

Surface Science Division

Room A220-221 - Session SS+2D+HC-TuM

Atom Manipulation and Synthesis/Oxide Surface Reactions & Flash Session

Moderators: Liney Arnadottir, Oregon State University, Stephen McDonnell, University of Virginia, Martin Setvin, TU Wien, Austria

8:00am SS+2D+HC-TuM-1 Angstrom Scale Chemical Analysis of Metal Supported *Trans*- and *Cis*-Regioisomers by Ultrahigh Vacuum Tip-Enhanced Raman Mapping, *S Mahapatra, J Schultz, L Li, Nan Jiang*, University of Illinois at Chicago

Real space chemical analysis of two structurally very similar components i.e. regioisomers lies at the heart of heterogeneous catalysis reactions, modern-age electronic devices and various other surface related problems in surface science and nanotechnology. One of the big challenges in surface chemistry is to identify different surface adsorbed molecules and analyze their chemical properties individually. Herein, we report a topological and chemical analysis of two regioisomers, *trans*- and *cis*-tetrakis(pentafluorophenyl)porphodilactone (*trans*- and *cis*-H₂F₁₀TPPDL) molecules by high resolution scanning tunneling microscopy (STM), and ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Both isomeric structures are investigated individually on Ag(100) at liquid nitrogen temperature. Following that, we have successfully distinguished these two regioisomeric molecules simultaneously through TERS with an angstrom scale (8 Å) spatial resolution. Also, the two-component organic heterojunction has been characterized at large scale using high resolution two-dimensional (2D) mapping. Combined with time-dependent density functional theory (TDDFT) simulations, we explain the TERS spectral discrepancies for both isomers in the fingerprint region.

8:20am SS+2D+HC-TuM-2 Theoretical Modeling of Metal Release from Complex Oxide Surfaces, *Sara Mason*, University of Iowa

Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. Our studies have shown that the oxidation states of the metals in these types of materials with adjust according to the chemical environment. The oxidation states also determine the stability of that metal in the lattice of the material, and can facilitate dissolution of the potentially toxic ions into aqueous environments. We have developed an analysis, based on Hess's Law, which combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the surface dissolution of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO₂ (LCO) and compositionally tuned variants with general chemical formula Li(NixMnyCoz)O₂ (NMC). We find that adjusting surface terminations, compositions and pH will change the oxidation states of the metals. These changes in oxidation state alters the dissolution properties of this family of materials. We track the changes in oxidation state with respect to changes in the environment with electronic structure calculations such as, band structure and projected density of states. Our confirms the incongruent dissolution trend seen by our experimental collaborators. Our further investigations show that increasing the amount of Mn in the lattice will facilitate dissolution from all the metals and increasing the amount of Ni will stabilize the lattice and have similar dissolution to the equistoichiometric NMC. Since the release of Ni, Mn, and Co has shown to have adverse biological effects, we employ database mining to generate a new set of materials where we have replaced Ni, Co, and Mn with metals that will keep the same functionality while reducing biological impact. We then predict the thermodynamics of metal release to give insight on tailorable properties that can be used to formulate sustainable design principles for future generations of functional CMO materials.

8:40am SS+2D+HC-TuM-3 On-surface Synthesis by Atom Manipulation Studied with Atomic Force Microscopy, *Leo Gross*, IBM Research - Zurich, Switzerland

INVITED

Elusive molecules are created using atomic manipulation with a combined atomic force/scanning tunneling microscope (AFM/STM). Employing high-resolution AFM with functionalized tips provides insights into the structure, geometry, aromaticity, charge states and bond-order relations of the molecules created and into the reactions performed [1].

We created radicals, diradicals [2], non-Kekulé molecules [3] and polyynes [4] and studied their structural and electronic properties. We recently showed that the reorganization energy of a molecule on an insulator can be determined [5]. In addition, we expanded the toolbox for the synthesis of molecules by atomic manipulation, demonstrating reversible cyclisation reactions [2], skeletal rearrangements [4] and controlled reactions on insulating substrates by electron attachment/detachment [6].

On insulating substrates we can control the charge state of molecules and resolve changes within molecular geometry, adsorption and aromaticity related to the oxidation state.

References:

- [1] L. Gross *et al. Angew. Chem Int. Ed* **57**, 3888(2018)
- [2] B. Schuler *et al. Nat. Chem.* **8**, 220 (2016)
- [3] N. Pavliček *et al. Nat. Nano.* **12**, 308 (2017)
- [4] N. Pavliček *et al. Nat. Chem.* **10**, 853 (2018)
- [5] S. Fatayer *et al. Nat. Nano.* **13**, 376 (2018)
- [6] S. Fatayer *et al. Phys. Rev. Lett.* **121**, 226101 (2018)

9:20am SS+2D+HC-TuM-5 The Large Effect of Solvents on Heats of Adsorption versus Gas Phase Explained with a Simple Bond-additivity Model: A Case Study with Phenol on Pt(111) in Water, *Charles T. Campbell*, University of Washington; *N Singh*, University of Michigan; *J Rumpitz*, University of Washington

