPA toxicity test using *Daphnia magna* colonies exposed to NE mucilage extract in concentrations ranging from 0 to 2000 mg/L for 48 hours. It has shown that mucilage can be classified as practically non-toxic to the *Daphnia magna* colonies with a LC_{50} above 500 mg/L, while the LC_{50} of COREXIT 9500 was below 2 mg/L, which is moderately toxic to the *Daphnia magna* colonies.

5:00pm **SS+AS+HC-MoA11 The Effect of Humidity on Chemical Interactions at Hybrid Interfaces: An In Situ Investigation of Polymer/Metal Oxide Bonds**, *Sven Pletincx*, Vrije Universiteit Brussel, Belgium, *L. Trotochaud*, Lawrence Berkeley National Laboratory, *L.-L. Fockaert*, TU Delft, Netherlands, *A.R. Head*, *O. Karshoğlu*, Lawrence Berkeley National Laboratory, *J.M.C. Mol*, TU Delft, Netherlands, *H. Bluhm*, Lawrence Berkeley National Laboratory, *H. Terryn*, *T. Hauffman*, Vrije Universiteit Brussel, Belgium

Probing interactions at the interface of polymer coatings and passivated metal oxide surfaces under humid conditions has the potential to reveal the local chemical environment at solid/solid interfaces under real-world, technologically relevant conditions. Common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*. Stability of formed bonds in aqueous environments between carboxylic acid functional groups of a polymer and a hydroxide surface of aluminum oxide has a great relevance to a broad range of applications. Although this region is very important for understanding adhesion of the polymer coating, it is very challenging to get useful information directly from the solid/solid interface, let alone characterize the effect of water on the formed chemical bonds.

Recent developments in the field of ambient-pressure photoelectron spectroscopy (APXPS) make it possible to set up a novel approach with respect to interface studies. [1] This is done by making the polymer layer sufficiently thin to access the interface with this surface analysis technique. A broad range of relative humidity can be simulated in the analysis chamber, to unravel interfacial chemistry changes of the hybrid system *in situ*. Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. [2]

Complementary *in situ* ATR-FTIR Kretschmann experiments on a similar model system are conducted. An Al layer is sputtered on an IR transparent crystal, the IR signal at the interface is amplified because of the Kretschmann effect and a near-interface spectrum of the oxide/polymer surface is obtained. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H₂O) can be probed. An integrated setup of ATR-FTIR Kretschmann and Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) allows to probe the transport of water (and other ions) through the polymer towards the interface. The subsequent interface processes can be followed with infrared spectroscopy while simultaneously the protective properties of the overall hybrid system are studied by ORP-EIS. [3]

[1] D. F. Ogletree, H. Bluhm, E. D. Hebenstreit, and M. Salmeron. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 601, 1–2, 151–160, 2009.

- [2] S. Pletincx, L. Trotochaud, L. Fockaert, J.M.C Mol, A. Head, O. Karshoğlu, H. Bluhm, H. Terryn, T. Hauffman. *Sci. Rep.* 7 (45123), 2017.
[3] M. Öhman and D. Persson, *Surf. Interface Anal.*, 44, 2, 133–143, 2012.

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