Nanometer-scale Science and Technology Division
Room 19 - Session NS+HC+SS-MoA

Oxides in Nanotechnology

Moderator: Nancy Burnham, Worcester Polytechnic Institute

2:00pm **NS+HC+SS-MoA-2 Epitaxial Growth and Characterization of WO3 and $WO_{3-\delta}$ Thin Films***, **Yingge Du**, Z Yang, Z Zhu, C Wang,* Pacific Northwest National Laboratory

Tungsten trioxide (WO_3) based thin-film materials are of significant importance because of their diverse structures and wide range of properties. These materials have found widespread applications in display devices, electrochromic “smart” windows, gas sensors, catalysis, and photocatalysis. Investigations of WO_3 films in epitaxial form offer definite advantages over porous or polycrystalline forms for fundamental science studies. For example, the ability to detect and eliminate secondary phases and surfaces simplifies the material system and makes it easier to establish defensible cause-and-effect relationships. While amorphous, polycrystalline, and epitaxial WO_3 films have been prepared by several methods such as evaporation of WO_3, sputtering, and pulsed laser deposition, the growth of epitaxial WO_3 films by molecular beam epitaxy (MBE) is much less explored.

We examined three different ways to grow epitaxial WO_3 films by MBE – by evaporating WO3 powders from an effusion cell, by evaporating WO_x surface layers formed on W metal surface, and by evaporating tungsten metal in an oxidizing environment. Epitaxial films are formed in all three cases but the growth characteristics vary significantly. The films from the first two methods are found to grow as stoichiometric islands first, while the third method leads to layer by layer growth, with significant amount of ordered oxygen vacancies. The films are characterized *in-situ* by RHEED and XPS, and *ex-situ* by XRD, SIMS, and STEM.

2:20pm **NS+HC+SS-MoA-3 Oxide Surfaces: Structure, Adsorption, Growth***, **Ulrike Diebold**,* TU Wien, Austria **INVITED**

Fundamental investigations into the surface properties of oxides have experienced a continued growth. The reasons for this increasing interest are quite clear: after all, most metals are oxidized under ambient conditions, so in many instances it is the oxidized surface that deserves our attention. In addition, metal oxides exhibit an extremely wide variability in their physical and chemical properties. These are exploited in established and emerging technologies such as catalysis, gas sensing, and energy conversion schemes, where surfaces and interfaces play a central role in device functioning. Hence a more complete understanding of metal oxide surfaces is desirable from both fundamental and applied points of view.

By using Scanning Probe Microscopy measurements, in combination with Density Functional Theory calculations and area-averaging spectroscopic techniques, great strides have been made in understanding the atomic-scale properties of the surfaces of these complex materials.

In the talk I will give examples drawn from recent studies on several metal oxide systems, including TiO_2, Fe_3O_4, In_2O_3, ZrO_2, and perovskites. I will point out the advantages of directly viewing, and manipulating, point defects and single molecules with atomic precision, and how inspecting central processes such as charge transfer to adsorbates can further a deep mechanistic understanding. I will also discuss new opportunities based on recent technique development such as Scanning Force Microscopy, and the challenges and possible rewards in exploring more complex materials.

3:00pm **NS+HC+SS-MoA-5 Imaging and Sensor Applications of infiltrated Zinc Oxide***, **Leonidas Ocola**,* Argonne National Laboratory*; V Sampathkumar,* University of Chicago*; N Kasthuri, R Winarski,* Argonne National Laboratory*; Y Wang, J Chen,* University of Wisconsin - Milwaukee

With the increased portfolio of materials that can be deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples in electron and X-ray microscopy and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

Most biological materials have problems with charging when imaging with electrons and low contrast when imaging with hard X-rays. In this presentation we describe the use of infiltrated ZnO as a means to address both charge dissipation in electron microscopy and contrast enhancement for X-ray microscopy. With ZnO infiltration it is feasible to coat a 2 – 3 nm conductive metal oxide film throughout a porous biological sample, and image both the surface and the interior of a sample without any further sample recoating. We demonstrate this technique can be applied on tooth and brain tissue samples. We show that high resolution X-ray tomography can be performed on biological systems using Zn K edge (1s) absorption to enhance internal structures, and obtained the first nanoscale 10 KeV X-ray absorption images of the interior regions of a tooth.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

- Use of the Center for Nanoscale Materials and the Advanced Photon Source, both Office of Science user facilities, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Additional funding by IARPA, (ARIADNE) under Contract D16P00002

3:20pm **NS+HC+SS-MoA-6 Plasma Modified Gas Sensors: Bridging the Gap Between Tin Oxide Nanomaterials and Paper-Based Devices***, **Kimberly Hiyoto**, E Fisher,* Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their low manufacturing cost and ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. The substrates that support these materials, however, are often brittle and their smooth surface limits the amount of nanomaterial that can be exposed to target gases. Recent attempts to address these issues utilize paper substrates, that are not only low cost, but flexible to allow for a more robust device. Moreover, the porous, fibrous morphology of paper substrates provides significantly increased surface area for attaching more nanomaterials when compared to a traditional substrate of the same size. Despite recent improvements to paper-based metal oxide gas sensors, tin(IV) oxide (SnO_2) nanomaterials require high operating temperatures, thus have not yet been successfully translated to paper-based sensors. Here, we describe how low power (30 – 60 W) Ar/O_2 plasma modification, can be used to enhance gas-surface interactions of SnO_2 paper-based sensors while maintaining desirable bulk nanomaterial and substrate architecture. X-ray photoelectron spectroscopy revealed plasma treatment increased adsorbed oxygen, which is thought to improve sensor response by promoting gas-surface interactions. Indeed, plasma modified SnO_2 nanomaterials on a paper substrate exhibit improved response to ethanol, carbon monoxide, and benzene at ambient temperature. Furthermore, scanning electron microscopy demonstrates that plasma treatment does not damage the morphology of SnO_2 or the paper substrate. Response and recovery studies on these devices will be discussed along with SnO_2 nanomaterial gas sensors created on more traditional substrates (e.g. ZrO_2) as another measure of sensor performance. A better understanding of how plasma modification and the resulting changes in surface chemistry affect sensor performance is an important step towards achieving improved paper-based gas sensors using SnO_2 nanomaterials.

4:00pm **NS+HC+SS-MoA-8 Understanding the Initial Stages of Oxidation in Nickel-Chromium Alloys***, P Reinke, **William H. Blades**, G Ramalingam,* University of Virginia

Through a combined experimental and computational effort, the interaction of oxygen with Nickel-Chromium alloys is studied. Prior to the formation of a full oxide layer, the physical and chemical processes behind the initial stages of oxidation are not well understood. This work fills a significant gap in our understanding of binary alloy oxidation. Scanning Tunneling Microscopy and Spectroscopy were used to observe the onset of oxide formation. These surface techniques are combined with Bandgap and Density of States maps, which lend themselves as powerful tools when studying surfaces with heterogeneity at the nanoscale. Ni-Cr(100) thin films with a range of compositions were prepared on MgO(100) in UHV and exposed to controlled amounts of oxygen up to 400L. Previous experiments have shown chromia to be the dominant oxide when Ni-Cr alloys are oxidized with a partial pressure of $p(O_2)<10^{-7}$mbar at 300°C. Under these oxidation conditions the Ni prefers the kinetically favorable Ni(100)-c(2x2)-O reconstruction. Our experiments demonstrate that a combination of increased chromium concentration, which locally catalyzes the Ni, and an elevated oxidation temperature of 500°C can overcome the activation barrier for NiO formation. The statistical analysis of island densities and sticking coefficient, in direct comparison of Ni and Ni-Cr surfaces, support the idea that NiO nucleation is facilitated by the presence of Cr. Early oxidation steps reveal that initial NiO nucleation and growth occurs along the step edges of the Ni-Cr alloy. This is in contrast to Ni(100)-c(2x2)-O where the step edges are passivated and devoid of reactive kink sites. We suggest that the presence of Cr at the step edges lowers the activation barrier and thus promotes rapid NiO formation. Anneal periods have shown that at low coverage, the NiO is readily desorbed from the surface leaving behind small oxides particles and regions with chemisorbed oxygen. Further oxidation steps create a high quality crystalline oxide layer, which is significantly more stable at elevated temperatures. Density Functional Theory is used to develop an understanding of the electronic and geometric structure of the oxidized Ni-Cr alloys and the effect of chromium on the local bonding environment. This collective experimental and theoretical approach has offered greater insight into alloy-oxide interface structure, and the role of transition metal dopants in the oxidation process in the pre Cabrera-Mott regime. This work is supported by the Office of Navel Research MURI "Understanding Corrosion in Four Dimensions," Grant N00014-14-1-0675.

4:20pm **NS+HC+SS-MoA-9 Evaluation of Titanium Doped β-Ga_2O_3 Thin Films in Extreme Environment for Application in Oxygen Sensors***, **Sandeep Manandhar**, A Battu, C Ramana,* University of Texas at El Paso

The reliable and efficient operation of power generation systems has become one of the grand challenges of today's research in order to meet the ever-increasing demand for energy and sustainability. The improvement in power/energy generation processes, in particular, for those depend on fossil fuels, the higher temperature and accurate measurement of the combustion environment and the emissions produced by the combustion via proper selection of sensing materials can enhance the efficiency and reliability. While several candidate metal oxides (SnO_2, ZnO, TiO_2, WO_3, and Ga_2O_3) exhibit high sensitivity chemical gases, β-Ga_2O_3 has shown to function as oxygen sensor at high temperatures (>700°C). However, the response time and sensitivity must be improved in order to utilize them in practical applications. While improved sensor characteristics are seen in various metal/ion doped β-Ga_2O_3, fundamental understanding of the long term effects of high temperature exposure on the structure and properties of doped β-Ga_2O_3 films is missing at this time. However, such studies are quite important to predict the thermodynamic stability and performance in extreme environments. In this work, we performed a detailed study to understand the effect of extreme environment on titanium (Ti) doped β-Ga_2O_3. The real environment condition for sensor (>700°C) application were simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-Ga_2O_3. The results will be presented and compared with as prepared Ti doped β-Ga_2O_3 films in the context of utilizing these materials in oxygen sensor applications.

4:40pm **NS+HC+SS-MoA-10 Characterization of Infiltrated ZnO in PS-b-PMMA Nanostructures***, **Paris Blaisdell-Pijuan**,* University of Chicago*; L Ocola,* Argonne National Laboratory

We have characterized the growth of ZnO using sequential infiltration synthesis (SiS) on PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. Investigation of these structures was done using atomic force microscopy (AFM), spectrofluorometry, Raman spectroscopy, and scanning electron microscopy (SEM). We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. Rapid thermal annealing of samples in air above 500 °C began to coalesce and show photoemission characteristic of bulk ZnO at 370nm (3.35eV). Our work demonstrates that ZnO nanostructures grown on PS-b-PMMA via SiS are advantageous in uniformity and size, and exhibit unique fluorescence properties. These observations suggest that infiltrated ZnO in PS-b-PMMA nanostructures lends itself to a new regime of applications in photonics and quantum materials.

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-MoA-3 Photochemistry of CO, Acetone and O_2 on Reduced Rutile TiO_2(110)***, **Greg Kimmel**, N Petrik, M Henderson,* Pacific Northwest National Laboratory **INVITED**

TiO_2 is an important photocatalyst with many practical applications. However, a fundamental understanding of the thermal and non-thermal reactions on TiO_2 surfaces is still lacking. We use ultrahigh vacuum (UHV) surface science techniques to investigate in detail representative reactions on single crystal rutile TiO_2(110). For this talk, I will focus on the ultraviolet (UV) photon-stimulated reactions of CO, acetone and oxygen adsorbed on TiO_2(110). For CO co-adsorbed with O_2, CO_2 is produced during UV irradiation. The CO_2 preferentially desorbs in the plane perpendicular to the bridge-bonded oxygen (BBO) rows at an angle of 45°. Furthermore, the production rate of CO_2 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 O_2 is adsorbed on TiO_2(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 O_2 that photodesorbs is ~45%. While photo-generated holes are responsible for the O_2 photodesorption, photo-generated electrons are responsible for the photo-induced O_2 dissociation. In general, these studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO_2.

3:00pm **SS+AS+HC-MoA-5 The Role of Band Alignment in Ketone Photooxidation on TiO_2(110)***, **Amanda Muraca**,* Stony Brook University*; M White,* Brookhaven National Lab and Stony Brook University

Organic photooxidation processes on the TiO_2(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 TiO_2, 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 ($R(CH_3)CO$; 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 photoxidation 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 $TiO_2(110)$ 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-MoA-6 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 Veyan,* University of Texas at Dallas; *H Wang, J Li,* Rutgers University; *T Thonhauser,* Wake Forest University; *Y 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, CO_2, SO_2, C_2H_4, 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 disposition (ALD) precursor trimethylaluminum (TMA). Aluminum oxide is not able to grow inside MOFs since the reactivity of TMA with adsorbed H_2O is significantly reduced due to nano-confinement effects; another convenient way is post-exposure of gas-loaded MOF-74 to NH_3. NH_3 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, CO_2, SO_2 in NH_3 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-MoA-8 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 (Ce^{4+}) ions was observed up to a concentration corresponding to CeO_2 phase segregation. We propose a strong promoting effect of Ce^{4+} 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 $Co\text{-}_3O_4$-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 Ce^{4+} 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-MoA-10 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-MoA-11 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 Fockaert,* TU Delft, Netherlands; *A Head, O Karslıoğlu,* Lawrence Berkeley National Laboratory; *A 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. H_2O) 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. Karslıoğlu, 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.

Surface Science Division
Room 25 - Session SS+HC-TuM
Controlling Mechanisms of Surface Chemical Reactions

Moderators: Daniel Killelea, Loyola University Chicago, Andrew Teplyakov, University of Delaware

8:00am **SS+HC-TuM-1 Multifunctional Adsorption on Ge(100)-2x1 Surface: The Role of Interadsorbate Interactions***, **Tania Sandoval**[1 2], S Bent,* Stanford University

Adsorption of multifunctional molecules onto semiconductor surfaces provides a pathway to functionalize the surface while leaving unreacted functional groups available for reaction. These hybrid interfaces are important for applications in biosensors, microelectronics, and energy storage. These applications require homogeneous and controllable adsorption of these complex molecules. In this presentation, we will discuss two studies that help elucidate the driving forces governing the overall product distribution during adsorption of multifunctional molecules.

The first example describes the adsorption of homobifunctional pyrazine on the Ge(100)-2x1 surface. Pyrazine ($C_4H_4N_2$) is a six-membered ring molecule with two nitrogen atoms in the para position. The electron-rich nitrogen possesses a lone pair that can easily react with the surface through a dative bond. While benzene is not known to react with germanium, the addition of nitrogen to the aromatic ring opens up additional reaction channels. Previous studies of pyridine (C_5H_5N) on Ge(100) showed that reaction through the nitrogen can yield a mix of adsorption products. Our X-ray photoelectron spectroscopy (XPS) results suggest that pyrazine reacts with Ge(100)-2x1 to form a mix of reaction products. Analysis of the N(1s) and C(1s) spectra indicates that reaction of pyrazine occurs through the N-dative bond and via N=C and C=C cycloaddition reactions. The product distribution was found to be a function of temperature and coverage. This dependence suggests differences in the reaction channels as well as cooperative effects between adsorbate molecules.

The second example describes the adsorption of homotrifunctional 1,2,3-benzenetriol on Ge(100)-2x1 surface. 1,2,3-benzenetriol ($C_6H_6O_3$) is a trihydroxy phenol with three neighboring hydroxyl groups. The proximity between OH-groups promotes intra and inter-molecular hydrogen bonding. XPS and Fourier transform infrared spectroscopy results demonstrated that the reaction occurs through an OH-dissociative pathway. Coverage dependent shows that the extent of surface reactions per molecule decreases as the surface becomes crowded, and we predict this behavior is due to a combination of sterics and intermolecular hydrogen bonding. It has been previously shown that intermolecular hydrogen bonding can lower the reactivity of an OH group and prevent further reactions. Our theoretical analysis confirms that adsorbed molecules will preferentially interact with each other if unreacted OH groups are in close proximity. We expect that these interactions contribute to lowering the saturation coverage, as well as decrease the amount of dissociation events per molecule.

8:20am **SS+HC-TuM-2 Steering the Chemical Reactions on Surfaces Toward Targeted Products***, Q Fan, T Wang, **Junfa Zhu**,* University of Science and Technology of China, China

The bottom-up construction of low-dimensional macromolecular nanostructures directly on a surface is a promising approach for future application in molecular electronics and integrated circuit production. However, challenges still remain in how to control the reaction pathways toward the formation of targeted nanostructures or dimensions. In this presentation, I will report our recent studies on the on-surface synthesis of low dimensional organic nanostructures on different substrate surfaces. These studies were performed under ultra-high vacuum (UHV) conditions using a combination of scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and high-resolution X-ray photoelectron spectroscopy (HR-XPS). Several examples will be shown to demonstrate that by employing different substrate templates,[1-4] special high-dilution synthesis condition[5] or hydrogen bond protection with dedicated precursor molecules on surfaces[6], surface reactions can be driven with different pathways towards the desired products. For example, on Cu(111) and Cu(110), after depositing the same precursor molecule, 4,4’’-dibromo-meta-terphenyl (DMTP), at elevated temperatures, Ullmann coupling reaction can proceed via different pathways to form different nanostructures.[1-3] While on the Cu(110)-(2x1)O surface, by controlling the width of the Cu stripes, the spatial confinement effect can steer the reaction of DMTP to form either 1D zigzag organometallic oligomeric chains with different lengths or organometallic macrocycles with different widths.[4] More interestingly, when recently we transplanted the (pseudo-) high dilution method in solution to the conditions of on-surface synthesis in UHV, we found that the reaction of DMTP on Ag(111) can be tailored to specially form cyclic hyperbenzene with high-yield (84%) in contrast to the commonly formed zig-zag open-chain polymers.[5] Except for the presentation of these different structures on surfaces, we will also discuss the principles and mechanisms behind.

This work is supported by the National Natural Science Foundation of China (21473178) and the National Basic Research Program of China (2013CB834605)

References:

(1) Fan, Q.; Wang, C.; et al., *Angew. Chem. Int. Ed.***2013**, *52*, 4668.

(2) Fan, Q.; Wang, C.; et al., *ACS Nano***2014**, *8*, 709.

(3) Dai, J.; Fan, Q.; et al., *Phys. Chem. Chem. Phys.***2016**, *18*, 20627.

(4) Fan, Q.; Dai, J.; et al., *ACS Nano***2016**, *10*, 3747.

(5) Fan, Q.; Wang, T.; et al., *ACS Nano***2017,** DOI: 10.1021/acsnano.7b01870.

(6) Wang, T.; Lv, H.; et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 4762.

8:40am **SS+HC-TuM-3 Spectroscopic Characterization of Reaction Pathways over a Pd-Cu(111) Single-Atom Alloy***, C Kruppe, **Michael Trenary**,* University of Illinois at Chicago **INVITED**

Low coverages of catalytically active metals deposited onto less active metal surfaces can form single atom alloys (SAAs), which often display unique catalytic properties. Such alloys are particularly attractive for selective hydrogenation reactions. It is therefore of interest to probe the surface structure and chemistry of such alloys in the presence of gas phase reactants. We have used polarization dependent reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the in-situ hydrogenation of acetylene to ethylene over a Pd/Cu(111) SAA surface. The coverage and morphology of the deposited Pd is characterized with Auger spectroscopy (AES), temperature programmed desorption (TPD) of H_2 and CO, and PD-RAIRS of CO. After exposing clean Cu(111) and Cu(111) with various Pd coverages to 10 L of CO at 100 K, the RAIR spectra show that the surface is largely unchanged by the presence of less than 0.5 ML of Pd. In the presence of 1×10^{-2} Torr of CO at 300 K, significant CO coverages are only achieved when Pd is present on the surface. The Pd coverage determined from CO peak areas obtained with RAIRS yields a value lower by about a factor of two than the Pd coverage obtained with AES. This is attributed to the presence of both surface and subsurface Pd, with only the former detectable by RAIRS of CO, but both detectable with AES. Surface species and gas phase products of C_2H_2 hydrogenation are monitored between 180 and 500 K on clean Cu(111) and Pd/Cu(111). With a total pressure of 1 Torr and a C_2H_2:H_2 ratio of 1:100, annealing a SAA-Pd/Cu(111) surface to 360 K results in complete conversion of all gas phase C_2H_2 to gas phase ethylene (C_2H_4), without producing any gas phase ethane (C_2H_6). The hydrogenation reaction is accompanied by acetylene coupling reactions that occur both on clean Cu(111) and on Pd-Cu(111).