The low-coverage heat of adsorption of phenol on Pt(111) facets of a Pt wire in aqueous phase is approximately 21 kJ/mol (relative to aqueous phenol)¹, much smaller than the heat for gas phase phenol adsorption at this same low coverage on single-crystal Pt(111) in ultrahigh vacuum (200 kJ/mol from adsorption calorimetry²). Here we quantitatively analyze the individual contributions that give rise to this large solvent effect using a simple pairwise bond-additivity model, taking advantage of experimental data from the literature to estimate the bond energies. The dominant contribution to the lowering in heat when adsorbing phenol in water is the energy cost to break the strong bond of liquid water to Pt(111) ($E_{\text{adhesion}} \sim 116$ kJ per mole of phenol area). The water-phenol bonding is lost on one face of the phenol and this costs ~ 50 kJ/mol, but this is nearly compensated by the new water-water bonding (~ 53 kJ/mol of phenol area). The results indicate that the intrinsic bond energy between phenol and Pt(111) is not very different when in gas versus aqueous phase, provided one takes into consideration the expectation that water forces phenol into 2D islands of high local coverage even at low average coverage (for the same reason that oil and water don't mix). This also explains the lack of a strong coverage dependence in the heat of adsorption when measured in aqueous phase, whereas it decreases by ~ 60 kJ/mol with coverage when measured in gas phase. This bond-additivity analysis can be extended to other surfaces and solvents for any flat adsorbate. It clarifies why catalysis with molecules like phenol which have very strong bonding to Pt group metals can proceed rapidly at room temperature in liquid solvents like water, but would never proceed in the gas phase at room temperature due to irreversible site poisoning. We also present many new measurements of solvent / metal adhesion energies that will aid future analyses of solvent effects in adsorption.

(1) Singh, N.; Sanyal, U.; Fulton, J. L.; Gutiérrez, O. Y.; Lercher, J. A.; Campbell, C. T. Quantifying Adsorption of Organic Molecules on Platinum in Aqueous Phase by Hydrogen Site Blocking and in Situ X-Ray Absorption Spectroscopy. *Submitted 2019*.

(2) Carey, S.; Zhao, W.; Mao, Z.; Campbell, C. T. Energetics of Adsorbed Phenol on Ni(111) and Pt(111) by Calorimetry. *J. Phys. Chem. C* **2019**, *123*, 7627–7632.

9:40am SS+2D+HC-TuM-6 Atomic-Scale Growth Mechanisms of Niobium Hydrides on Hydrogen Infused Nb(100), *Rachael Farber, D Veit, S Sibener*, The University of Chicago

Particle accelerator technology and science, while commonly associated with fundamental high-energy physics applications, is also a crucial

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component in biological, chemical, and industrial scientific technologies. In order to increase the accessibility and applicability of accelerator-based technologies in multiple sectors, it is imperative to develop technologies that will enable the production of a more intense particle beam at a lower price point. As such, it is essential to identify structural and chemical features that inhibit beam intensity and develop methods to suppress such surface features.

Niobium (Nb) is the current standard for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance (R_s) and high cavity quality factor (Q) at operating temperatures of ~ 2 K. It is known that SRF cavity surface composition and contaminant incorporation is directly related to Q , and much work has been done to understand factors influencing SRF cavity performance for the clean and oxidized Nb surface. Hydrogen incorporation, which results in the formation of Nb hydrides, has been identified as a major source of decreased Q . There is not, however, a fundamental understanding of the growth mechanism for Nb hydrides. In this work, we have investigated the atomic-scale growth mechanism of Nb hydrides on oxidized Nb(100) under ultra-high vacuum (UHV) conditions using temperature programmed desorption (TPD), low-temperature scanning tunneling spectroscopy (LT-STM), and scanning tunneling spectroscopy (STS). The incorporation of relevant concentrations of hydrogen into the Nb(100) crystal was confirmed using TPD, LT-STM experiments revealed novel, real space information regarding the atomic-scale growth mechanism of Nb hydrides, and STS was used to elucidate the relationship between Nb hydride formation and the surface density of states.

11:00am **SS+2D+HC-TuM-10 Water induced restructuring of Vanadium oxide clusters**, *Kræn Christoffer Adamsen, J Lauritsen, S Chiriki, B Hammer*, Aarhus University, Denmark

Fundamental knowledge of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is important for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on a VO_x/TiO_2 based catalysts. It is well established that vanadium in the V^{+5} -state is most catalytic active state, though is still debated whether it is a hydroxylated- or an unhydroxylated- species that is most active species. Here we investigate the structure of vanadium oxide (V_2O_5) before, under and after exposure of water.