9:20am **SS+HC-TuM-5 Reactivity of Pt and Rh Adatoms, Dimers, and Small Clusters on Fe_3O_4 (001)***, **Jan Hulva**[3],* TU Wien, Austria*; M Meier,* University of Vienna, Austria*; M Setvin, Z Jakub, R Bliem, M Schmid, U Dieblod,* TU Wien, Austria*; C Franchini,* University of Vienna, Austria*; G Parkinson,* TU Wien, Austria

The rapidly emerging field of “single-atom catalysis” aims to drastically reduce the amount of precious metal required to catalyze chemical reactions by replacing nanoparticles with single-atom active sites. Although there are now many reports of active single-atom catalysts [1], the concept itself remains controversial because it is challenging to characterize real catalysts and determine the reaction mechanism. In our work, we study fundamental properties of supported single metal atoms using a surface science approach. We employ the Fe_3O_4 (001) surface as a model support, because it can stabilize dense arrays of single metal atoms to temperatures as high as 700 K [2,3]. In this contribution, we address the adsorption behavior and reactivity of the Pt and Rh adatoms, dimers, and small

---

[1] **Morton S. Traum Award Finalist**

[2] **National Student Award Finalist**

[3] **Morton S. Traum Award Finalist**

clusters using a combination of atomically resolved STM and non-contact AFM, high-resolution spectroscopy, and density functional theory. We conclude that Pt adatoms are inactive because CO adsorption results in mobility, and rapid sintering into Pt_2 dimers [5]. Pt dimers, on the other hand, are stable, and highly efficient CO oxidation catalysts. By isotopically labelling the oxide surface with ^{18}O, we unambiguously show that a Mars van Krevelen mechanism is responsible for the catalytic activity. Rh adatoms interact more strongly with the oxide, and do not sinter upon adsorption of CO. As a result, we find that Rh adatoms do catalyze CO oxidation, also via an MvK mechanism.

[1] – Acc. Chem. Res. 46(8), pp.1740-1748.

[2] – Phys.Rev.Lett.108(2012): 216103

[3] – Science 346 (2014): 1215-1218.

[4] – Angew. Chem. Int. Ed. 54.47 (2015): 13999-14002.

[5] – PNAS 113.32 (2016): 8921-8926.

9:40am **SS+HC-TuM-6 An AP-XPS Study to Investigate the Reaction Mechanism of the Oxidation of CO on Pt/TiO_2 Nanoparticles: A Step Towards Closing both the Pressure and the Materials Gap***, **Randima Galhenage**, J Bruce, D Ferrah,* University of California Irvine*; I Waluyo, A Hunt,* Brookhaven National Laboratory*; J Hemminger,* University of California Irvine

Platinum supported on oxides, such as TiO_2, are widely studied catalysts to drive oxidation reactions. Even though there are fundamental studies that have been done on single crystal Pt and TiO_2 to understand the reactivity and the mechanism, there lies a sizable knowledge gap due to the complexity of the real catalytic systems compared to the single crystal studies. We studied CO oxidation on a unique model system where Pt nanoparticles (NPs) are deposited on TiO_2 NPs supported on an inert HOPG surface. Our study takes the complexity of the material a step forward. In-operando Ambient Pressure X-ray photoelectron spectroscopy (AP-XPS) was used to study the oxidation states of Pt, Ti, and O during the reaction to understand the role of different oxidation states of the elements on the reaction mechanism. Ex-situ prepared model catalyst which mostly contains a mixture of Pt(4) and Pt(2) were first heated to obtain a mixture of Pt(0) and Pt(2). During the reaction, the TiO_2 remains stoichiometric with no indication of any change in the oxidation state. At 400 K, CO is adsorbed on Pt resulting in a decrease of the Pt(2)/Pt(0) ratio. O1s spectra show the formation of Pt-O bond at 450 K. A rapid decrease of O1s (Pt-O) and a decrease of Pt(2)/Pt(0) ratio were observed simultaneously with CO_2 production at 500 K. In conclusion, we were able to study CO oxidation on a more complex model system of Pt/TiO_2 and followed the reaction mechanism. CO first adsorb on Pt and reacts with the oxygen that is dissociated on Pt sites which agree with the existing Langmuir–Hinshelwood (LH) mechanism. Furthermore, we found out that CO gets adsorbed on Pt(2) rather than on Pt(0) when there is a mixture of Pt(2) and Pt(0).

11:00am **SS+HC-TuM-10 Oxygen Reduction Reaction of Graphite Decorated by the Pyridinic-Nitrogen Contained Molecules with High Density***, **Riku Shibuya**, T Kondo,* University of Tsukuba, Japan*; J Nakamura,* University of Tsukuba, Japam

Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction (ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Here we report model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule). The DA molecules were deposited on HOPG with different coverage by simply dropping solutions of the DA molecules at room temperature. Scanning tunneling microscopy (STM) measurements revealed that a well-ordered two-dimensional structure of DA monolayer is formed on HOPG surfaces with high densities via π-π interaction, rather than aggregates to form three-dimensional clusters. The nitrogen concentration of the DA-covered HOPG surfaces was estimated to be 0.5~1.5 at.% by XPS. The DA-covered HOPG model catalysts reveled activities of ORR. The specific activity per pyridinic nitrogen atom was estimated to be 0.08 (e sec^{-1} $pyriN^{-1}$) at 0.3 eV, which is comparable to that for pyridinic nitrogen incorporated graphene sheets (0.07 ~ 0.14 (e sec^{-1} $pyriN^{-1}$))[1]. The current densities at 0.1, 0.2, and 0.3 V vs RHE were in proportional to the surface coverage of DA molecules, indicating that the ORR active site was created by DA molecule adsorbed on HOPG. The present studies clearly show that fixing nitrogen-containing aromatic molecules on graphitic carbon materials is one of promising approaches to prepare active ORR carbon catalysts.

References

[1] D.Guo, R.Shibuya, T.Kondo, J.Nakamura, et al., Science, 351 (2016), 361-365.

11:20am **SS+HC-TuM-11 Spectroscopic and Computational Studies of Room-Temperature Decomposition of a Chemical Warfare Agent Simulant on Copper Oxide***, **Lena Trotochaud**,* Lawrence Berkeley National Laboratory*; R Tsyshevsky, S Holdren,* University of Maryland, College Park*; K Fears,* U.S. Naval Research Laboratory*; A Head,* Lawrence Berkeley National Laboratory*; Y Yu,* University of Maryland, College Park*; O Karslioglu,* Lawrence Berkeley National Laboratory*; S Pletincx,* Vrije Universiteit Brussel, Belgium*; B Eichhorn,* University of Maryland, College Park*; J Owrutsky, J Long,* U.S. Naval Research Laboratory*; M Zachariah, M Kuklja,* University of Maryland, College Park*; H Bluhm,* Lawrence Berkeley National Laboratory

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metal oxides, including CuO_x. Despite decades of work to develop highly effective and versatile filtration materials, little is known about the mechanisms of CWA degradation by material surfaces and filter deactivation/poisoning, in part due to the challenges involved with spectroscopic characterization of filtration material surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present work detailing the mechanism of adsorption and decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant, on polycrystalline copper oxide surfaces. Ambient-pressure XPS enables examination of these surfaces and adsorbed species upon exposure to DMMP and other common atmospheric gases, such as water vapor and NO_x. Multiple decomposition products are observed on CuO_x surfaces, and the oxidation state of the metal appears to influence the mechanistic pathway. Complementary density functional theory (DFT) and *in situ* FTIR studies corroborate our experimental findings and are used to propose likely decomposition pathways. Exposure of the CuO_x surfaces to water vapor or NO_x prior to introducing DMMP affects the decomposition product distribution, but does not appear to significantly inhibit the initial DMMP adsorption.

11:40am **SS+HC-TuM-12 Atomic View of Acid Zeolite Chemistry: Surface Chemistry Studies on 2D Silicate Materials***, **Jin-Hao Jhang**, G Hutchings, C Zhou, U Schwarz, E Altman,* Yale University

Although zeolites have been used in facilitating numerous catalytic reactions for decades, it is still a long-term challenge to understand how surface properties of zeolites promote catalytic reactions. Recently, two-dimensional (2D) silicate materials were discovered and prepared successfully on different substrates, including transition metals and alloy. This achievement makes surface science approaches possible for understanding zeolite chemistry from an atomic view. In this work, we seek to establish that 2D silicates are capable of promoting acid catalyzed reactions in a manner analogous to 3D zeolites. The 2D silicates were prepared on a Pd(111) substrate via physical vapor deposition (PVD) at room temperature followed by annealing at 1000 K in an oxygen background. The probe molecule 2-propylamine reacts through a deammination process and produces propene on the 2D aluminosilicate indicating the existence of acid sites capable of catalysis. In contrast, no propene or other products were detected on the 2D silica surface. We also generated atomic deuterium (D) on both silica and aluminosilicate by a D_2-plasma treatment and a D_2-recombination feature at 540 K assigned to the decomposition of surface OD groups was only observed from the aluminosilicate sample. These findings show the similarity between the 2D aluminosilicate and the acid zeolites which allows us to consider the 2D material as a zeolite model to explore zeolite chemistry.

12:00pm **SS+HC-TuM-13 Establishing Rules for Oriented SURMOF Growth Beyond Template Effects***, X Yu,* University of Frankfurt, Germany*; J Zhuang,* Guizhou Normal University, P.R. China*; **Andreas Terfort**,* University of Frankfurt, Germany

The surface deposition of metal-organic frameworks (MOFs) opens the opportunity to use these highly designable materials for applications in electronics, data storage, sensing or biointerfaces. Several protocols have been reported to grow or attach MOFs onto a variety of surfaces, but nevertheless, the bandwidth of successfully deposited MOFs is still extremely limited: Besides the archetypical HKUST-1 and ZIF-5, only a family of tetragonal layer systems (with or without pillars) could be grown into well-defined SURMOF layers [1]. Although with some of these systems impressive results for different devices, such as photovoltaic cells, have been reported, the limitation to these classes of MOFs is unsatisfactory.

In this talk, we wish to discuss that the lack of success with other systems is related to the fact that most projects relied solely on the well-established surface-template effects, in which the coordination of surface-bound, functional groups to the metal SBU defines not only the binding mode but the orientation of the whole film. We will show that the rules on the surface differ from the ones in solution by a reduced number of trajectories, which in turn hamper certain reactions [2]. It is also of importance to keep in mind the different surface energies of the crystal surfaces, which can dictate a reorientation of the preformed system by Ostwald ripening during the deposition process [3]. All these processes involve different activation energies, the careful control of which opens the opportunity to grow well-oriented films of MOF systems, which have behaved notoriously difficult up to now.

References

[1] Zhuang, J.-L.; Terfort, A.; Wöll, C. *Coord. Chem. Rev.* 307 (**2016**) 391-424.

[2] Zhuang, J.-L.; Kind, M.; Grytz, C. M.; Farr, F.; Diefenbach,M.; Tussupbayev, S.; Holthausen, M. C.; Terfort, A. *J. Am. Chem. Soc.* 137 (**2015**) 8237-8243.

[3] Yu, X.-J.; Zhuang, J.-L.; Scherr,J.; Abu-Husein,T.; Terfort, A. *Angew. Chem. Int. Ed.* 29 (**2016**) 8348-8352.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 25 - Session HC+SS-TuA

Advances in Theoretical Models and Simulations of Heterogeneously Catalyzed Reactions

Moderator: Xiaofeng Feng, University of Central Florida

2:20pm **HC+SS-TuA-1 Hindered Translator/Rotor Models for Calculating the Entropy of Adsorbed Species for Improved Micro Kinetic Models Based on Density Functional Theory Calculations***, **Liney Arnadottir**, L Sprowl,* Oregon State University*; C Campbell,* University of Washington **INVITED**

With the recent explosion in computational catalysis and related microkinetic modeling, the need for a fast, yet accurate, way to predict equilibrium and rate constants for surface reactions has become more important. Here a method to calculate partition functions and entropy of adsorbed species and equilibrium constants is presented. Instead of using the vibrational frequencies estimated from DFT and the harmonic oscillator approximation to calculate all modes of motion in the partition function, we use a hindered translator and hindered rotor model for the three modes of motion parallel to the surface, one for each of the two translations in the directions parallel to the surface and one for rotation about the axis perpendicular to the surface. This hindered translator and hindered rotor model joins the two limiting cases for adsorbates on a surface, the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model, making it valid over large temperature range. At the limit of low temperature, or high energy barrier, only vibrations are present and this model is the same as the harmonic oscillator approximation, while at high temperature, or low energy barrier, translations and rotations readily occur and this model becomes identical to the 2D ideal gas model for translations or the 1D free rotor model for rotations. The transition between the 2D ideal lattice gas (harmonic oscillator) model and the 2D ideal gas (free translator) model is surprisingly sharp, but modeled very closely by the hindered translator/rotor model. To verify this model, density functional theory was used to calculate adsorbate entropies of four different adsorbate species and found to agree well with experimental results.

3:00pm **HC+SS-TuA-3 CO_2 Dynamics as a Product of Formate Decomposition on Cu(111)***, **Fahdzi Muttaqien**, H Oshima, Y Hamamoto, K Inagaki, I Hamada, Y Morikawa,* Osaka University, Japan

Formate (HCOO) synthesis has been experimentally clarified to occur by the Eley-Rideal (ER) mechanism,[1] which suggests that the reaction rate depends on the initial energy of impinging CO_2. Since HCOO synthesis and decomposition are reversible reactions, the energy of impinging CO_2 must be related to the energy states of desorbed CO_2 from formate decomposition. Therefore, elucidation of HCOO decomposition dynamics is important to deduce optimal conditions for catalytic HCOO synthesis.

We performed ab initio molecular dynamics analysis to elucidate the dynamics of CO_2 from HCOO decomposition on Cu(111). We first investigated the translational energy of desorbed CO_2 from the velocity of center of mass of CO_2. The calculated translational energy (shown in Fig. 1 of Supp. Info) using PBE, PBE-D2, vdW-DF1, rev-vdW-DF2, and optB86b-vdW are 0.30 eV, 0.05 eV, 0.18 eV, 0.16 eV, and 0.11 eV, respectively. Those calculated CO_2 translational energy using PBE-D2 and vdW-DFs are in reasonable agreement with the experimental estimation (0.10 eV),[2] while PBE fails in predicting this energy.

We then explored the rotational and vibrational energies of CO_2 from HCOO decomposition. The rotational energy of CO_2 was calculated from its moment of inertia and angular momentum. We obtained that calculated CO_2 rotational energy varies between 0.08−0.11 eV. The CO_2 vibrational energies are evaluated based on the time evolution of the bond angle, C−O bond length, and difference between two C−O bond lengths of desorbed CO_2 (shown in Fig. 2 of Supp. Info). The vibrational energy of bending, symmetric stretching, and antisymmetric stretching modes are 0.25 eV, 0.11 eV, and 0.0015 eV, respectively. The vibrational energy of desorbed CO_2 bending mode is close to the third excitation energy of the vibrational energy of bending of isolated CO_2.

In summary, the vibrational energy of desorbed CO_2 bending mode is twice larger than the translational energy. Since HCOO synthesis from CO_2 and H_2, reverse reaction of the HCOO decomposition, is experimentally suggested to occur by the ER mechanism, our results indicate that the reaction rate of formate synthesis can be enhanced if the bending vibrational mode of CO_2 is excited rather than the translational, rotational, and/or stretching modes. These results are in contrast to the case of CO_2 dissociation, in which the CO_2 symmetric and antisymmetric stretching modes are more important to increase the dissociation rate.[3,4]

References:

1. H. Nakano *et. al.*, *J. Phys. Chem. B***105**, 1355 (2001).
2. J. Quan *et. al.*, *Angew. Chem. Int. Ed.* **56**, 3496 (2017).
3. T. Yamanaka, *Phys. Chem. Chem. Phys.***10**, 5429 (2008).
4. B. Jiang and H. Guo, *J. Chem. Phys.***144**, 091101 (2016).

4:20pm **HC+SS-TuA-7 Reaction Mechanisms and Nature of Active Sites on Alloy Catalysts: Combining First-principles, Microkinetic Modeling, and Reaction Kinetics Experiments***, **Manos Mavrikakis**,* University of Wisconsin - Madison **INVITED**

Using a combination of first-principles calculations, microkinetic modeling, and reactivity experiments, we establish a rigorous framework for developing a fundamental mechanistic understanding of chemical reactions catalyzed by heterogeneous catalysts. First, and through an iterative process between these three components of our research, we demonstrate unique insights derived on the nature of the active site. Then, based on that understanding, and insights derived for the importance of atomic-scale structure sensitivity, we show how we can provide guidance to inorganic synthesis for preparing alloys, which are predicted to hold promise for improved activity and selectivity for the reactions of interest.

5:00pm **HC+SS-TuA-9 CO_2 Hydrogenation on Defect-Laden Hexagonal Boron Nitride***, **Tao Jiang**, T Rawal, D Le, R Blair, T Rahman,* University of Central Florida

Defect-laden hexagonal boron nitride (*dh*-BN) has recently been shown [1] to be an excellent metal-free hydrogenation catalyst. Here, we employ density functional theory based calculations, including van der Waals interaction, to examine the reactivity of single layer *dh*-BN with N vacancy (V_N) or N substitution by B (B_N), toward the CO_2 hydrogenation to alcohols. To begin with, we find that CO_2 binds strongly at the B sites (near the vacancy) with binding energy of 1.66 eV. Next, we find that formic acid, an important reaction intermediate, chemisorbs molecularly on *dh*-BN with these defects (V_N and B_N) with adsorption energy of -1.82 eV and -0.83 eV, respectively. Through detailed comparison of the adsorption geometries and energetics of the various reactants and intermediates, we conclude that *dh*-BN with V_N defect, rather than B_N, is more suitable a catalyst for purposes here. The potential energy for the decomposition of formic acid ($HCOOH \rightarrow HCO + OH$) on *dh*-BN with V_N is found to be -1.12 eV, indicating an exothermic reaction. The activation barrier for this reaction turns out to be 0.39 eV. We present the reaction pathways and their energetics for further hydrogenation of formic acid to form methanol or to dissociate into CO and H_2O. Reaction rates and turn over frequencies are next calculated using kinetic Monte Carlo simulations to obtain evaluate the propensity of *dh*-BN to serve as a catalyst for CO_2 hydrogenation.

[1] D. Nash et al., ACS Omega, 1, 1343 (2016).

Work supported in part by NSF grant CHE-1465105.

5:20pm **HC+SS-TuA-10 Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface***, **Sara Isbill**, S Roy,* University of Tennessee

Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.

5:40pm **HC+SS-TuA-11 Electronic Structure and Catalytic Properties of Au/h-BN Composite System***, **Takat Rawal**, T Jiang, D Le,* University of Central Florida*; P Dowben,* University of Nebraska - Lincoln*; T Rahman,* University of Central Florida

Rational designing of functionalized materials owning superior properties than those of their constituents is of great importance for potential applications. Herein, we study the electronic structure and catalytic properties of subnanometer sized gold nanoparticle (Au_{13}) supported on hexagonal boron nitride (h-BN) with single boron vacancy, employing density functional theory including van der Waals (vdW) interaction. The electronic interaction between Au_{13} and h-BN is strongly facilitated by the formation of covalent bonds between an Au atom and three N atoms (the first-nearest neighbors of B vacancy), giving rise to the frontier states (near Fermi energy), which spatially distribute around the corner Au atoms as well as the Au atom that occupies the B vacancy site. We examine CO oxidation, as a prototype reaction, on Au_{13}/h-BN via the peroxo-type (OOCO) reaction path. Our results reveal that the highly active sites for CO activation are the corner Au atoms where the frontier states are localized. The strong affinity of CO to bind at those sites, with binding energy of 0.84 eV, can also be understood in terms of the negatively charged Au atoms. The reaction energy and the activation barriers for the reaction OOCO*’ CO_2(g)+O*, are found to be -2.28 eV and 0.10 eV, respectively whereas they are -1.89 eV and 0.12 eV for the reaction CO*+O*’ CO_2(g). These results suggest that Au/h-BN composite can catalyze the CO oxidation even at the low temperature.

Work is supported by DOE grant DE-FG02-07ER15842.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 9 - Session SA+AS+HC+SS-TuA

Frontiers of Photoelectron Spectroscopy: Surface & Interface Processes with Variable Depth Probe, High Spatial or Temporal Resolution

Moderators: Geoff Thornton, University College London, Carla Bittencourt, University of Mons, Belgium

2:20pm **SA+AS+HC+SS-TuA-1 AVS 2017 Medard W. Welch Award Lecture: Ionic Liquid Surface Science***, **Hans-Peter Steinrück**[1],* University Erlangen-Nuernberg, Germany **INVITED**

Ionic liquids (ILs) are molten salts with a melting point below 100∘C. They represent a new class of liquid materials with unique property profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van der Waals interactions of their ions. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as ’task-specific ionic liquids’. Applications range from catalysis and organic synthesis to tribology, protective coatings and gate dielectrics. In catalysis, two important concepts are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. The interface of the IL with the gas phase/vacuum or with the solid support plays an important role. Therefore, knowledge about surface and interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. In contrast to most other liquids, ionic liquids have a very low vapor pressure, and thus can be studied with the methods of ultrahigh vacuum-based surface science. One particularly powerful method is angle-resolved X-ray photoelectron spectroscopy. Thereby, detailed information on their surface composition, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes, on the growth of ultrathin IL-layers, and even on reactions in the liquid phase, can be obtained. Several examples will be discussed illustrating the power of surface science to study this new materials class. Many of the derived conclusions are considered representative for liquid surfaces in general.

F. Maier, I. Niedermaier, and H.-P. Steinrück, *"Perspective: Chemical Reactions in Ionic Liquids Monitored through the Gas (Vacuum)/Liquid Interface",* J.Chem. Phys. **2017** (in press)

H.-P. Steinrück and P. Wasserscheid, "*Ionic Liquids in Catalysis*", Catal. Lett. **2015**, *145*, 380.

H.-P. Steinrück, "*Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions*", Phys. Chem. Chem. Phys. **2012**, *14*, 2510.

H.-P. Steinrück, "*Surface Science goes liquid !*", Surf. Sci. **2010**, *604*, 481.

3:00pm **SA+AS+HC+SS-TuA-3 *In Situ* Characterization of Semiconductor Nanowire Devices by Nano-Focus X-ray Photoemission Microscopy and Spectroscopy***, S McKibbin, **Andrea Troian**, S Yngman,* Lund University, Sweden*; H Sezen, M Amati, L Gregoratti,* Elettra-Sincrotrone Trieste, Italy*; A Mikkelsen, R Timm,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1,2], mainly due to their flexibility in creating heterostructures by axial stacking during epitaxial growth. Because of their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. X-ray photoemission spectroscopy (XPS) has been proven highly suitable for studying surface composition and electronic properties of homogeneous NWs [3]. However, in order to better understand NW device performance, it is essential to also investigate NW heterostructures, with nm-scale lateral resolution and during device operation.

Here, we will present nano-focus XPS results from material and doping heterostructures in InP and GaInP NWs intended for photovoltaic application [2]. We used scanning photoemission microscopy (SPEM) at the ESCAMicroscopy beamline of the ELETTRA synchrotron, providing a lateral resolution of about 120 nm, for imaging individual NWs. In addition, we revealed the change in local surface potential across (Ga)InP *pn*-junctions and InP/GaP tunnel junctions, obtained from In 3d, In 4d, and P 2p XP spectra acquired along the heterostructure NW. Electrical contacts were provided to both ends of the investigated NW, allowing to vary the source-drain bias along the NW during SPEM characterization. We will present detailed results on the influence of built-in potential and external forward and backward bias on the surface potential distribution across NW interfaces.

In another approach, we aim at revealing *in-situ* the interplay of surface chemical composition and local electronic properties. As a model system, we chose InAs NWs consisting of several segments of wurtzite and zincblende crystal structure [4]. At the interface between such segments, we confirmed a staggered type-II electronic band alignment, obtained from nano-focus XP spectra along externally biased NWs. After removing the native oxide from the NW surface by atomic hydrogen annealing [4] in the XPS UHV chamber, the same NW instead showed flat-band conditions, which is preferential for electronic application [1]. We will discuss future plans of using the dynamic high pressure option of the ESCAMicroscopy beamline for changing the surface chemistry of NWs while simultaneously investigating them with SPEM and nm-scale spectroscopy.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015).

[2] J. Wallentin *et al*., Science **339**, 1057 (2013).

[3] R. Timm *et al.,* Appl. Phys. Lett. **99**, 222907 (2011); J. Webb *et al.,* Nano Lett. **15**, 4865 (2015).

[4] M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

---

[1] **Medard W. Welch Award Winner**

3:20pm **SA+AS+HC+SS-TuA-4 Introducing Ionic-Current Detection for X-ray Absorption Spectroscopy in Liquid Cells*, Daniela Schoen,*** Helmholtz-Zentrum Berlin, Germany

Photons and electrons are two common relaxation products upon X-ray absorption, enabling fluorescence yield and electron yield detections for X-ray absorption spectroscopy (XAS). The ions that are created during the electron yield process are relaxation products too, which are exploited in this study to produce ion yield for XA detection. The ionic currents measured in a liquid cell filled with water or iron(III) nitrate aqueous solutions exhibit characteristic O K-edge and Fe L-edge absorption profiles as a function of excitation energy. Application of two electrodes installed in the cell is crucial for obtaining the XA spectra of the liquids behind the membrane. Using a single electrode can only probe the species adsorbed on the membrane surface. The ionic-current detection, termed as total ion yield (TIY) in this study, also produces an undistorted Fe L-edge XA spectrum, indicating its promising role as a novel detection method for XAS in liquid cell.

5:00pm **SA+AS+HC+SS-TuA-9 Non-destructive Depth Profiling of $LaAlO_3/SrTiO_3$ Interfaces*, Conan Weiland,*** NIST*; A Rumaiz,* National Synchrotron Light Source II, Brookhaven National Laboratory*; G Sterbinsky,* Advanced Photon Source, Argonne National Laboratory*; J Woicik,* NIST

The interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) is known to be conductive, even though both LAO and STO are insulators. The interface may also host a variety of interesting phenomena such as a two-dimensional electron gas, ferromagnetism, and superconductivity. Various mechanisms have been proposed to explain the formation of the conductive interface, including the 'polar catastrophe', wherein the polar discontinuity at the interface leads to a diverging potential allowing electronic reconstruction, oxygen vacancies at the interface or at the LAO surface, and chemical intermixing, amongst others.

Synchrotron-based variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) is a unique and powerful tool to non-destructively probe the chemical and electronic structure of buried interfaces such as that between LAO and STO. Using VKE-XPS, we have analyzed a series of LAO films on STO and have observed compositional variations in the LAO films as a function of depth: Al-enrichment occurs at the LAO surface. Additionally, an electric field was observed in some samples. In this presentation we will discuss the relevance of these results on the formation of conductive LAO/STO interfaces.

5:20pm **SA+AS+HC+SS-TuA-10 Hard X-ray Photoelectron Spectroscopy Study of the Resistive Switching in Te-based Conductive Bridging Random Access Memories*, Munique Kazar Mendes*,** *E Martinez, O Renault, R Gassilloud, M Bernard, M Veillerot,* CEA/LETI-University Grenoble Alpes, France*; J Ablett,* Synchrotron SOLEIL, France*; N Barrett,* SPEC, CEA Saclay - University Paris-Saclay, France

Conductive bridging random access memories (CBRAM) are emerging devices for the next generation of non-volatile memories (NVM) (1). The CBRAM mechanism is related to ionic transport and electrochemical reactions, which give rise to the formation and dissolution of a conductive filament through the insulating dielectric layer (2). Data storage relies on switching the resistivity between two high (HRS) and low (LRS) resistance states by applying voltage or current pulses. We investigate the electrochemical reactions involved in the switching mechanism of Al_2O_3-based CBRAMs with different active electrodes (TiTe and ZrTe) (3). We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The HAXPES experiments were performed at the Galaxies beamline (Soleil) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between these different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. For the $TaN/TiTe/Al_2O_3/Ta$ stack, results highlight, the reduction of Ti together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the O^{2-} form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte (Al_2O_3). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode. These results reveal the important role of oxygen migration in the filament formation/dissolution. ToF-SIMS measurements are also performed to get complementary in-depth chemical information. We will finally compare the two active electrodes to investigate the influence of the composition on the switching mechanism.

References

1. Kozicki MN, Barnaby HJ. Conductive bridging random access memory—materials, devices and applications. Semicond Sci Technol. 2016;31(11):113001.

2. Waser R, Dittmann R, Staikov G, Szot K. Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges. Adv Mater. 2009 Jul 13;21(25-26):2632–63.

3. Jameson JR, Kamalanathan D. Subquantum conductive-bridge memory. Appl Phys Lett. 2016 Feb 1;108(5):053505.

5:40pm **SA+AS+HC+SS-TuA-11 Correlation of the Magnetic and Magnetotransport Properties, Electronic and Atomic Structure of Strongly Correlated Complex-oxide Thin Films with the Oxygen Vacancies and Films Thickness*, German Rafael Castro,*** Spanish CRG BM25 Beamline at the ESRF, France*; J Rubio Zuazo,* SpLine Spanish CRG BM25 Beamline at the ESRF, France

Herewith, we present structural, electronic, morphological and magnetotransport properties of thin films of perovskite-manganese oxides (maganites) grown on SrTiO3(001) by oxygen assisted pulsed laser deposition (PLD) methods, using Hard X-ray Photoelectron Spectroscopy (HAXPES), and Grazing Incidence X-ray diffraction (GIXRD).

Perovskite-manganese oxides exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. $La_{1-X}CaxMnO_3$–type perovskite-manganese oxides are strongly correlated electron systems and exhibit, in the Ca doping range between 0.15 and 0.5, a ferromagnetic–paramagnetic (FM) phase transition accompanied by a metal–insulator (MI) transition that results in a colossal magneto-resistance behaviour. In bulk $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), the transition temperature TFM, TMI rises for 33% Ca doping level reaching values close to room temperature. The results shown here are focused on the study of the influence of buried interfaces and the oxygen vacancies on the electric and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films grown on $SrTiO_3(001)$

The growth of these materials in thin film form opens possibilities for magneto-electronic devices applications. The atomic and electronic structures, as well as the oxygen content, are followed simultaneously by GIXRD and HAXPES. Combining GIXRD, HAXPES and transport techniques, we have established a correlation between the electronic, atomic structure and magnetic and magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films as a function of the oxygen vacancies and films thickness.

6:00pm **SA+AS+HC+SS-TuA-12 Synchrotron–Based X-ray Spectroscopy Studies of Inorganic-Organic Hybrid Halide Perovskite Materials Surfaces and Properties*, Deidra Hodges*,** *S Shahriar, A Mishra, V Castaneda, V Vidal, M Martinez, N Garcia, J Munoz, J Lopez,* University of Texas at El Paso

Recently, the methylammonium lead iodide $CH_3NH_3PbI_3$ perovskites have attracted a lot of attention as a possible absorber material for thin film solar cells due to their bandgap energy, high optical absorption coefficients and low-cost solution-processing deposition approaches. Methylammonium lead iodide $CH_3NH_3PbI_3$ perovskite solar cells have evolved with transformative potential with laboratory efficiencies greater than 20%. Perovskite absorber materials are very inexpensive to synthesize and simple to manufacture, making them an extremely commercially viable option. Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to a Newport certified 20.1% in 2015, making this the fastest-advancing solar cell technology to date. These devices are known for their high photon absorptivity, tunable large direct band gaps with superior carrier charge transports, and low-cost methods of fabrication. Methylammonium lead tri-iodide $CH_3NH_3PbI_3$ perovskites thin films and single crystals were prepared for synchrotron-based X-ray spectroscopy studies of the perovskite materials surfaces and properties. The perovskite thin films and single crystals were characterized at the National Synchrotron Light Source (II) (NSLS-II) at Brookhaven National Laboratory (BNL). Synchrotron-radiation-based chemical analysis using X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES) spectroscopy were performed on samples for detailed analysis into chemical composition, stoichiometry, and material surface properties.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 24 - Session HC+NS+SS-WeM

Nanoscale Surface Structures in Heterogeneously-Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

8:00am **HC+NS+SS-WeM-1 The Role of Nanoparticle Edges in Water Dissociation and Oxidation/reduction Reactions in Layered Cobalt Oxides Supported on Au(111) and Pt(111)***,* ***Jakob Fester****, J Lauritsen,* Aarhus University, Denmark*; M Garcia-Melchor,* Trinity College Dublin*; A Walton,* University of Manchester, UK*; M Bajdich,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; A Vojvodic,* University of Pennsylvania*; Z Sun, J Rodríguez-Fernández,* Aarhus University, Denmark

Nanostructured cobalt oxides show great promise as earth-abundant and cheap heterogeneous catalysts, in particular for the oxygen evolution reaction (OER) in electrochemical water splitting and low temperature CO oxidation. However, despite the strong potential in this system as catalysts, we still lack basic knowledge on the active sites and the exact reaction pathways as well as an understanding of the underlying principles behind observed synergistic effects with gold.

To study the possible structure and location of catalytically active sites under controlled conditions, we created a model system consisting of 2-dimensional layered cobalt oxide (CoO_x) nanoislands supported on Au(111) [1] and Pt(111) [2] substrates. This system offers the possibility to reveal the structures in atomic detail by Scanning Tunneling Microscopy (STM) combined with high-resolution X-ray Photoelectron spectroscopy (XPS).

By recording in-situ STM movies during exposure of Co-O bilayer nanoislands to H_2O we showed that H_2O dissociates on edge sites of the nanoclusters followed by migration of H to the basal plane which serves as a reservoir [3] . In combination with Density Functional Theory (DFT) calculations, a preferable dissociation pathway was revealed, also highlighting an assisting role of a second water molecule in the dissociation process.

The determining role of edge sites in the nanoparticle reactivity was further emphasized by STM and XPS studies capturing several stages in both of the gradual oxidation- and reduction processes leading to transitions between layered Co-O bilayer and O-Co-O trilayer morhphologies. In particular, atom-resolved STM images showed changes in edge structure and high densities of defect lines prior to the intercalation of oxygen. The onset of the O-Co-O trilayer formation is located at the island edges on both Au(111) and Pt(111), however several substrate effects were observed on the process rate, mechanism and reversibility. In general, the microscopic picture revealed in these studies suggests that special sites at CoO_x nanoparticle edges may be important for the integral description of CoO_x as a catalyst.

1. Fester, J., et al., *Gold-supported two-dimensional cobalt oxyhydroxide (CoOOH) and multilayer cobalt oxide islands.* Physical Chemistry Chemical Physics, 2017. **19**(3): p. 2425-2433

2. Fester, J., et al., *Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au (111), Pt (111) and Ag (111).* Topics in Catalysis, 2016: p. 1-10

3. Fester, J., et al., *Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands.* Nature Communications, 2017. **8**

8:20am **HC+NS+SS-WeM-2 Analysis of Bulk and Surface Properties of Catalytically-Active Nickel Carbide/Nitride Nanostructures using X-ray Techniques***,* ***Samuel Gage****, K Fong, C Ngo, S Shulda,* Colorado School of Mines*; C Tassone, D Nordlund,* SLAC National Accelerator Laboratory*; R Richards, S Pylypenko,* Colorado School of Mines

Transition metal carbides and nitrides are an ever-growing topic in the scientific community. These materials can be synthesized with varying composition and morphology to exhibit properties similar to platinum-group metal catalysts, which are relevant to industrial heterogeneous catalysis and energy development. Studies, which report promising catalytic performances of nickel carbide and nitride catalysts, have continued to increase in recent years. Wet-chemical approaches involving a top-down thermal decomposition of nickel salt precursors in the presence of product-directing solvents are particularly interesting. The degree of nitrogen present in the nickel salt precursor, as well as the choice of molecular ligand-based solvents, can influence the material properties of the nickel carbide/nitride (Ni_3C/Ni_3N) products.

A series of nitrogen-rich and nitrogen-poor nickel salt precursors were thermally degraded in the presence of oleylamine. X-ray diffraction confirms the bulk hexagonal crystal structure belonging to Ni_3C/Ni_3N. However, a combination of bulk and surface X-ray characterization techniques, including the X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), small angle- and wide angle X-ray scattering (SAXS and WAXS) indicate that the material properties of the Ni_3C/Ni_3N nanostructures do vary depending on the precursor. Computationally guided experiments reveal that the unique bulk and surface properties of these nanostructures influence their catalytic activity, giving Ni_3C/Ni_3N nanostructures the potential to be earth-abundant substitutes for precious metal catalysts.

9:00am **HC+NS+SS-WeM-4 Grain-Boundary-Supported Active Sites for Electrochemical Catalysis***,* ***Xiaofeng Feng****,* University of Central Florida

Identification of active sites on a catalyst surface is the key to a rational design of heterogeneous catalysts. For nanoparticle catalysts, most efforts to tailor their surfaces have focused on controlling particle size, shape, and composition. The atomic surface sites underlying these structural features are mainly facets, steps, edges, and corner sites. These efforts have led to important progresses in heterogeneous catalysis, but it is unclear if the accessible structure space is sufficient for finding optimal catalysts. One alternative is to use bulk defects such as grain boundaries (GBs) to stabilize catalytically active surfaces. Here we show that the GBs in metal nanoparticles create new active sites for electrochemical catalysis. Through a careful design of metal nanoparticle catalysts with different GB densities, extensive TEM characterization, and electrochemical measurements, we discovered that the catalytic activity for CO_2 reduction on Au and CO reduction on Cu is linearly correlated with the GB density in the catalysts [1, 2]. The quantitative GB-activity relationship implicates GB surface terminations as new active sites and lead to highly active and stable electrocatalysts for a two-step conversion of CO_2 to liquid fuels such as ethanol and acetate. In addition, we found that the GBs in Au enhance its activity for oxygen reduction reaction, suggesting that GB engineering may be a general strategy to improve heterogeneous catalysis for renewable energy conversion.

References:

(1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.***2015**, *137*, 4606–4609.

(2) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *ACS Cent. Sci.***2016**, *2*, 169−174.