By evaporation of Vanadium in an oxygen-rich atmosphere (10^{-6} mBar) on an anatase- TiO_2 (101) substrate, we can create well-dispersed single V_2O_5 -clusters. Confirm the oxidation state of vanadium with X-ray Photo electron Spectroscopy (XPS) and image the size and structure with high resolution Scanning Tunneling Microscopy (STM). Prior to water exposure V_2O_5 -clusters appear predominately as elongated features extending across two bridging oxygen rows of the anatase- TiO_2 (101) substrate. Utilizing the high scanning speed of the Aarhus STM we can follow the water induced restructuring of the clusters in situ. We observe a clear change in appearance of the vanadium oxide cluster, where a vanadium atom moves across on of the bridging oxygen rows of the a- TiO_2 substrate. Removal of water causes another change in appearance, but re-exposure of water the previous appearance is restored. We therefore observe a reversible reaction with exposure and removal of water, however with several hour of pumping we cannot return to the initial state directly after evaporation.

Together with Theoreticians, we are able to suggest structure models of the interactions between the vanadium oxide and water. We are able to explain both the irreversible restructuring in the first water exposure and the reversible restructuring with re-exposure of water. Understanding the structure and its dynamical behavior under water exposure bring us closer to understand the catalyst under working conditions.

11:20am **SS+2D+HC-TuM-11 Hydrogenation of Titanium Dioxide with Low-energy Hydrogen Ions and Atomic Hydrogen**, *N Nagatsuka, Y Ohashi*, Institute of Industrial Science, The University of Tokyo, Japan; *M Fujimoto, M Matsumoto*, Tokyo Gakugei University, Japan; *Katsuyuki Fukutani*, Institute of Industrial Science, The University of Tokyo, Japan

Interaction of hydrogen with TiO_2 surfaces is of interest and importance in view of photocatalytic H_2 generation and hydrogen sensors. Furthermore, hydrogenated TiO_2 has recently acquired much attention due to its excellent photocatalytic activity [1]. In our previous study, we have investigated the interaction of hydrogen with the rutile $\text{TiO}_2(110)$ surface with nuclear reaction analysis (NRA) and ultraviolet photoemission (UPS) [2]. Whereas the former allows us to quantify hydrogen in the sample in a depth-resolved manner [3], the latter provides us with the information on the electronic states. In the present study, we have studied interaction of low-energy hydrogen ions with TiO_2 single-crystal surfaces, where the

hydrogen ion penetrates the surface being distributed in the near-surface region [4]. We also report atomic hydrogen interaction with TiO_2 nanoparticles in relation with hydrogenation of TiO_2 .

When the rutile $\text{TiO}_2(110)$ and anatase $\text{TiO}_2(101)$ surfaces are exposed to atomic hydrogen, NRA shows adsorption of hydrogen on the surfaces with a coverage of about 0.5 monolayer [2]. When the rutile $\text{TiO}_2(110)$ surface is exposed to a hydrogen ion beam at 500 eV, on the other hand, NRA reveals a maximum at a depth of about 1 nm extending to ~ 30 nm with an average concentration of 5.6 at. % and UPS shows an in-gap state (IGS) at ~ 0.8 eV below the Fermi level with a downward band-bending by 0.5 eV. The IGS intensity is about ten times as large as that of the H-adsorbed surface. Upon annealing at 673 K, the IGS intensity is reduced by about 40 % and H with a coverage of 1.4 monolayer remains in the near-surface region, which suggests stable H occupation of subsurface sites. When the H-ion-irradiated surface is exposed to oxygen molecules, on the hand, the hydrogen distribution remains unchanged although the IGS intensity is substantially reduced. The effect of hydrogen in the near-surface region on the surface electronic state is discussed.

[1] Z. Wang et al., *Adv. Func. Mater.* 23, 5444 (2013).

[2] K. Fukada et al., *J. Phys. Soc. Jpn.* 84, 064716 (2015); N. Nagatsuka et al., in preparation.

[3] M. Wilde, K. Fukutani, *Surf. Sci. Rep.* 69, 196 (2014).

[4] Y. Ohashi et al., *J. Phys. Chem. C* in press.

11:40am **SS+2D+HC-TuM-12 Direct Observation of Atomic Exchange during Surface Self-diffusion**, *Matthew Koppa, P Schwoebel, D Dunlap*, University of New Mexico

The growth of crystals from the vapor phase is widely used in many technological applications, ranging from the microfabrication of microprocessors to the development of biological sensors. The dynamics of processes such as the surface diffusion of adatoms are key phenomena governing mass transport and the resulting crystal growth. Atomic exchange with substrate atoms during surface self-diffusion has been inferred from previous field ion microscope (FIM)-based experiments by mapping adatom visitation sites. Here iridium enriched to $>93\%$ ^{193}Ir was deposited onto an atomically clean and smooth $\text{Ir}(100)$ plane as observed in an atom-probe field ion microscope. Following thermally activated surface self-diffusion the adatom was field desorbed and mass analyzed. Observation of the ^{193}Ir isotope in one-half of the cases demonstrates conclusively that atomic exchange can occur during surface self-diffusion.

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