9:20am **HC+NS+SS-WeM-5 Molecule-Surface Interaction on TiO_2 and MoS_2***,* ***Zhenrong Zhang****,* Baylor University **INVITED**

Interaction of molecules with surfaces of catalysts is critical for understanding catalytic reaction mechanisms. We have studied the interaction of various probe molecules with TiO_2 and MoS_2 using scanning tunneling microscopy (STM) and tip-enhanced Raman scattering (TERS). Two-dimensional material, MoS_2, has attracted tremendous attention due to promising applications in electronics, photonics, and catalysis. Here we compared the difference in the interaction of sub-monolayer copper phythalocyanine (CuPc) molecules with MoS_2 and Au. The relative Raman peak ratio and Raman peak position shift from s patial TERS mapping show the difference in the adsorbates-adsorbates interaction and the adsorbates-substrates interaction on Au and MoS_2 substrates. We have investigated the limits of Raman signal enhancement on MoS_2. Employing carboxylic acid, acetone, and formaldehyde as probe molecules, we studied how reactive sites affect the chemical activity of TiO_2(110). This unique methodology enables us to achieve the atomic-level understanding of the key elemental reaction steps — adsorption, dissociation, diffusion, and coupling reaction — taking place in heterogeneous catalytic reactions.

11:00am **HC+NS+SS-WeM-10 Enantioselectivity: The Quintessential Structure Sensitive Surface Chemistry***,* ***Andrew Gellman****, P Kondratyuk, A Rienicker, M Payne,* Carnegie Mellon University **INVITED**

Enantioselective heterogeneous catalysis and surface chemistry are quintessential forms of structure sensitive surface processes. Selectivity is driven purely by the diastereomeric relationship between the structural handedness of a chiral reagent or transition state and the structural handedness of a chiral surface. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are described as having flat low Miller index terraces separated by kinked step edges, therefore lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on ~500 different single crystal planes exposed by the surfaces of Cu(111) and Cu(100) Surface Structure Spread Single Crystal (S^4C). S^4Cs are single crystals polished into a spherical shape that exposes continuous distributions of surface orientations vicinal to primary orientation. During isothermal decomposition of TA and Asp , XPS has been used to map the temporal evolution of coverage at points across the Cu(111) and Cu(100) S^4Cs. The D- and L-TA (D- and L-Asp) coverage maps across the S^4Cs following heating at 450 K to decompose ~70% of the initially adsorbed molecule reveal the symmetry of the substrate surface and the enantiospecific decomposition kinetics on the chiral surfaces with R- and S-orientations. The fourfold symmetry of the Cu(100) substrate is apparent, and the enantiospecificity of the decomposition kinetics is revealed by the spiral nature of the two maps and their opposite sense of handedness for D- and L-TA. These data can be analyzed to yield the enantiospecific rate constants for TA decomposition as functions of surface orientation.

11:40am **HC+NS+SS-WeM-12 Understanding the Growth and Chemical Activity of Pt-Re Clusters on HOPG and Titania Surfaces*, Donna Chen,* *T Maddumapatabandi, A Brandt, G Seuser,* University of South Carolina

The growth and chemical activity of bimetallic Pt-Re clusters supported on highly-oriented pyrolytic graphite (HOPG) and $TiO_2(110)$ surfaces are studied as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) and methanol oxidation reactions. STM experiments demonstrate that both Pt and Re atoms are mobile on unmodified HOPG surfaces and form large clusters that preferentially located at step edges. However, Ar^+ sputtering creates defect sites that serve as nucleation sites and result in smaller clusters with uniform size distributions. At high metal coverages, exclusively bimetallic clusters are formed from both the deposition of Pt on Re or Re on Pt. The cluster surfaces are Pt-rich even for the Re on Pt clusters due to the lower surface free energy of Pt compared to Re and the high mobility of atoms within clusters. Similarly, Pt-rich Pt-Re clusters have also been grown on titania supports. The activities of the Pt-Re bimetallic clusters are investigated in a microreactor coupled to an ultrahigh vacuum chamber so that the surfaces can be characterized by X-ray photoelectron spectroscopy (XPS) before and after reaction. In the WGS reaction, Re remains metallic, and Pt on Re surfaces exhibit higher activity than pure Pt. In methanol oxidation, oxygen-diffusion of Re to the surface occurs under reaction conditions, and the formation of volatile Re_2O_7 results in Re sublimation from the surface. Furthermore, the titania support appears to stabilize Re_2O_7 against sublimation, whereas Re oxidation is enhanced by the presence of Pt in the bimetallic clusters.

12:00pm **HC+NS+SS-WeM-13 *Single Atom Alloys* for Efficient and Cost-effective Catalysis*, E. Charles Sykes,*** Tufts University

Catalytic hydrogenations are critical steps in many industries including agricultural chemicals, foods and pharmaceuticals. In the petroleum refining, for instance, catalytic hydrogenations are performed to produce light and hydrogen rich products like gasoline. Typical heterogeneous hydrogenation catalysts involve nanoparticles composed of expensive noble metals or alloys based on platinum, palladium, rhodium, and ruthenium. We demonstrated for the first time how single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst. High-resolution imaging allowed us to characterize the active sites in single atom alloy surfaces, and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the system's unique synergy.

Our *single atom alloy* approach may in fact prove to be a general strategy for designing novel bi-functional heterogeneous catalysts in which a catalytically active element is atomically dispersed in a more inert matrix. Very recently we demonstrated that this strategy works in the design of real catalysts. Palladium/copper nanoparticles containing <2% palladium exhibited highly selective hydrogenation of phenylacetylene under realistic reaction conditions and platinum/copper nanoparticles perform the industrially important butadiene hydrogenation at lower temperature using just 1% platinum. Moreover, some of the best industrial alloy catalysts to date may already be operating via this mechanism, but there is currently no method to directly probe the atomic geometry of a working catalyst. Our scientific approach allows one to parse out the minimal reactive ensembles in an alloy catalyst and provide design rules for selective catalytic nanoparticle. *From another practical application standpoint, the small amounts of precious metal required to produce single atom alloys generates a very attractive alternative to traditional bimetallic catalysts.*

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 24 - Session HC+SA+SS-WeA

Bridging Gaps in Heterogeneously-Catalyzed Reactions

Moderator: Yu Lei, University of Alabama in Huntsville

2:20pm **HC+SA+SS-WeA-1 Oxygen Reduction Reaction Activity for Pt/Co/Pt(111) and Pt/Co-N/Pt(111) Model Catalyst Surfaces Fabricated by Arc-plasma Depositions***, S Kaneko, R Myochi, S Takahashi, N Todoroki,* ***Toshimasa Wadayama,*** Graduate School of Environmental Studies, Tohoku University, Japan*; T Tanabe,* Graduate School of Engineering, Tohoku University, Japan

Comprehensive understanding of oxygen reduction reaction (ORR) activity enhancement mechanisms for Pt-based alloy (Pt-M) catalysts is a key for developing highly-efficient, low-Pt-loading cathode catalysts for polymer electrolyte fuel cell. To clarify the effects of the alloy surface structures (e.g., Pt shell atomic arrangements, Pt/M ratio etc.,) on activity and durability, a number of studies have been performed. We have, thus, investigated ORR properties for the well-defined Pt-based bimetallic single crystal surface alloys prepared by vacuum depositions of metals on single crystal substrates in ultra-high vacuum (UHV) [1]. In this study, ORR activities are investigated for Pt/Co and Pt/Co-N model catalysts prepared on Pt(111) substrate by alternative arc-plasma depositions (APDs) of Pt and Co (Co-N).

The UHV-APD-EC apparatus is described elsewhere [2]. Pt and Co (Co-N) layers were alternately deposited onto a clean Pt(111) substrate by the APDs at 573K in UHV. As for the preparations of Co-N layers, Co was deposited by APD under 0.1 Pa of N_2. Total thickness of the Pt/Co(Co-N) and thickness of the topmost-surface Pt and bottom Co layers are fixed to be 6 nm, 1.6nm, and 0.4nm, respectively; the $Pt_{1.6nm}/Co_{0.4nm}/Pt_{3.6nm}/Co_{0.4nm}/Pt(111)$ (denoted as U_Co_4A), U_Co_8A, U_Co_16A, and U_Co_32A samples are prepared. Structural analysis is performed by in-plane XRD, cross-sectional TEM. Then, the Pt/Co/Pt(111) and Pt/Co-N/Pt(111) samples were transferred to an N_2-purged glove box without air exposure. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted in N_2-purged and O_2-saturated 0.1M $HClO_4$ in the glove-box. To discuss EC stability, square-wave potential cycling between 0.6(3s) ~ 1.0(3s) V vs. RHE was applied.

ORR properties (initial activity & durability) of the samples closely correlate with the Co (Co-N) thickness underlying the topmost Pt layer. For example, the activity enhancement factor for the U_Co_16A is highest (13-fold vs. Pt(111)) for the Pt/Co/Pt(111). ORR activity enhancement well corresponds to in-plane lattice distance estimated by the XRD. The results suggest that the ORR enhancements are determined by compressive surface strains that work on the topmost Pt(111) layers induced by underlying Co (Co-N) layers.

We wish to acknowledge the NEDO and JSPS.

[1] T.Wadayama et al., Electrochem.Commun. **12**, 1112 (2010). N.Todoroki et al., PCCP, **15**, 17771 (2013). M.Asano et al., ACS catal. **6**, 5285 (2016).

[2] S. Takahashi et al., PCCP, **17**, 18638 (2015). S. Takahashi et al., ACS Omega **1**, 1247 (2016).

2:40pm **HC+SA+SS-WeA-2 The Mechanism of Oxygen Induced p(2×3) Reconstruction on Mo(112)***,* ***Teng Ma,*** Shenyang Agricultural University, PR China

Oxygen induced reconstruction and oxidation of Mo(112) surface has shown various surface structures in model catalysis and surface studies. Because of its complexity, the p(2 × 3) reconstruction has been modeled as several patterns and its formation mechnism was not well clarified. In this report, a critical precursor of forming p(2 ×3) reconstruction has been observed by using STM, XPS and HREELS methods. For the Mo(112) surface exposed to 5.0×10^{-8} mbar O_2, the formation of the p(2×3) reconstruction is a process of two consecutive steps, during which the clean metallic surface experience the initial oxidation to form dispersed oxide particles at nanoscale, and then reduction and structural rearrangement of molybdenum oxides to the ordered nanostructures. The features of surface structures are also temperature dependent, a mixture of dispersed nanoparticles of molybdenum oxide and one-dimensional nanostructures occurs after O_2 dose at 605 K, while two-dimensional nanostructures or the p(2×3) reconstruction occurs until above 710 K. Our results would give a good explanation about some hurdled questions about the appearance of LEED streaky points and antidomain dislocations in the STM images of the p(2× 3) reconstruction.

3:00pm **HC+SA+SS-WeA-3 Gas-Liquid Scattering Studies of Atmospheric Reactions at the Surfaces of Sea-Spray Mimics***, M Shaloski, J Gord,* University of Wisconsin - Madison*; S Staudt,* University of Wisconsin-Madison*; S Quinn, T Bertram,* University of Wisconsin - Madison*;* ***Gilbert Nathanson,*** University of Wisconsin-Madison **INVITED**

Heterogeneous reactions between atmospheric gases and sea-spray aerosols are fascinating examples of complex interfacial processes involving water, ions, and surface-active molecules. These reactions are also important because of the controlling role they play in regulating pollution and greenhouse gases in the troposphere. Of particular interest is the atmospheric molecule N_2O_5, created indirectly by fossil fuel burning. During the day, N_2O_5 is photolyzed to NO_2 and NO_3, ultimately producing O_3 and then OH· radicals that destroy CH_4. During the night, N_2O_5 can be removed by dissolving into sea-spray aerosols near coastal regions. This dissolution is followed by rapid hydrolysis to HNO_3 or reaction with Cl^- to produce $ClNO_2$, a gas that potentially supplies reactive Cl atoms and returns half of the NO_2 to the atmosphere. The fate of N_2O_5 upon collision with an aerosol droplet is enormously difficult to predict because the droplets are chemically diverse and often possess an outer layer of lipid-like organic molecules. Such surface-active species can inhibit or even enhance uptake and reactivity by orders of magnitude.

We have implemented gas–liquid scattering experiments to investigate the dynamics of these interfacial N_2O_5 reactions. By directing a well-defined beam of N_2O_5 at a stream of salty water emerging from a liquid microjet in vacuum, we can track the uptake and reactivity of N_2O_5 with seawater and sea-spray mimics. We have also used similar experiments involving liquid glycerol to explore the ability of cationic and zwitterionic surfactants to increase ion concentrations of Br^- or Cl^- at the surface and to stabilize reaction intermediates created by N_2O_5. These studies provide insight into interfacial ionization and bimolecular reactions at the surfaces of complex liquids found in the atmosphere.

4:20pm **HC+SA+SS-WeA-7 In-situ Investigation of Methane Activation on MO_x/CeO_2 (111) Surfaces {M=Co, Ni and Cu} using Ambient-Pressure XPS***, J Rodriguez,* ***Zongyuan Liu,*** Brookhaven National Laboratory

Natural gas has transformed the energy landscape of this nation and has fast become a cheap and abundant fuel stock. Methane is the primary component of natural gas but is difficult to convert it to upgraded fuels or chemicals due to the strong C-H bond in methane (104 kcal/mol). This challenge constitutes one of the most difficult problems in heterogeneous catalysis. We have discovered a catalyst with small Ni nanoparticles supported on ceria that has shown promising activity for both methane activation and dry reforming of methane. Then we expanded the study to other transition metals (Co and Cu) supported on ceria in order to rationalize the structure-reactivity relationships for methane activation. Due to the chemically inert nature of methane, the experiment needs to be conducted at elevated pressure via the utilization of Ambient Pressure of XPS. Nanoparticles or clusters of Co and Cu were deposited onto the well-defined CeO_2(111) surface. Strong metal-oxide interactions were found upon annealing the deposited surfaces to 700 K, leading to the generation of MO_x. In-situ AP-XPS showed that the CoO_x/CeO_2(111) interacted strongly with 50 mTorr of methane, resulting in the formation of Co/CeO_x(111), while no obvious changes were observed on the CuO_x/CeO_2(111) surface (figure 1). By comparing it with the NiO_x/CeO_2(111) surface, it can be found that the methane activation on these MO_x/CeO_2 (111) surfaces follow the order: Co > Ni > Cu. The methane dry reforming activity was also investigated on the CoO_x/CeO_2(111) surface by sequentially adding another 50 mTorr of CO_2 into the system. The slight reoxidation of the ceria surface indicates the participation of CO_2 in the catalytic cycle by the following steps: $CH_4(g) \rightarrow CH_{4-x}(a) + H(a)$ with x=1-4; $CO_2(g) \rightarrow CO(a) + O(a)$; $C(a) + O(a) \rightarrow CO(g)$; $H(a) + H(a) \rightarrow H_2(g)$.

4:40pm **HC+SA+SS-WeA-8 Ambient Pressure XPS Study of Catalytic Conversion of Carbon Dioxide by CuO_x Nanoparticles Photodeposited on TiO_2 Nanoparticles***,* ***Djawhar Ferrah,*** *R Galhenage, J Bruce, A Babore, J Hemminger,* University California, Irvine

The chemical conversion of carbon dioxide to useful products has attracted great interest both from a scientific and industrial perspective. It is widely known that Cu is active for the catalytic hydrogenation of CO_2. However, the detailed structure and oxidation state of the active site is not well understood. Recently, Cu nanostructures were reported to be a promising catalyst for hydrogenation of CO_2. The main challenge in the development of Cu based transition - metal nanoparticles is thereby bring selectivity and efficiency to heterogeneous catalysis. Due to the wide range of accessible oxidation states (Cu^0, Cu^I, Cu^{II}, and Cu^{III}), CuO_x-nanoparticules can promote and undergo a variety of reactions which enable reactivity via both one- and two-electron pathways. The size and shape of the particles can play an important role in reactant adsorption and activation at defects and dangling bonds.

In this study, we investigated the reaction mechanisms in carbon dioxide conversion with CuO_x nanoparticles synthesized through the photodeposition process on TiO_2 nanoparticles supported on HOPG. We utilize ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to monitor the surface chemistry during in-situ catalytic reaction of CO_2 and H_2 (H_2O) on the surface under ambient pressure conditions. To track the structural and morphological evolution of catalytic nanoparticles, SEM and TEM investigation will be reported.

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, as follows: The specific development of CuOx nanoparticles on TiO2 nanoparticles was supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993; The ambient pressure XPS experiments were carried out at the CSX2 end station at NSLS-II. RG is supported by funding from the Provost Office of the University of California, Irvine.

5:00pm **HC+SA+SS-WeA-9 Atomic-Scale Characterization of Pt/Ag Surface Alloys***, **Dipna Patel**, E Sykes,* Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt is catalytically active towards hydrogenation, it is very costly, can suffer from poisoning by CO, and coke. On the other hand, bulk Ag is catalytically inert towards hydrogenation reactions, but cheaper than Pt and more resilient to poisoning. Previously, Ag based catalysts have been modified for applications in highly selective heterogeneous catalysis. By analogy to our single-atom alloy approach in other systems such as Pt/Cu and Pd/Cu, alloying Pt into Ag has the potential to greatly enhance catalytic selectivity while reducing the cost of precious metal required to catalyze industrially relevant reactions and reduce poisoning. The atomic-scale surface structure of dilute Pt-Ag alloys has not been reported to date. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of low coverage Pt deposited on Ag(111) as a function of temperature. At low temperatures, intermixing of Pt-Ag is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. This characterization of Pt-Ag surface alloys will enable us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and potentially tune catalytic selectivity and resilience to poisoning via both ligand and ensemble effects.

5:20pm **HC+SA+SS-WeA-10 Structural Consequences of High Oxygen Coverages on Rh(111)***, **Rachael Farber**[12], M Turano, D Killelea,* Loyola University Chicago

Partial oxidations of small molecules over metal surfaces are central to many heterogeneously catalyzed reactions. However, the identity of the actual surface species that promote or hinder these reactions has remained elusive for a variety of reasons. Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, they are now believed to be effective promoters of selective catalysis.

We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Our approach is to first elucidate the uptake of oxygen on Rh(111) and the surface structures formed for a range of oxygen coverages and then characterize them with a variety of techniques under ultra-high vacuum conditions. Exposure to O_2 yields coverages up to 0.5 monolayers (ML), and higher coverages, well in excess of 1 ML, were achieved by dosing with gas-phase atomic oxygen (AO). The surface oxygen coverage was determined with Auger electron spectroscopy (AES), the total oxygen abundance with temperature programmed desorption (TPD), and the surface structures with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Careful control of the exposure parameters allowed for the selective growth of the RhO_2 surface oxide, surface adsorbed oxygen, and subsurface oxygen. The combination of AES, TPD, LEED, and STM revealed that despite total oxygen coverages in excess of 3 ML, the surface oxygen coverage was less than 1 ML and the thermodynamically favored surface phase was the (2x1)-O adlayer corresponding to a surface oxygen coverage of 0.5 ML. The RhO_2 surface oxide was observed to form during extended oxygen exposures, but the (2x1) adlayer persisted. Our findings highlight the complexity of the surface chemistry of oxygen on transition metals and reveal the consequences of incorporating oxygen into the near-surface region of the solid. Furthermore, formation of the surface oxide was shown to rely not only on the presence of defects, but also on high concentrations of oxygen absorbed below the surface of the metal.

5:40pm **HC+SA+SS-WeA-11 Reactivity and Electronic Properties of Supported Metal Oxide and Sulfide Clusters***, **Michael White**,* Brookhaven National Laboratory*; X Meng, K Goodman,* Stonybrook University*; P Liu,* Brookhaven National Laboratory **INVITED**

Small clusters exhibit electronic and chemical properties that can differ significantly from that of the bulk and offer a unique opportunity for preparing novel catalysts whose reactivity can be modified at the atomic level. Here, we use mass-selected cluster deposition to prepare model "inverse" catalysts comprised of small metal oxide (M_xO_y: M = Ti, Nb, Mo, Ce, W) and sulfide (M_xS_y: M = Mo, W) clusters deposited on Cu, Cu_2O/Cu and Au surfaces for studies the water-gas-shift reaction (WGSR) and for CO/CO_2 activation. A key advantage of cluster deposition is that it allows control over cluster stoichiometry which provides a means of introducing oxygen/sulfur "vacancies" and varying the average cation oxidation state. Recent work has focused on the correlation of electron transfer at the cluster-support interface and activity for water dissociation, the latter being a key step in the WGSR mechanism. Electron transfer is probed by XPS core level spectra and 2PPE photoemission measurements of coverage-dependent work function shifts to extract surface dipoles. All the oxide clusters on Cu(111) exhibit negative surface dipoles, indicative of Cu to cluster charge transfer, with smaller dipoles for sub-stoichiometric and reducible oxides (Ti, Nb). Temperature programmed reaction (TPR) experiments show that the Ti_xO_y and Nb_xO_y clusters promote water dissociation on Cu(111), with the 'reduced' Ti_xO_y clusters being more active, while both stoichiometric and reduced Nb_xO_y clusters are active. Overall, these results suggest that local cation coordination is most important for determining water activity. Recent ambient pressure XPS (CO+H_2O, 100's mTorr) measurements at NSLS-II show that small Ti_nO_{2n} (n = 3, 4, 5) clusters on Cu(111) are active for the WGSR reaction through the observation of reaction-induced O-vacancy formation (Ti^{3+} 2p) and the appearance of formate intermediates (C 1s) at room temperature. Results will also be presented on investigations of CO_2 activation on alkali modified surfaces of Mo_6S_8 clusters on Au(111), which had been previously predicted to be active for CO_2 hydrogenation to methanol. Combined TPR and XPS measurements show that co-deposition of K-atoms and Mo_6S_8 clusters strongly enhances CO_2 adsorption above room temperature, whereas the CO_2 is only weakly bound on the bare clusters. The results will be compared with DFT calculations of the possible CO_2 binding sites for the K-cluster-Au interfaces.

This work was performed at Brookhaven National Laboratory under Contract No. DE-SC0012704 with the U.S DOE, Office of Science, and supported by its Division of Chemical Sciences, Geosciences, and Biosciences.

---

[1] **Morton S. Traum Award Finalist**

[2] **National Student Award Finalist**

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 9 - Session SA+AS+HC+SS-WeA

In Situ and Operando Characterization of Interfacial Reactions in Energy & Electronic Devices

Moderators: Karen Chen-Wiegart, Stony Brook University/Brookhaven National Laboratory, Elke Arenholz, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-WeA-1 Probing Solid-Gas and Solid-Liquid Interface Using APXPS*,* *Zhi Liu,*** ShanghaiTech University, PR China, China*; J Cai, Q Liu,* ShanghaiTech University, PR China*; Y Han,* Chinese Academy of Sciences, PR China*; J Liu,* ShanghaiTech University, PR China*; M Mao, H Zhang,* Chinese Academy of Sciences, PR China*; Y Li,* ShanghaiTech University, PR China **INVITED**

Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Most of the research has been focused on the solid-gas interfaces. [1] Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. [2] In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell. I will also give a brief introduction on the APXPS development in Shanghai.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study interface phenomena at Solid-Gas and Solid-Liquid Interfaces.

References

1. D. E. Starr et.al, Chemical Society reviews 42, 5833-57 (2013).

2. S. Axnanda et. al, Scientific Reports, 5,9788 (2015).

3:00pm **SA+AS+HC+SS-WeA-3 Graphene Capped Static and Fluidic Systems for In-Liquid Atmospheric Pressure XPS/AES/SEM and PEEM Studies of Electrochemical Interfaces*,* *Hongxuan Guo*,** *E Strelcov, A Yulaev,* NIST, Center for Nanoscale Science and Technology*; S Nemšák, D Mueller, C Schneider,* Peter Grünberg Institute and Institute for Advanced Simulation, Germany*; A Kolmakov,* NIST, Center for Nanoscale Science and Technology

The liquid-solid electrochemical interfaces are a central topic of modern energy-related electrochemistry and catalysis research. For the last two decades, this research line benefited greatly from the development of differentially pumped electron optics and refreshable sample delivery systems which became an experimental core of the modern ambient pressure electron spectroscopy. An alternative experimental approach to atmospheric pressure electron microscopy (SEM[1], SPEM[2], PEEM[3]) and spectroscopy (XPS[4-5], XAS[3,6]) has been recently tested. In this approach, high electron transparency and molecular impermeability of the graphene membrane was employed to separate the liquid or gaseous sample from ultra-high vacuum environment of electron spectrometer.

In this presentation, we will show our recent work on design and performance of the static and fluidic microfabricated arrays (MCA) capped with bilayer graphene. With such a liquid cell, we characterized water and aqueous solution employing synchrotron-based and standard laboratory XPS, SEM, EDX, and Auger spectroscopy setups[7]. In particular, Cu electroplating and copper sulfate electrolyte polarization at the graphene working electrode have been studied spectroscopically in real time and nanoscopic spatial resolution.

Acknowledgement

ES, HG, and AY acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

Reference

1. J. D. Stoll and A. Kolmakov, Nanotechnology 23 (50), 505704 (2012).

2. A. Kolmakov, D. A. Dikin, L. J. Cote, J. Huang, M. K. Abyaneh, M. Amati, L. Gregoratti, S. Günther and M. Kiskinova, Nature nanotechnology 6 (10), 651-657 (2011).

3. H. Guo, E. Strelcov, A. Yulaev, J. Wang, N. Appathurai, S. Urquhart, J. Vinson, S. Sahu, M. Zwolak and A. Kolmakov, Nano letters (2017).

4. J. Kraus, R. Reichelt, S. Günther, L. Gregoratti, M. Amati, M. Kiskinova, A. Yulaev, I. Vlassiouk and A. Kolmakov, Nanoscale 6 (23), 14394-14403 (2014).

5. R. S. Weatherup, B. Eren, Y. Hao, H. Bluhm and M. B. Salmeron, The journal of physical chemistry letters 7 (9), 1622-1627 (2016).

6. J.-J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J. Guo, D. Prendergast and M. Salmeron, Science 346 (6211), 831-834 (2014).

7. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlassiokiv and A. Kolmakov, ACS Applied Materials & Interfaces (accepted) (2017).

3:20pm **SA+AS+HC+SS-WeA-4 A 3D Printed Liquid Cell for Soft X-ray Absorption Spectroscopy*,* *Tom Regier,*** *T Boyko, J Dynes,* Canadian Light Source, Inc., Canada*; Z Arthur,* Canadian Light Source, Inc.*; M Banis,* University of Western Ontario, Canada

Research methods that enable operando studies on energy materials are an important tool for the rational design of materials for renewable energy and carbon neutral technologies. Of particular value is the ability to observe the change in configuration of the 3d orbitals in transition metal based catalysts. Using the excitation of 2p electrons into vacant 3d orbitals, synchrotron based L-edge measurements allow for clear observation of chemical state and co-ordination geometry information from the first row transition elements. Challenges related to the operating in-situ flow cells in soft x-ray beamline endstations have been overcome and operando measurements are now possible at several facilities.

We report on the design of a 3D printed liquid flow cell with built-in electrodes for operando measurements of the transition metal L-edges. The disposable cells can be quickly customized for specific experiments and can be pre-ordered for lab-based characterization before attempting synchrotron measurements. Beamline instrumentation allows for highly sensitive fluorescence yield measurements with 10 micron spatial resolution or 1 minute time resolution.

4:20pm **SA+AS+HC+SS-WeA-7 In Operando Quantification of Valence Changes in Memristive Devices*,*** *R Dittmann,* ***Christoph Baeumer,*** Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany*; D Cooper,* Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France*; C Schmitz, S Menzel, C Schneider, R Waser,* Peter Gruenberg Institute, Forschungszentrum Juelich GmbH, Juelich, Germany **INVITED**

Memristive devices based on resistive switching in transition metal oxides are attractive candidates for next-generation non-volatile memory applications. It is suspected that voltage-driven oxygen-ion migration and the resulting nanoscale redox processes drive the resistance change in these materials[1, 2]. Direct observation and quantification of the switching mechanism itself, however, remain challenging because the net changes of structure, stoichiometry, and valence state during switching are very small and occur primarily at electrode interfaces or within nanoscale filaments.

Here we will present local changes in the chemical and electronic structure of $SrTiO_3$-based memristive devices utilizing *in operando* characterization tools like transmission electron microscopy (TEM) and photoemission electron microscopy (PEEM). $SrTiO_3$ is chosen as a single crystalline model material, which offers a well-understood platform and well-characterized spectroscopic signatures.

To overcome the surface sensitivity typically limiting PEEM investigations of memristive devices, photoelectron-transparent graphene top electrodes are used to attain spectroscopic information from the buried $SrTiO_3$ layer[3]. During *in situ* switching, reversible changes of the O K-edge absorption spectra within spatially confined regions provide a quantitative map of the oxygen vacancy concentration, confirming that the resistance change is caused by localized oxygen evolution and reincorporation reactions rather than purely internal movement of oxygen vacancies[4].

A remarkable agreement between experimental quantification of the redox state and device simulation reveals that changes in oxygen vacancy concentration by a factor of 2 at electrode-oxide interfaces cause a modulation of the effective Schottky barrier and lead to >2 orders of magnitude change in device resistance. These findings allow realistic device simulations, opening a route to less empirical and more predictive design of future memory cells.

[1] R. Waser and M. Aono, Nat. Mater. **6**, 833 (2007).

[2] R. Waser, R. Dittmann, G. Staikov, and K. Szot, Adv. Mater. **21**, 2632 (2009).

[3] C. Baeumer, C. Schmitz, A. Marchewka, D. N. Mueller, R. Valenta, J. Hackl, N. Raab, S. P. Rogers, M. I. Khan, S. Nemsak, M. Shim, S. Menzel, C. M. Schneider, R. Waser, and R. Dittmann, Nat. Commun. **7**, 12398 (2016).

[4] C. Baeumer, C. Schmitz, A. H. H. Ramadan, H. Du, K. Skaja, V. Feyer, P. Muller, B. Arndt, C. Jia, J. Mayer, R. A. De Souza, C. Michael Schneider, R. Waser, and R. Dittmann, Nat. Commun. **6**, 9610 (2015).

5:00pm **SA+AS+HC+SS-WeA-9 Magnetic Skyrmions in Ultrathin Magnetic Films and Nanostructures***, **Jan Vogel,*** Institut Néel, CNRS/UGA, Grenoble, France*; O Boulle, R Juge,* SPINTEC, CNRS/CEA/UGA, Grenoble, France*; D Chaves, S Pizzini,* Institut Néel, CNRS/UGA, Grenoble, France*; S Je, G Gaudin,* SPINTEC, CNRS/CEA/UGA, Grenoble, France*; T Mentes, A Locatelli,* Elettra-Sincrotrone Trieste, Italy*; M Foerster, L Aballe,* ALBA Synchrotron Light Facility, Spain **INVITED**

Magnetic skyrmions are chiral spin structures with a whirling spin configuration. Their topological properties, small size and sensitivity to small current pulses have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion were first experimentally observed in bulk materials [1] and in epitaxial ultrathin films [2], under a strong external magnetic field or at low temperature. More recently, it was predicted that they can also be created in thin magnetic films in stacks with structural inversion asymmetry [3]. We have used high lateral resolution PhotoEmission Electron Microscopy combined with X-ray Magnetic Circular Dichroism (XMCD-PEEM) to show that skyrmions with a size around 150 nm can indeed be stabilized at room temperature and without external magnetic field, in nanostructures of Pt/Co/MgO with a Co thickness of 1 nm [4]. The high sensitivity of the technique allows measuring very thin Co layers buried under protecting cover layers. The vectorial information obtained by rotating the sample with respect to the incoming x-ray direction allowed us obtaining information on the 3-dimensional spin structure of the skyrmions, directly showing the chiral spin configuration with left-handed chirality.

We investigated the dependence of the skyrmion size on an applied magnetic field, revealing that already a moderate field of 4 mT can reduce the skyrmion diameter to a size of 70 nm. We also studied the motion of skyrmions in micron-wide strips of Pt/Co/MgO induced by current pulses. The results show that skyrmions can be moved with moderate current pulses with current densities of some 10^{11} A/m^2, leading to velocities of several tens of m/s.

Our measurements show that synchrotron-based magnetic imaging using PEEM is very powerful for studying the static and dynamic properties of skyrmions in ultrathin magnetic films.

[1] X.Z. Yu et al., Nature 465, 901 (2010). [2] N. Romming et al., Science 341, 636 (2013). [3] A. Fert, V. Cros & J. Sampaio, Nature Nanotech. 8, 152 (2013). [4] O. Boulle, J. Vogel et al., Nature Nanotech. 11, 449 (2016).

5:40pm **SA+AS+HC+SS-WeA-11 O_2 Pressure Dependence of SiO_2/Si Interfacial Oxidation Rate Studied by Real-time Photoelectron Spectroscopy***, **Shuichi Ogawa,*** Tohoku University, Japan*; A Yoshigoe,* JAEA, Japan*; S Ishidzuka,* National Institute for of Technology, Akita College, Japan*; Y Takakuwa,* Tohoku University, Japan

Thermal oxidation of Si surfaces under the non-equilibrium conditions were used to form a high-quality Si oxide films and/or enlarge the oxidation rate. For example, rapid thermal oxidation (RTO) is performed under the raising the temperature, and then thick oxide can be formed without preventing the dopant diffusions[1]. In addition, the oxidation rate of RTO process is faster than that of constant temperature oxidation (CTO) though the highest temperature of RTO is as same as that of CTO[2]. Based on these knowledges, it is predicted that the oxidation rate at the SiO_2/Si interface can be quickened even by increase of the O_2 pressure. In this study, the increased O_2 pressure dependence of the interface oxidation rate which proceeds contentiously after Si(001) surface oxidation was investigated using real-tile photoelectron spectroscopy.

The oxidation experiment was performed using the surface reaction analysis apparatus placed at the BL23SU of SPring-8, Japan. A clean Boron doped p-type Si(001)2×1 surfaces were oxidized at 400℃ under the O_2 pressure of 3.2×10^{-5} Pa. When clean surfaces were completely covered by the Si oxide, the O_2 pressure was elevated to P_{O2}(int) in order to enhance the interfacial oxidation. The P_{O2}(int) was changed between 6.4×10^{-5} Pa to 3.2×10^{-3} Pa. O 1s and Si 2p spectra were measured repeatedly during the oxidation. The time evolution of O 1s photoelectron intensity (I_{O1s}) was used for investigation of the oxidation rate.

From the I_{O1s}, we can estimate the completion of surface oxidation as 3200 s. An O_2 pressure was increased up to 1.5×10^{-3} Pa at this time, and then the interface oxidation was enhanced. The enhanced interfacial oxidation rates were obtained from the differential of I_{O1s}. The P_{O2}(int) dependence of the interfacial oxidation rate shows that the O_2 pressure increase makes the interfacial oxidation rate fast, and the interface oxidation rate is proportional to the square root of P_{O2}(int).

This result cannot be explained using traditional oxidation models, because the proportional relationship between the interface oxidation rate and square root of P_{O2}(int) indicates that the interface oxidation rate is limited by an O_2 diffusion through the oxide. However, the thickness oxide is much thinner than 1 nm, so that it cannot be thought that the rate-limiting reaction of interfacial oxidation is O_2 diffusion. To explain the kinetics, we propose the new interface oxidation model named "Unified Si oxidation model mediated by point defects"[3].

[1] H.Y.A. Chung, *et al.*, Mater. Sci. Eng. B, **118,** 55 (2005).

[2] S. Ogawa *et al.*, J. Chem. Phys., **145,** 114701 (2016).

[3] S. Ogawa *et al.*, Jpn. J. Appl. Phys., **46,** 7063 (2006).

6:00pm **SA+AS+HC+SS-WeA-12 Highly Time-resolved Insights into the Sputter Deposition of Metal Electrodes on Polymer Thin Films for Organic Electronics***, **Franziska Löhrer**, V Körstgens,* Technische Universität München, Germany*; M Schwartzkopf,* Deutsches Elektronensynchrotron DESY, Germany*; A Hinz, O Polonskyi, T Strunskus, F Faupel,* Christian-Albrechts-Universität zu Kiel, Germany*; S Roth,* Deutsches Elektronensynchrotron DESY, Germany*; P Müller-Buschbaum,* Technische Universität München, Germany

With their easy processability, high flexibility and tuneable optical properties, organic electronics (OE) offer a wide range of potential applications. Especially photoactive polymers have received attention in recent years as candidates for organic photovoltaics (OPV) and light emitting diodes (OLEDs). Although based on organic materials, their electrodes are typically made from metals due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OE devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes happening at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ grazing incidence small and wide angle x-ray scattering (GISAXS/GIWAXS) [1]. These techniques allow insights into the structural evolution of the metal on the organic film, which depends on various parameters such as the deposition rate or the film morphology. Making use of the brilliant synchrotron light source Petra III at DESY [2], we can study the deposition behavior of the metal on the polymer film with outstandingly high spatial and temporal resolution. The acquired large data sequences are tracked in real-time and further analyzed using the fast data reduction software DPDAK [3]. The final film morphology is characterized via scanning electron microscopy and X-ray reflectometry. UV/Vis absorption and reflection measurements complete our work. The metal layer formation can be described by applying an appropriate growth model based on our earlier work. [4] The model is refined in an iterative process of GISAXS simulations and data fitting. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

[1] A. Hexemer, P. Müller-Buschbaum, IUCrJ 2, 106-125 (2015)

[2] A. Buffet, et al., J. Synchrotron Radiat., 19(4), 647-653 (2012)

[3] G. Benecke, et al., J. Appl. Crystallogr., 47(5), 1797-1803 (2014)

[4] M. Schwartzkopf et al., ACS Appl. Mater. Interfaces, 7(24), 13547-13556 (2015)

Surface Science Division
Room 25 - Session SS+HC+NS-WeA
Dynamical Processes at Surfaces

Moderators: Ashleigh Baber, James Madison University, Kathryn Perrine, Michigan Technological University

3:00pm **SS+HC+NS-WeA-3 Quantum Molecular Machines***, **Saw-Wai Hla,*** Ohio University and Argonne National Laboratory **INVITED**

One of the goals of nanotechnology is the development of complex molecular machines that can be operated with atomic level control in a solid-state environment. Most biological molecular machines have the sizes from tens of nanometers to a few microns –a range where classical machine concepts hold. However, artificially designed molecular machines can be in the size range down to a few nanometers or less, which is in the range of quantum processes. In this talk, we will present various artificial molecular machines such as molecular motors and linear transport devices such as molecular cars operating in the quantum regime on materials surfaces. Fundamental operations of these synthetic molecular machines are investigated at one molecular machine-at-a-time in an atomically clean environment using low temperature scanning tunneling microscopy (STM), tunneling spectroscopy, and molecular manipulation schemes [1,2]. These investigations reveal how charge and energy transfer are taken place within single molecular machines as well as among the molecular machines in the molecular networks. Moreover by introducing dipole active components in the rotor arms of the molecular motors, communication among the molecules can be introduced via dipolar interaction. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and the strength of applied electric field energy. Here, all the molecular motors can be rotated in a synchronized manner using 1V or higher electric field supplied from the STM tip. Below this bias, the rotor arms of the molecular motors can reorient into different directions. Careful analyses reveal that such reorientations of the molecular motors are not random, but they are coordinated to minimize the energy. Furthermore, individual molecular motors can be charged using the inelastic tunneling scheme with the STM tip. This introduces spin-active components within the molecular motors and enables us to investigate spintronic properties of individual molecular motors at the sub-molecular scale using tunneling spectroscopy. For the controlled linear transport at the nanoscale, we will present the latest development of molecular nanocars.This work is supported by US DOE grant DE-FG02-02ER46012.

[1] U.G.E. Perera . F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, and S.-W. Hla. ***Nature Nanotechnology 8***, 46-51(2013).

[2] Y. Zhang, H. Kersell, R. Stefak, J. Echeverria, V. Iancu, U. G. E. Perera, Y. Li, A. Deshpande, K.-F. Braun, C. Joachim, G. Rapenne, and S.-W. Hla. ***Nature Nanotechnology* 11**, 706-711 (2016).

4:20pm **SS+HC+NS-WeA-7 Collective, Multi-atom Diffusion in Epitaxially Grown Metallic Films*, Matt Hershberger*,** *M Hupalo, P Thiel,* Iowa State University Ames Laboratory –USDOE*; M Man, M Altman,* Hong Kong University of Science and Technology, Hong Kong*; C Mullet, S Chiang,* University of California-Davis*; M Tringides,* Iowa State University Ames Laboratory –USDOE

Surface diffusion is the main process controlling mass transport of many important phenomena such as nucleation, nanostructure growth, pattern formation, and chemical reactions. In practically all cases, it is described as a random walk of independently moving adatoms. Such process is inherently stochastic and therefore very slow as a route to self-organization in nature.

A series of experiments in different epitaxially grown metallic films over the last 5 years using different techniques has challenged the classical picture. The experiments have shown unusually fast, collective diffusion is present in nature, observed in a range of experiments over different length and time scales.

STM experiments show that fully completed Pb crystalline islands emerge "explosively" out of the compressed wetting layer on Si(111) after a critical coverage q_c=1.22ML is reached. The unexpectedly high island growth rates and directional correlations show that mass transport is through the correlated motion of the wetting layer.[1] Additional deposition of Pb shows island density that does not reach steady state; it shows abrupt jumps in island density with new generations of smaller islands continuing to nucleate (in contrast to classical nucleation). Real time experiments with LEEM, monitoring the refilling of an initial vacant area in Pb/Si(111), show that the initial steep profile does not disperse and that the profile propagates at constant velocity x~t. The profile follows a non-Fickian form with two moving highly correlated fronts, one inward and the other outward.[2] The formation of long anisotropic multi-height Ag islands on Ge(110) is exceedingly fast, when compared to the rates expected from random walk Ag diffusion barriers. A wetting layer is also present prior to the crystallization and is responsible for the fast growth rates, although the temperature is above room temperature.[3] Evidence for collective diffusion has been seen in Pb/Si(100), Pb/Ge(111), Pb/Ni(111), Pb/W(110), Ag/Si(110).

A better understanding of these processes can guide the search of collective transport in other systems, especially to identify the relevant growth "window" (of temperature and coverage). It can further clarify the role of stress since the compression of the non-crystalline wetting layer is critical for these effects.[4]

References:

1. M. T. Hershberger et al., .Phys. Rev. Lett. 113, 236101 (2014)
2. K. L. Man et al., Phys. Rev. Lett. 110, 036104 (2013)
3. C. H. Mullet et al., manuscript submitted.
4. E. Granato et al., Phys. Rev. Lett. 111, 126102 (2013)

4:40pm **SS+HC+NS-WeA-8 Quantitative Molecular Beam Study for CO₂ Hydrogenation on Cu (111) and Cu(100) Surfaces*, Jiamei Quan*,** *T Kondo, T Kozarashi, T Mogi,* University of Tsukuba, Japan*; J Nakamura,* University of Tsukuba, Japan, Japam

Catalytic conversion of CO_2 into valuable fuels and chemicals such as methanol, especially if activated by a precise energetic control, represents a potentially economic strategy for utilization of fossil feedstock and reducing CO_2 emissions and their contributions to climate changes. The formation of formate intermediates ($2CO_2 + H_2 \rightarrow 2H\ COO_a$) on Cu catalysts is an important initial step, in which the reaction probability is reported as low as 10^{-12} at 340 K.[1] Our previous reports suggested that the reaction proceeds via an Eley-Rideal type mechanism, where CO_2 directly reacts with pre-adsorbed H to form $HCOO_a$.[2] Recently, we have clarified using supersonic molecular beam apparatuses that the reaction probability is promoted up to ~10^{-3} by increasing both translational and vibrational energies, while insensitive to the Cu surface structure (Cu(111) and Cu(100)) and the surface temperature (120 - 210K). The energy efficacy on the reaction probability is found to be larger as much as 100 times for the vibrational energy compared to the translational energy, suggesting that the vibrational excitation significantly enhances the formate formation. Based on the comparison with DFT calculations, we conclude that the excitation of the bending mode of CO_2 at the transition is crucially important to form the C-H bond of HCOO via lowering LUMO level of CO_2. The small pre-exponential factor derived by the experiment is ascribed to the preferential orientation of the CO_2 molecule (C-end collision to H_a on Cu) for the reaction. The discovered thermal non-equilibrium channel in CO_2 conversion, which doesn't require the heating of catalysts, is expected to provide a prototypical surface reaction dynamics and open up novel industrial pathways of efficient CO_2 conversion into useful chemicals and fuels.

[1] (a) T. Fujitani, J. Nakamrua et al., *App. Surf. Sci.* 121–122 (**1997**) 583; (b) H. Nakano, J. Nakamrua et al., *J. Phys. Chem. B* 105 (**2001**) 1355.

[2] (a) J. Quan, J. Nakamrua, et al., Angew. Chem. Int. Ed. 56 (**2017**) 3496; (b) G. Wang, J. Nakamura, et al., *J. Phys. Chem. B* 110 (**2005**) 9.

5:00pm **SS+HC+NS-WeA-9 A New Approach for Controlling the Rotational Orientation of a Molecule and Studying the Stereodynamics of a Molecule-Surface Collision*, Gil Alexandrowicz,*** Technion – Israel Institute of Technology, Israel **INVITED**

The interaction between a molecule and a solid surface is fundamental to a huge variety of research fields and applications, ranging from industrial heterogeneous catalysis to ultra-cold astrochemical reactions on cosmic dust. One molecular property that affects molecule-surface interactions, but is also particularly difficult to control and resolve, is the orientation and alignment of the rotational axis of the molecule i.e. the quantum rotation projection states. The existing paradigm is that control over this molecular property can be obtained either by photo-excitation schemes and/or by deflecting experiments using strong electric or magnetic fields. Using these approaches valuable insight was obtained and the crucial role the rotation projection states have on the outcome of molecule-surface collision was demonstrated. However, the two approaches mentioned above can only be applied to a very small sub-group of systems (typically excited/paramagnetic species). In this presentation I will describe a completely different approach which utilizes the rotational magnetic moment, which is a general molecular property, to control and resolve the projection rotation states of ground-state molecules.

Our new experimental approach combines an atomic interference setup, originally built to perform ultra-fast surface diffusion measurements[1], with magnetic manipulation techniques we developed for separating quantum states of molecular beams[2]. The result is a unique setup which can both control and resolve the rotational orientation of a molecule as it collides with a solid surface. In this presentation I will show some recent experiments where we controlled the rotational orientation of a ground state hydrogen molecule, and correspondingly modified the outcome of a collision event with flat and stepped copper surfaces[3].The possibilities this new technique opens for studying the stereodynamic nature of molecule-surface interactions as well as ultra-fast surface dynamics will be briefly discussed.

[1] Progress in Surface Science, 84, 323 (2009).

[2] Science, 331, 319 (2011).

[3] Nature communications, (DOI: 10.1038/ncomms15357), in press (2017).

5:40pm **SS+HC+NS-WeA-11 Surface Temperature Effects in CH_4 Dissociation on Flat and Stepped Nickel Single Crystals***, **Eric High**, E Dombrowski, A Utz,* Tufts University

A modified King and Wells molecular beam reflectivity method was used to obtain thermal and quantum state resolved initial sticking probabilities (S_0) for CH_4 on nickel single crystals at elevated surface temperatures (500 to 1000K). We recorded the reactivity of a supersonic molecular beam of methane with and without laser excitation to v=1 of the v_3 antisymmetric C-H stretching vibration. Square wave modulation of the laser source during CH_4 deposition provided simultaneous real-time measurement of $S_0^{LaserOff}$ and S_0^{v3}, resulting in a dramatic reduction in data acquisition time, a significant reduction in experimental error, and the opportunity to measure S as a function of accumulating surface coverage. On a Ni(111) surface, both laser-off and vibrational state-resolved measurements of S_0 were essentially independent of surface temperature, within error, from 1000 to 800K and then decreased linearly as T_{surf} dropped from 800 to 500K. These findings are consistent with the predictions of Reaction Path Hamiltonian calculations by Jackson and Guo over a wide range of incident kinetic energies (96 to 167 kJ/mol). The calculations suggest that at low incident energies, reactivity occurs predominantly at on-top sites, but as energy increases, reactions begin to occur at bridge sites as well. We will also present more recent measurements on the low step density Ni(997) surface that provide insight into the role of step-edge nickel atoms at these industrially relevant surface temperatures.

6:00pm **SS+HC+NS-WeA-12 Experimental and Theoretical Study of Rotationally Inelastic Diffraction of $H_2(D_2)$ from Methyl-Terminated Si(111)***, **Kevin Nihill**[1], Z Hund,* University of Chicago*; A Muzas, C Diaz, M del Cueto,* Universidad Autónoma de Madrid, Spain*; T Frankcombe,* University of New South Wales, Australia*; N Plymale, N Lewis,* California Institute of Technology*; F Martin,* Universidad Autónoma de Madrid, Spain*; S Sibener,* University of Chicago

Fundamental details concerning the interaction between H_2 and CH_3-Si(111) have been elucidated by the combination of diffractive scattering experiments and electronic structure and scattering calculations. Rotationally inelastic diffraction (RID) of H_2 and D_2 from this model hydrocarbon-decorated semiconductor interface has been confirmed for the first time *via* both time-of-flight and diffraction measurements, with modest $j = 0 \rightarrow 2$ RID intensities for H_2 compared to the strong RID features observed for D_2 over a large range of kinematic scattering conditions along two high-symmetry azimuthal directions. The Debye-Waller model was applied to the thermal attenuation of diffraction peaks, allowing for precise determination of the RID probabilities by accounting for incoherent motion of the CH_3-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of H_2 and D_2 have been quantitatively evaluated as a function of beam energy and scattering angle, and have been compared with complementary electronic structure and scattering calculations to provide insight into the interaction potential between H_2 (D_2) and hence the surface charge density distribution. Specifically, a six-dimensional potential energy surface (PES), describing the electronic structure of the $H_2(D_2)/CH_3$-Si(111) system, has been computed based on interpolation of density functional theory (DFT) energies. Quantum and classical dynamics simulations have allowed for an assessment of the accuracy of the PES, and subsequently for identification of the features of the PES that serve as classical turning points. A close scrutiny of the PES reveals the highly anisotropic character of the interaction potential at these turning points. This combination of experiment and theory provides new and important details about the interaction of H_2 with a hybrid organic-semiconductor interface, which can be used to further investigate energy flow in technologically relevant systems.

---

[1] **Morton S. Traum Award Finalist**

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 24 - Session HC+SA+SS-ThM

Mechanisms and Reaction Pathways in Heterogeneously Catalyzed Reactions

Moderator: David Payne, Imperial College London

8:00am **HC+SA+SS-ThM-1 Effects of Phosphorus and Alkyl Substituents on C-H, C-C, and C-O Bond Rupture within Carboxylic Acids on Ru(0001)**, ***SiWei A. Chang**, D Flaherty,* University of Illinois at Urbana-Champaign

Transition metal phosphide (TMP) catalysts are selective towards C-O bond rupture during hydrodeoxygenation reactions used to upgrade bio-oil. However, the manner in which bond rupture mechanisms and intrinsic barriers (i.e., C-H, C-C, and C-O bond) differ between transition metals and TMP catalysts are not well understood. In this study, a phosphorus (P) modified Ru(0001) surface is created using sequences of PH_3 adsorption and annealing treatments followed by Auger electron spectroscopy to determine the P:Ru ratio. Synthesized $P_{0.4}$-Ru(0001) surfaces have a (r7xr7) low energy electron diffraction pattern and appear to resemble the (111) facet of bulk Ru_2P materials. The results from temperature programmed desorption of CO and NH_3 demonstrate that the addition of P atoms to Ru(0001) decreases the binding energy of CO and NH_3 by ~12 kJ mol^{-1} compared to Ru, suggesting that P atoms decrease the extent of electron exchange between Ru surfaces and adsorbates (i.e., CO and NH_{-3}).

Results from temperature programmed reaction (TPR) of C_1-C_4 carboxylic acid decomposition on Ru(0001) and $P_{0.4}$-Ru(0001) surfaces indicate that both P atoms and the length of alkyl substituents on carboxylic acids (i.e., R = H, CH_3, CH_2CH_3, and $CH_2CH_2CH_3$) alter the intrinsic activation energy (E_a) of bond ruptures. On both surfaces, TPR and reactive molecular beam scattering (RMBS) results are consistent with carboxylic acid decomposition mechanism, that involves the reaction of carboxylate intermediates to form alkyl surface species with either CO (by C-O bond rupture followed by C-H/C-C bond rupture) or CO_2 (by direct C-H/C-C bond rupture). The addition of P atoms to Ru(0001) increases E_a values for the rupture of all bonds (i.e., C-O, C-H and C-C bonds) by 5-50 kJ mol^{-1} and increases also the ratio of CO to CO_2 production (in the case of formic acid and acetic acid decomposition). In addition, P atoms weaken the linear correlation that exists between E_a for C-C and C-H bond rupture and the homolytic bond dissociation energies (BDE) of the involved bonds (e.g., R-COOH), thereby decreasing the strength of the correlation from near parity on Ru(0001) (i.e., slope m = 1) to moderate changes with BDE on $P_{0.4}$-Ru(0001) (i.e., slope m = 0.2). The RMBS results from formic acid in the presence of P atoms show a higher production of CO than CO_2, which reflects the catalytic consequences of the differences between the C-H and C-O bond rupture energy barriers on $P_{0.40}$-Ru(0001) and those for Ru(0001). Collectively, these results suggest that P atoms alters the production selectivity of CO and CO_2 through a greater increase in the energy barriers of C-O bond relative to C-H/C-C bond rupture.

8:20am **HC+SA+SS-ThM-2 Monitoring Cu(111) Restructuring under Elevated CO Pressures via Polarization Dependent Infrared Spectroscopy**, ***Christopher Kruppe**, M Trenary,* University of Illinois at Chicago

Recently it was shown that a Cu(111) surface will reconstruct to form nanoclusters when exposed to 0.1 – 100 Torr of CO.[1] We present the use of polarization dependent – reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the Cu(111) restructuring in real time. Under 10 Torr of CO, PD-RAIR spectra display a peak for CO on top of Cu atoms. Scans were taken periodically and displayed new peaks related to CO bound to the nanoclusters that grow over a period of 30 minutes. Spectra obtained at 10 Torr and 300 K show that the creation of the Cu nanoclusters is correlated with an increase in intensity of these C-O vibrational features, which are only visible due to removal of gas phase CO features from the RAIR spectra. Dissociation of H_2O in UHV occurs on the nanoclusters, which is negligible on unreconstructed Cu(111). Previously the splitting of H_2O was thought to be a geometric effect caused by the nanoclusters as under UHV conditions CO does not adsorb on Cu(111) at room temperature. However, after exposing Cu(111) to 10 Torr of CO at room temperature for 30 minutes strong C-O vibrations are observed upon evacuation of the IR cell. In UHV, the H_2O partial pressure is increased in the IR cell to 2×10^{-8} Torr and flowed over the reconstructed Cu(111) crystal. The RAIR spectra indicates there is a reactive CO species that interacts with H_2O to create formaldehyde. This is further confirmed by observing formaldehyde with temperature programmed desorption following H_2O exposure. Auger electron spectroscopy confirms the presence of oxygen on the Cu(111) surface after water exposures in the IR cell. Detailed interpretation of the data requires consideration for the formation of Fe-carbonyls, which can be present in the CO bottle, or produced in the reaction cell. The possibility of Fe as the cause for the CO bound in UHV will be presented.

1. Eren, B.; Zherebetskyy, D.; Patera, L. L.; Wu, C. H.; Bluhm, H.; Africh, C.; Wang, L.-W.; Somorjai, G. A.; Salmeron, M. Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption. *Science* **2016**, *351*, 475 LP - 478.

8:40am **HC+SA+SS-ThM-3 Thermal and Plasma Heterogeneous Catalysis Compared: CO_2 and Hydrocarbon Dry Reforming**, *Q Huang, D Zhang,* Center of Interface Dynamics for Sustainability, Chengdu, PR China, China*; E Schuler, M Ronda Lloret, G Rothenberg, N Shiju,* van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands, Netherlands*; **Aart Kleyn**,* Center of Interface Dynamics for Sustainability, PR China, China **INVITED**

Endothermic catalytic reactions require operation at elevated temperatures. The heating required is usually obtained by combustion of hydrocarbons and contributes to CO_2 emission. Instead electricity obtained in a sustainable should drive the reaction. In addition, it is desirable that the energy transfer involved is done in a bond specific manner. Plasma excitation and dissociation of molecules can serve this purpose. In plasma, all molecular degrees of freedom are not in equilibrium and dissociation of CO_2 can be realized much more efficiently than in thermodynamic equilibrium. There is a preferential vibrational excitation of CO_2.

In Chengdu we use a plasma chemical reactor with mass spectroscopy, infrared spectroscopy, optical emission spectroscopy and a Langmuir probe to study the characteristics of the plasma, reaction products and the catalyst. In Amsterdam we use a thermal reactor and gas chromatography to study reaction products. The reactions are carried out at pressures of several hundreds of Pa up to atmospheric in Ar buffergas. Catalysts are prepared in the usual way.

The simplest reaction studied in the plasma reactor is the dissociation of CO_2 into CO and O_2. We find energy efficiencies higher than 45%, indicating that the system is not in thermodynamic equilibrium and plasma favors vibrational excitation to translational heating. Adding a catalyst like AgO or NiO on Al_2O_3 does not enhance the yield. However, a purely metallic catalyst does significantly enhance the yield.

Optical emission spectroscopy shows that the radiofrequency (RF) and microwave (MW) plasma behave quite different. In the MW plasma predominantly emission from the C_2 Swann-band is seen, whereas the RF plasma shows mainly chemiluminescence from excited CO. This is due to a different electron excitation mechanism.

In the case of dry reforming of CH_4 with CO_2 in the plasma reactor we find that addition of an oxidic catalyst does not enhance the yield of CO + H_2. In the case of dry reforming of butane (C_4H_{10}) to yield butene (C_4H_8), plasma reforming with or without catalyst does shows only small conversion. Mainly cracking of butane into C_2H_x is seen and polymerization. However, running the same reaction under high temperature conditions in a thermal reactor yields a satisfactory conversion. A Co based catalyst has the best performance.

These studies allow us to obtain mechanistic information on the conversion of simple molecules, pretreated by plasma, on various catalysts. We are exploring to what extend direct Eley-Rideal reactions are relevant in the plasma reactor. This reaction mechanism is very unlikely under thermal conditions.

9:20am **HC+SA+SS-ThM-5 Imaging the Molecular Origins of Symmetry Breaking on Well-defined Surfaces**, ***Amanda Larson**, R Hannagan, E Sykes,* Tufts University

Understanding the interaction of prochiral reactants with chiral modifiers on surfaces is a key step towards controlling heterogeneous enantioselective catalysis. We have chosen a simple model system composed of interacting chiral propylene oxide and propene molecules on a Cu(111) surface that is amenable to both scanning probe and desorption studies. Low temperature scanning tunneling microscopy (STM) enables an unprecedented level of spatial resolution of the enantioselective molecule-molecule interactions and their dynamics. STM imaging of propylene oxide and propene molecules at 5 K reveals that both molecules, when in isolation on the surface, behave as molecular rotors. Furthermore, the chirality of individual propylene oxide molecules can be discerned from the STM images of the rotating molecule. While propene is achiral in the gas phase it become chiral when bound to surfaces and STM also allows us to distinguish between its surface-bound enantiomers. When studied separately, repulsive forces between both sets of molecules disperse them on the surface at low coverages. However, when co-dosed we observe an attraction between propylene oxide and propene and they form complexes in which their rotation is inhibited. Temperature programmed desorption measurements are used to quantify these chiral modifier-molecule interaction strengths. Finally, the geometry of individual propene and propylene oxide molecules can be determined within the complexes and 1:1 chiral interactions deciphered.

11:00am **HC+SA+SS-ThM-10 A Surface Science Approach for New Heterogeneous Catalyst***, **Ib Chorkendorff**,* Technical University of Denmark, Denmark **INVITED**

First, we shall discuss how surface science and mass-selected nanoparticles can be used to make efficient model systems for heterogeneous catalysts. We shall demonstrate how mass-selected nanoparticles of CuZn alloys can be used to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from CO_2 and H_2 [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8]. Finally, we shall also discuss how planar surface science can be used to identify new catalysts for ammonia oxidation. We shall demonstrate how Copper deposited on Ruthenium can enhance the activity substantially and give rational explanations for this enhancement which also can be transferred to high area catalysts used for diesel exhaust treatment [9].

References

1. S. Kuld,....... I. Chorkendorff and J. Sehested, Angew. Chemie 53 (2014) 1.

2. C. Holse,....., I. Chorkendorff,S. Helveg, J. H. Nielsen, J. Chem. Phys. 119 (2015) 2804-2812.

3. S. Kuld,..... I. Chorkendorff,J. Sehested, SCIENCE 352 (2016) 969-974.

4. F. Studt, ..., I. Chorkendorff, and J. K. Nørskov, Nature Chemistry. 6 (2014) 320.

5. J. Greeley, ... I. Chorkendorff, J. K. Nørskov, Nature Chemistry. 1 (2009) 522.

6. M. Escudero-Escribano, ..., I. Chorkendorff, SCIENCE 352 (2016) 73-76.

7. P. Hernandez-Fernandez, ... I. Chorkendorff, Nature Chemistry 6 (2014) 732-8.

8. A. Velázquez-Palenzuela,.....I. Chorkendorff, J. Catal. 328 (2015) 297-307.

9. D. Chakraborty, ..., I. Chorkendorff, Accepted Angew. Chemie. (2017).

11:40am **HC+SA+SS-ThM-12 Chemisorption and Oxidation of H_2 on $IrO_2(110)$***, **Tao Li**, Z Liang,* University of Florida, Gainesville*; M Kim, A Asthagiri,* The Ohio State University*; J Weaver,* University of Florida, Gainesville

Understanding the interactions of hydrogen with IrO_2 surfaces is central to improving applications of electrocatalysis as well as exploiting the high-reactivity of IrO_2 for promoting methane activation. In this talk, I will discuss our recent investigations of the dissociative chemisorption and oxidation of H_2 on stoichiometric and oxygen-rich $IrO_2(110)$ surfaces. We find that H_2 dissociation is highly facile on s-$IrO_2(110)$, with more than 90% of a saturated H_2 layer dissociating below 225 K during temperature-programmed reaction spectroscopy (TPRS). We observe only H_2O desorption in a broad TPRS peak from about 400 to 780 K after generating low H_2 coverages on s-$IrO_2(110)$ at about 90 K. At high H_2 coverages, we also observe small H_2 desorption peaks at 200 and 530 K which we attribute to molecular and recombinative desorption processes, respectively. We present evidence that H_2 dissociation on $IrO_2(110)$ occurs through a mechanism wherein H_2 σ-complexes adsorbed on the coordinatively-unsaturated (cus) Ir atoms serve as precursors for H_2 dissociation. We show that oxygen atoms adsorbed on the cus-Ir sites, so-called on-top O-atoms, hinder H_2 dissociation on $IrO_2(110)$, while also facilitating H_2O desorption and promoting H-atom transfer from bridging O-atoms to on-top O-atoms. I will also discuss the results of density functional theory calculations of H_2 dissociation and initial steps of H_2O formation on stoichiometric and O-rich $IrO_2(110)$.

Surface Science Division
Room 25 - Session SS+EM+HC+MI-ThM

Oxides: Structures and Reactions

Moderators: Valeria Lauter, Oak Ridge National Laboratory, Charles Sykes, Tufts University

8:00am **SS+EM+HC+MI-ThM-1 Influence of Iron Doping on Cobalt Oxide Bilayers on Au(111): Toward a Model of Synergistic Catalytic Effect in Oxygen Evolution Reaction***, **Jonathan Rodriguez-Fernandez**, Z Sun, J Fester, J Lauritsen,* Aarhus University, Denmark

Iron doped cobalt oxides have been shown enhanced activity for promoting the oxygen evolution reaction (OER) compared with unary iron oxides and cobalt oxides, respectively[1]. However, the nature of such synergistic catalytic effect and in particular the way of iron species incorporate with cobalt oxides are only understood on a superficial level, which presents a significant obstacle to further exploration on rational design of efficient OER catalysts. Noble metal supported transition metal oxides have been previously applied as model catalysts, which enables the powerful surface science techniques, and successfully reveal the catalytic active sites and help researchers understand the catalytic process further[2].

Here, aiming to study the origin of the synergistic catalytic effect, we dope iron into well-characterized cobalt oxide bilayer nanoislands supported on a single crystal Au(111) substrate[3]. Atomic-resolved scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) are used to compare the growth of cobalt oxide and cobalt-iron oxide bilayers. We perform a comprehensive analysis of the iron doping induced influence on the atomic structure of the nanoislands and oxidation states of both the dopant and host species.

We find that doped iron species integrate into the cobalt oxide nanoislands and are mostly under oxidative condition. The Co atoms surrounding the doped Fe appear brighter and form 6-fold flower-like features under STM due to the local modification of electronic structure, which indicates changed chemical activities of these atoms. Similar situation happens on O atoms near doped Fe and form 3-fold triangle-like features. XPS spectra imply that Co keeps 2+ oxidation state whereas Fe shows 3+ oxidation state, which is not the same with the oxidation state of 2+ in the iron oxide nanoislands, indicating that iron species in the cobalt-iron oxides have stronger oxidizing ability. Further water exposure experiments demonstrate that hydroxyl groups usually appear next to the doped iron sites while almost randomly distributed on the basal plane of pure cobalt oxide nanoislands, suggesting that iron species in the cobalt-iron oxide play an important role in promoting the catalytic activity.

References

1. Burke, Michaela S., et al., Journal of the American Chemical Society 137.10 (2015): 3638-3648.

2. Fester, J., et al., Nature Communications 8 (2017): 14169.

3. Walton, Alex S., et al., ACS Nano 9.3 (2015): 2445-2453.

8:20am **SS+EM+HC+MI-ThM-2 An Ordered Mixed Oxide Monolayer formed by Iron Segregation on Rutile-$TiO_2(011)$***, **Sandamali Halpegamage**,* University of South Florida*; L Bignardi, P Lacovig,* Elettra-Sincrotrone Trieste, Italy*; A Kramer,* University of South Florida*; Z Wen, X Gong,* East China University of Science and Technology, PR China*; S Lizzit,* Elettra-Sincrotrone Trieste, Italy*; M Batzill,* University of South Florida

Ternary oxide monolayers supported on or intermixed with a second oxide surface have attracted great interest in designing new materials with unique chemical functional properties including selective heterogeneous catalysts and nanocatalysts. Due to the complexity of the structure and composition, it is challenging to discover and characterize such phases. Here we synthesized an ordered mixed oxide monolayer of $FeTi_2O_5$ on rutile-$TiO_2(011)$ via two different experimental pathways; firstly, by annealing the clean $TiO_2(011)$ in $1x10^{-7}$ mbar of O_2 at ~450 ^{0}C and secondly, by physical vapor depositing Fe on clean $TiO_2(011)$ in $1x10^{-7}$ mbar of O_2 at ~450 ^{0}C.In both procedures the Fe atoms intermixe with Ti atoms in the surface layer of the substrate and form an ordered mixed-oxide monolayer with $FeTi_2O_5$ composition. High resolution and fast X-ray photoemission spectroscopy (XPS) reveals that Fe and Ti are in 2+ and 4+ charge states respectively. The structure of this mixed oxide monolayer was predicted by a combination of atomically-resolved STM (Scanning Tunneling Microscopy) and DFT-based calculations and further confirmed by synchrotron based angle scanned x-ray photoelectron diffraction (XPD) studies. Multiple electron scattering simulations implemented in the Electron Diffraction in Atomic Clusters (EDAC) package were performed for comparing experimental XPD patterns with structural models. Judged by the reliability factor (R_p), the experimentally determined XPD patterns are in good agreement with the simulated XPD patterns. The study has been extended to a few of the other transition metals namely, V, Cr, and Ni. Due to the similarities in the bulk oxide structures of these transition metals they all are capable of forming similar intermixed monolayer oxide surfaces with the composition MTi_2O_5 (M=V,Ni,Cr). For all these monolayers, the valance band maximum (VBM) is above the VBM for TiO_2, suggesting that these monolayers may trap holes at the surface efficiently and thus may modify the photocatalytic activity of TiO_2.

8:40am **SS+EM+HC+MI-ThM-3 Growth and Chemistry of rutile IrO_2 Surfaces**, ***Jason Weaver****, Z Liang, T Li, R Rai,* University of Florida, Gainesville*; M Kim, A Asthagiri,* The Ohio State University **INVITED**

Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this talk, I will discuss our recent investigations of the growth and chemical properties of rutile IrO_2 surfaces. I will discuss our studies of the oxidation of metallic Ir surfaces by O-atom beams as well as O_2 at pressures above 1 Torr. We find that stoichiometrically-terminated $IrO_2(110)$ layers could only be formed by oxidizing Ir(111) and Ir(100) at sufficiently high temperature and O_2 pressure. I will discuss the binding characteristics of small molecules, and our recent discovery of highly facile CH_4 activation on the $IrO_2(110)$ surface at temperatures as low as 150 K.

9:20am **SS+EM+HC+MI-ThM-5 Formation and Manipulation of Water Clusters on Bilayer ZnO Surface***, **Junseok Lee**, D Sorescu, X Deng,* National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the clustering behavior of water on the bilayer ZnO surface grown on Au(111) has been studied at low coverage regime. Diffusion and clustering of water molecules at specific sites in the Moire pattern are observed after initial adsorption of water on bilayer ZnO at T = 77 K. Heating the surface to T < ~240 K reveals that the adsorbed water molecules form triangular shape clusters with two specific orientations in the STM images. The DFT calculations along with the experimental findings suggest that the clusters are comprised of mixed water and hydroxyl groups with a binding energy of 21 kcal/mol. The two types of clusters can be converted to each other by the injection of electron from the STM tip. The inelastic electron scattering process is considered to be responsible for the conversion of the clusters via O-H stretch vibration mode excitation.

9:40am **SS+EM+HC+MI-ThM-6 Formation of Metastable Water Chains on Anatase $TiO_2(101)$***, **Arjun Dahal**, Z Dohnálek,* Pacific Northwest National Laboratory

The interaction of water with metal oxide surfaces is of great importance in many diverse areas such as catalysis, electrochemistry, corrosion, atmospheric science, geology, astrophysics, and others. Anatase TiO_2 surface is particularly relevant because it is the most active polymorph of TiO_2 and its commercially employed nanomaterials grow preferentially as anatase. In this study, we employ scanning tunneling microscopy (STM) to study the adsorption of water on a model stoichiometric anatase $TiO_2(101)$ surface. Well-defined anatase $TiO_2(101)$ surface has saw-tooth-like morphology exposing alternating rows of two-fold-coordinated oxygen atoms (O_{2c}) and five-fold-coordinated Ti atoms (Ti_{5c}) along the [010] direction. Our STM data show that at 80 K isolated water monomers bind molecularly to the Ti_{5c} sites. The onset of diffusion is found at ~190 K where water monomers diffuse both along and across the Ti_{5c} rows. The analysis shows that the along-the-row diffusion is energetically favored by only 0.03 eV. Surprisingly, we find that at 80 K water molecules start to form linear chains along the Ti_{5c} rows as the coverage is increased. This indicates the presence of transient mobility of water molecules suggesting that the adsorption occurs via a precursor state. When the water chains are annealed at 190 K, they fall apart to monomers that reside on the next-nearest-neighbor Ti_{5c} sites. These results demonstrate that the water chains are metastable in nature. This is at odds with many other oxide surfaces where hydrogen-bonded water clusters are energetically preferred over the isolated monomers.

11:00am **SS+EM+HC+MI-ThM-10 The Structure of $Fe_2O_3(012)$ and its Reactivity to Water***, **Gareth Parkinson**, F Kraushofer, Z Jakub, M Bichler, J Hulva, M Schmid, U Diebold, P Blaha,* TU Wien, Austria

Hematite (α-Fe_2O_3) is a promising material for technological applications due to its abundance, low cost and chemical stability. Its 2.2 eV bandgap makes it potentially ideal as a photoanode for photoelectrochemical water splitting, [1] but performance is hampered by slow reaction kinetics and the need for a significant overpotential. Little is known about the atomic-scale structure of hematite surfaces, and even less about how this relates to photocatalytic activity.

To date, most surface science studies of α-Fe_2O_3 have focused on the (001) facet, but preparing a stoichiometric surface under UHV conditions has proven problematic. Some authors have investigated the equally relevant (012) surface, [2][3][4] and reported that a (1x1) and a reduced (2x1) termination can be reversibly prepared. Several models have been proposed for the (2x1) reconstruction, but as yet no scanning probe data exists to support or refute them.

Here we present a multi-technique study of the (1x1) and (2x1) surfaces of α-Fe_2O_3 (012), as well as their interaction with water. The data acquired for the (1x1) termination support a bulk termination model, as predicted by previous publications, but STM and nc-AFM images of the (2x1) reconstruction are inconsistent with previously proposed models. [3] We propose a new model based on ordered oxygen vacancies, the plausibility of which is confirmed by density functional theory (DFT) results. TPD and XPS data reveal that the (1x1) surface adsorbs water in a mixed-mode fashion, whereas the interaction with the (2x1) surface is entirely dissociative. We propose models for the structure of the adsorbed overlayers based on scanning probe microscopy data.

References

[1] Parkinson, G. S. *Surface Science Reports* **71**, 272-365 (2016).

[2] Henderson, M. A., Joyce, S. A. & Rustad, J. R. *Surface Science* **417**, 66-81 (1998).

[3] Henderson, M. A. *Surface science* **515**, 253-262 (2002).

[4] Gautier-Soyer, M., Pollak, M., Henriot, M. & Guittet, M. *Surface science* **352**, 112-116 (1996).

11:20am **SS+EM+HC+MI-ThM-11 Interaction of Water with anatase $TiO_2(001)$-1x4***, **Igor Beinik**, K Adamsen, S Koust, J Lauritsen, S Wendt,* Aarhus University, Denmark

The interaction of water with titanium dioxide (TiO_2) is pivotal for many practical applications of this material in heterogeneous catalysis because water is almost always present either as a reactant or a product in many catalytic reactions. In our model study, we focus on the anatase polymorph of TiO_2 that has demonstrated a higher catalytic activity in water splitting than rutile and is generally considered as a more technologically relevant polymorph. The nanocrystals of anatase that are present in powder catalysts normally expose a high fraction of low surface energy (101) facets and a significantly smaller fraction of high energy, but supposedly more reactive (001) facets. The (001) facet is intrinsically unstable and reconstructs upon annealing in vacuum forming 1x4 reconstructed terraces, where rows of bridging oxygen atoms in [100] and [010] directions are replaced by TiO_3 units [1]. This kind of reconstruction has been found both on the (001) facets of anatase single crystals and nanoparticles [2], however the interaction of water with this surface has been significantly less investigated.

In the present work, we study the adsorption and dissociation of water on the anatase (001) 1x4 reconstructed surface by means of STM, TPD, and synchrotron core-level and valence band PES under UHV conditions. Our results show that water dissociates to some extent even at 120 K and that low water exposures (up to 3 L) at this temperature results in a mixture of molecularly and dissociatively adsorbed molecules. A systematic analysis of the data obtained using all three techniques leads us to a conclusion that the A-TiO2(001)-1x4 surface is rather reactive - in agreement with an earlier study [3] we find that water dissociates at the ridges of the 1x4 reconstruction. Moreover, the 1x4 reconstruction remains stable upon water exposures at least up to ~45 L (at 120 K). However, after desorption of a multilayer ice film, the ridges themselves contain a high number of defects, which remain stable up to 800 K. The nature of these defects will be discussed.

References:

1. Lazzeri, M. & Selloni, A. Phys. Rev. Lett. **87**, 266105 (2001).

2. Yuan, W. et al. Nano Letters **16**, 132–137 (2016).

3. Blomquist, J., et al. J Phys Chem C **112**, 16616–16621 (2008).

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 24 - Session HC+SS-ThA

Combined Experimental and Theoretical Explorations of the Dynamics of Heterogeneously Catalyzed Reactions

Moderator: L. Gabriela Avila-Bront, College of the Holy Cross

2:20pm **HC+SS-ThA-1 Building the World's Greatest Microscope: Revealing the Atomic Scale Dynamics of Surface Chemistry**, *A Wodtke,* Max Planck Institute for Biophysical Chemistry, Germany*; O Buenermann, H Jiang, Y Dorenkamp,* Institute for Physical Chemistry University of Goettingen, Germany*; A Kandratsenka, S Janke, **Daniel Auerbach,*** Max Planck Institute for Biophysical Chemistry, Germany **INVITED**

In 1929, Nobel Laureate Paul Dirac made comments to the effect that Chemistry had been solved. With the advent of quantum mechanics "The underlying physical laws necessary for the mathematical theory of… …the whole of chemistry are… …completely known…. However, on a practical level computational chemistry is still in an early stage of development. Dirac went on: "the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." Despite electrifying advances in computational power since that time, Dirac is still right. The theory of chemistry requires approximations before theoretical descriptions and predictions of chemical reactions can be made.

The advent of the Born-Oppenheimer Approximation led to the development of the standard model of chemical reactivity where the electronically adiabatic potential energy surface for nuclear motion is derived and quantum motion of the nuclei on that surface can be calculated. For simple gas phase reactions, this approach has become an extraordinarily useful and reliable tool. For surface chemistry, additional approximations are commonly made: 1) classical mechanics for describing nuclear motion, 2) density functional theory (usually at the generalized gradient level) for calculating electronic states, 3) reduced dimensionality approximations and as before 4) the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom. I call this collection of approximations the provisional model for surface chemistry as we in the field are still testing and improving it.

In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will describe the very significant challenges surface chemistry presents including the problems of high dimensionality and the common failure of the Born Oppenheimer approximation. I will present two concrete examples. In the first, results of a full dimensional experimentally validated theoretical approach to hydrogen atom adsorption at a metal surface that includes the effects of Born-Oppenheimer failure leads to an atomic scale view of H-atom adsorption at a noble metal as well as an explanation for chemicurrents. In the second, energy loss dynamics occurring on a 25-fs time scale can be inferred from the scattering of hydrogen atoms from a graphene surface where a transient C-H chemical bond is formed. The H interaction on graphene is strongly influenced by the choice of metal substrate upon which the graphene is grown.

3:00pm **HC+SS-ThA-3 Calibrating Electronic Structure Calculations – A Joint Experimental-Theoretical Approach***, **Arthur Utz**, E Dombrowski, E High,* Tufts University

Computational chemistry holds great promise for guiding the design of new catalytic materials, but current density functional theory (DFT) methods typically do not provide the level of absolute chemical accuracy ($\Delta E \leq 1$kcal ≈ 4 kJ/mol) required to distinguish between potential catalysts with similar activation energies, nor can they accurately predict product selectivity when the rate-limiting barriers to different reaction products are similar. Two factors are primary contributors to this shortcoming. First, the most widely used DFT functionals for reactions on metals (PBE and RPBE) are not quantitatively accurate, and are prone to systematic errors that either over- or underestimate barrier heights. Second, few experimental measurements provide accurate and unambiguous benchmarks for testing DFT predictions.

In this contribution, we will describe recent results from a joint experimental-computational study to address these limitations. We performed conventional and internal state-resolved beam-surface reactivity measurements for tri-deutero methane (CHD_3) molecules incident on a clean Ni(111) surface to obtain robust benchmark data for comparison with theory. Our collaborators in the Kroes group at Leiden University then used these data to "calibrate" a hybrid functional based on a linear combination of PBE and RPBE functionals via the specific reaction parameter density functional theory (SRP-DFT) approach. *Ab initio* molecular dynamics (MD) calculations using the SRP-DFT functional yielded predictions of initial reaction probability, S_0 as a function of incident translational energy, E_{trans}, for comparison with experiment.

We used measurements of S_0 for CHD_3 molecules predominantly in their vibrational ground state (v=0) and incident at the lowest incident translational energy (E_{trans}) studied to constrain the define the SRP-DFT functional. We then used that functional, without further modification, to predict the reactivity of a thermal ensemble of CHD_3 molecules whose reactivity was dominated by C-D stretching and bending vibrations, as well as of the laser excited C-H stretching states, over a wide range of E_{trans}. We found that despite the significant difference in energy distribution within these three ensembles of molecules, the single SRP-DFT functional yielded chemically accurate predictions of reactivity. The presentation will outline our approach and results on this system, as well as more recent work exploring the generality of this approach to other chemical systems and surface structures.

3:20pm **HC+SS-ThA-4 CO_2, CO and H_2O on Copper Surfaces: A HPXPS Study Supported by DFT Calculations**, *A Regoutz, G Kerherve, J Kahk, J Lischner, **David Payne**,* Imperial College London, UK

CO_2 is a source for the production of carbon based fuels, including methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of CO_2, as it is able to direct reactions through stable intermediates, e.g. CO. For example important questions concern the influence of oxygen on the catalytic activity and whether oxides are formed on the surface, and the role of H_2O and CO (as co-adsorbents) during exposure to CO_2. As copper-based systems are an excellent material for the reduction of CO_2 a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in solid-state science but due to its nature as an ultra high vacuum technique (pressure 10^{-10} mbar) it is not possible to study more realistic gas-solid interfaces. High-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar [1]. Over the last few years, this technique has been applied to understanding the chemistry of CO_2 (and mixtures of gases) on copper surfaces [2-4] leading to a number of surface mechanisms being postulated.

This work presents results on the interaction of CO_2 with a variety of Cu surfaces (polycrystalline and single-crystals) by HPXPS. In contrast to previously published work, these experiments are supported by state-of-the-art density functional theory calculations, in an effort to enable accurate determinations of the binding energies of the various surface-bound species present during reaction.

It is hoped that the presented results provide a starting point for the detailed understanding of these copper surfaces, using HPXPS in conjunction with theory, and lead to the identification unknown phenomena.

[1] G. Kerherve, D.J. Payne et al., Rev. Sci. Instrum., **88** 033102 (2017)

[2] T. Koitaya at al. Topics in Catalysis, **59** 526 (2016)

[3] B. Eren et al. J. Am. Chem. Soc., **138**, 8207 (2016)

[4] X. Deng et al., Langmuir, **24**, 9474 (2008)

4:00pm **HC+SS-ThA-6 Dissociative Adsorption of Methane on Transition Metal Surfaces and Supported Atoms from First Principles Calculations**, ***Heriberto Fabio Busnengo***, CONICET and Universidad Nacional de Rosario, Argentina **INVITED**

The study of dissociative adsorption of methane on transition-metal surfaces and transition-metal atoms deposited on oxide surfaces is of great importance to understand the reaction mechanisms governing the catalytic steam reforming process used to produce molecular hydrogen. In particular, the understanding of the origin of the role of surface temperature, surface defects involving reduced coordination metal atoms, and possible effects of the oxide support have significantly increased during the last years thanks to both, experiments and first principles calculations.

In this talk we will describe and discuss some of these recent advances by focusing on theoretical developments allowing us today, to model with unprecedented accuracy the interaction of methane with transition metal atoms under ultra high vacuum conditions and in particular, molecular beam experiments. This has been possible in part, thanks to the increase of processing power of modern computers, to methodological developments allowing to describe quantum mechanically the molecule-surface interaction dynamics, and new methods to accurately represent full dimensional interaction potentials from first principles calculations.

4:40pm **HC+SS-ThA-8 Methane Steam Reforming: Using External Electric Fields to Enhance the Catalytic Performance of Ni-based Catalysts***, **Fanglin Che**,* University of Toronto, Canada*; J Gray, S Ha, J McEwen,* Washington State University

According to the Annual Energy Outlook, natural gas production in the U.S. is projected to continue rising through 2040. To make the most of this abundant natural resource and at the same time reduce emissions of harmful greenhouse gases it is imperative that we fully understand the catalytic reactions which are used in methane processing – particularly methane steam reforming (MSR). MSR is our reaction of interest also because the conversion of methane to syngas greatly affects the charge-transfer chemistry and consequently influences the SOFCs' performance. There are two significant issues facing MSR: (i) Coke formation; (ii) High temperatures of above 900 K. To address these issues, we are interested in the effect of an electric field on this process. [1,2]

Based on a field-dependent microkinetic model of the MSR reaction and corresponding experimental evidence, we find that a positive electric field can significantly enhance the methane conversion and reduce the formation of coke over a pure Ni surface. [3-8] The reason for such an improvement can be correlated with the fact that a positive field polarizes the Ni surface with a partial positive charge, which assists the first C-H bond cleavage of a methane molecule. [9] Changing the oxygen vacancy concentration and increasing the applied electric field value affects the charge of the Ni cluster in a Ni/YSZ cermet as well. Interestingly, we find that the C-H bond cleavage of methane becomes more favorable as the Ni cluster becomes more positively charged. We also find that the carbon complex resulting from the dissociation of a CH molecule at the triple phase boundary region of a Ni/YSZ cermet results in a more positively charged Ni cluster, which facilitates the cleavage of the first C-H bond in methane as compared to when the carbon complex is absent. This indicates that the initial carbon species resulting from the decomposition of methane assists in the first C-H bond cleavage of a methane molecule rather than the formation of coke that poisons the Ni-based catalyst. Overall, this work provides valuable information for a new design of electrochemical systems to enhance methane activation.

[1] Stüve, E. M. *Chem. Phys. Lett.***2012,***519*, 1.

[2] Kreuzer, H. J. *Surf. Sci. Anal.***2004,***36*, 372.

[3] Che, F. et al., *Catal. Sci. Technol.***2014,** 4020.

[4] Che, F. et al., *Phys. Chem. Chem. Phys.***2014,***16*, 2399.

[5] Che, F. et al., *J. Catal.***2015,***332*, 187.

[6] Che, F. et al., *Appl. Catal. B***2016,***195*, 77.

[7] Che, F. et al., *ACS Catal.***2017,***7*, 551.

[8] Che, F. et al., *ACS Catal.***2017,***under review*.

[9] Che, F. et al., *Angew. Chem. Int. Ed.***2017,***129*, 3611.

5:00pm **HC+SS-ThA-9 Mullite Support Boosts Active Oxygen Atoms for Enhanced Platinum Sub-nanometer Clusters Catalysis***, **Xiao Liu**, J Cai, B Shan, R Chen,* Huazhong University of Science and Technology, China

Platinum (Pt) catalysts have been widely utilized in catalysis due to their excellent catalytic activity, such as CO oxidation, water-shift gas reaction and preferential CO oxidation in hydrogen. As the high cost and large demand of Pt, the improvement of its catalytic efficiency has attracted great attention to reduce its loading. Since catalytic reactions usually happen on surface, the decreasing of Pt catalyst's size to increase the fraction of exposed atoms is a widely accepted strategy to try to utilize each Pt atom. However, the low temperature activities of the Pt sub-nanometer clusters and single atoms have been greatly limited due to the seriously CO poison effect, which prevents the supplying of active oxygen. Therefore, searching new approaches to supply active oxygen atoms at low temperature is important to enhance the activity and efficiency of Pt catalysts. In this work, the density functional theory (DFT) calculations shows that the designed Pt cluster supported on $SmMn_2O_5$ mullite structure exhibits high activity for O2 dissociation than pure $SmMn_2O_5$ surface. Inspired by the theoretical results, we have prepared uniform and high dispersed sub-nanometer Pt clusters on $SmMn_2O_5$ supports ($Pt_n/SmMn_2O_5$) via atomic layer deposition method. The interfacial structure of $Pt_n/SmMn_2O_5$ characterized by high-resolution transmission electron microscopy agrees well with our designed model. The as-prepared $Pt_n/SmMn_2O_5$ catalyst has shown outstanding room temperature CO oxidation activity and low apparent activation energy, which could result from the strong interfacial interactions as indicated by the X-ray photoelectron spectra and X-ray absorption fine structure results. The *in-situ* diffuse reflectance infrared Fourier transform spectroscopy, ^{18}O isotope-labelling experiments and DFT calculations shows that the active oxygen supplied by the $SmMn_2O_5$ surface is critical to the room temperature CO oxidation activity.

5:20pm **HC+SS-ThA-10 Calorimetric Energies of Small Adsorbates on Ni(111) and NiO(111) Surfaces, with Comparison to Pt(111) to Explain Differences in Catalytic Activity between Ni vs Pt***, **Wei Zhao**, S Carey, Z Mao, S Morgan, C Campbell,* University of Washington

Catalysts based on nickel and nickel oxides are of great importance in chemical industry, such as methane steam reforming and biomass conversions. We present here calorimetric measurements of the energies of several catalytically relevant adsorbed intermediates on Ni(111), including methyl, bidentate formate, H_2O, benzene and phenol, and also the enthalpies of H_2O and HCOOH dissociative adsorption on NiO(111). We will also give an extensive comparison of these energies on Ni(111) to previous calorimetric measurements on Pt(111), providing the insight into the catalytic properties and reaction efficiency for these two metals. Besides the crucial importance of these measured energies for understanding related catalytic relations, they also provide important experimental benchmarks that can be used to improve the accuracy of the related quantum mechanical calculations.

5:40pm **HC+SS-ThA-11 Defect Formation on MoS_2 via Methanol to Methoxy Conversion***, **Prescott Evans**, H Jeong, S Beniwal, P Dowben,* University of Nebraska - Lincoln*; D Le, T Rahman,* University of Central Florida

Coverage dependent defect formation, via methanol adsorption on MoS_2 and conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission and modeled by density functional theory (DFT). The adsorption of methanol on MoS_2 at 110 K followed by annealing of the sample near 350 K or the adsorption of methanol on MoS_2 at 350 K results in the formation of numerous point defects at the surface of the MoS_2 substrate. Larger multi-point defects, nominally ~1 nm in size as well as line defects on the MoS_2 sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of MoS_2 to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and the significant shifts in oxygen binding energies. The experimental results indicate a small but persistent activation energy for the reaction. The energy favorability of the combination of defect creation and methoxy formation is also suggested by density functional theory. A strongly bound methanol surface species is not favored on the defect free MoS_2 surface.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room Central Hall - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Poster Session

HC-ThP-2 Auger Electron Spectroscopy Analysis of Fresh and Aged Alumina Supported Ag Catalysts*, **Dennis Paul**, J Newman,* Physical Electronics*; W Suchanek,* Scientific Design Company, Inc.

Auger Electron Spectroscopy is a well known surface analysis method optimized for characterization of very small features. The technique has an inherent depth of analysis of ~5 nm and can provide analysis of features as small as ~20 nm. While Auger works well on conducting and semiconducting materials, it is much more challenging to analyze insulating samples due to uncompensated charge buildup that occurs during electron bombardment. Thus, for catalyst analysis on insulating supports (typically metal oxides) Auger can be extremely difficult. However, with careful sample preparation and appropriate Auger operating conditions, excellent data can still be obtained from these challenging materials.

In this investigation Auger elemental mapping and small area spectroscopy were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. The results show that while the size of the alumina support particles remains roughly the same during extended use, the Ag catalyst morphology has changed dramatically with the particle size increasing by over an order of magnitude. Conversely, the Cs Auger maps from the Fresh and Aged catalysts show that this constituent remains dispersed across the alumina support during the aging process.

HC-ThP-3 CO Adsorption on Size-selected Pt$_n$ Clusters Uniformly-Deposited on Al_2O_3/NiAl(110)*, **Yoshihide Watanabe**, A Beniya,* Toyota Central R&D Labs. Inc., Japan

Size-selected metal clusters on oxide surfaces are a subject of considerable interest because of their distinctive size-dependent catalytic properties. The most precise approach to prepare a model catalyst is deposition of size-selected clusters using a mass-filtered cluster ion beam. It is important to prepare a uniformly deposited surface and avoid cluster-aggregations for investigation of size-dependent catalytic activity.

Pt clusters produced using a DC magnetron-sputtering source were mass-selected using a quadrupole mass filter. The parallel plate deflectors were placed to scan the cluster ion beam. When two sine voltage waveforms are applied to the orthogonal deflectors, the ion trajectory on the surface produces a Lissajous pattern. The ion trajectory fills the sample surface uniformly with an irrational frequency ratio. The advantages of this method are simplicity and low cost of setup compared with raster scanning method.

In this study, size-selected Pt clusters were deposited uniformly on surfaces by scanning the cluster ions in the form of Lissajous pattern. We confirmed that size-selected clusters can be deposited uniformly on a surface by Pt 4f intensity mapping. A uniform cluster distribution was also confirmed using a scanning tunneling microscope.

In high-density condition, the Pt clusters deposited without Lissajous scan could aggregate and form different size clusters. Cluster aggregation probability depends on the deposited density. The isolated Pt$_n$ clusters and their aggregates were estimated to be distributed with position-dependence. At 0.1 ML of total coverage, 33% of the clusters coalesce to form larger clusters. This result indicates that the coverage needs to be low enough to neglect the cluster aggregation effect.

The adsorption states of CO molecules on size-selected Pt$_n$ (n = 7, 15, 20) clusters deposited on the Al_2O_3/NiAl(110) surface were also investigated with and without a Lissajous scan. Two peaks at 2020 and 2040 cm^{-1} are observed in infrared reflection absorption spectroscopy (IRAS) spectra of adsorbed ^{13}CO at saturation coverage. These peaks are assigned to adsorbed CO at the on-top site of slightly cationic Pt atoms interacting with substrate oxygen atoms (2040 cm^{-1}), and of neutral Pt atoms bound by the Pt–Pt bond (2020 cm^{-1}). Temperature programed desorption (TPD) spectra of saturated ^{13}CO were also investigated. Combining the IRAS and TPD results, we determined that CO molecules bind to slightly cationic Pt atoms with an adsorption energy of 0.7–1.0 eV, and bind to neutral Pt atoms with an adsorption energy of 1.4 eV.

HC-ThP-4 Unexpected Formation of Catalytically Active Palladium Nanoparticles on Silica Surface in Organic Solvents*, **Megan Bornstein**, A Quast, R Park, J Shumaker-Parry, I Zharov,* University of Utah

Supported palladium nanoparticles (PdNPs) have been found to be active catalysts for a variety of organic transformations, with more recent reports showing PdNPs can catalyze chemoselective hydrogenation, as well as the photocatalytic activity of PdNPs can be enhanced plasmonically. Having a method to reliably synthesize small PdNPs on inorganic supports is useful, and we will report on the formation of PdNPs on silica nanospheres in organic solvents, which can be used as a convenient method of PdNPs preparation.

While attempting to immobilize Pd^{2+} ions on ligand-modified silica nanospheres, we observed the formation of small (~5 nm) uniform PdNPs. The only reactants in this process were surface-functionalized silica spheres, $Pd(OAc)_2$, and reagent-grade acetone. This suggests that an impurity in the acetone is responsible for the reduction of Pd^{2+} to Pd^0. We obtained similar PdNPs when using high purity acetone containing a small amount of added ethanol, while no PdNPs formation was observed in acetonitrile. Thus, this suggests that PdNPs is due to the presence of reducing organic compounds, such as alcohols.

The oxidation state of palladium was confirmed using X-ray photoelectron spectroscopy (XPS), and the morphology of the particles was analyzed using Scanning Transmission Electron Microscopy (STEM). The PdNPs formed were very small, typically around 5 nm in diameter when the reaction was done at room temperature, and uniformly distributed on the surface of a silica support that had been functionalized with primary amines or BiPy ligands, which provide stabilization for the PdNPs. For reactions run at 40 °C, the average diameter of the PdNPs was larger than those run at -77 °C or room temperature. The materials synthesized were capable of catalyzing the reduction of 4-nitrophenol to 4-aminophenol and the oxidation of benzyl alcohol to benzaldehyde.

HC-ThP-5 Copper Activated Conversion of Ethanol to Higher Alcohols over Hydrotalcite Derived MgAl Mixed Oxides*, **Karthikeyan K. Ramasamy**, M Guo, M Gray, S Subramaniam,* Pacific Northwest National Laboratory*; A Karakoti,* Ahmedabad University, India*; V Murugesan, V Shutthanandan,* Pacific Northwest National Laboratory*; S Thevuthasan,* Pacific Northwest National Laboratory, Qatar

Unique physical and chemical properties of layered double hydroxide, hydrotalcite (HT) ($[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}x/n{\cdot}mH_2O$), derived materials have been used for selective and efficient transformations of organic compounds to higher value products. The catalytic properties of the HT derived mixed oxide material are a function of the morphology, local structure and oxidation state of the participating cations. In this work the effect of addition of copper ions on the catalytic properties of MgAl HT derived materials were studied for selective conversion of ethanol to higher alcohols. The ethanol to higher alcohol conversion goes thru a series of complex intermediate steps. The addition of copper is expected to promote the catalytic dehydrogenation of alcohols to aldehydes which is the first step in the complex cascade reaction and considered as the rate determining step in the overall chemistry. Various concentration of copper loading were attempted from 0 wt% to 6 wt % using different synthesis strategies in an attempt to achieve a homogenous dispersion of copper in the MgAl matrix. The selectivity and efficiency of copper substituted catalysts were analyzed by conversion of ethanol to higher alcohols in an indigenously designed plug flow reactor. Resulting physical and chemical changes in copper substituted catalysts were studied before and after the catalytic reaction using high resolution transmission electron microscopy, x-ray diffraction, x-ray absorption, X-ray photoelectron spectroscopy and nuclear magnetic resonance measurements. It was observed that different oxidation states of copper and the extent of dispersion of copper in the HT matrix influences catalytic efficiency and selectivity of the process by promoting various side reactions. Synthesis of copper substituted HT derived mixed oxide catalyst plays a major role in controlling the dispersion of the copper in the matrix. Fundamental challenges in achieving higher copper substitution without observing significant clustering and aggregation effects will be discussed in context of catalytic selectivity and efficiency.

HC-ThP-6 Methane Dissociation on Ni(111) at High Surface Temperatures: The Observed role of Surface and Subsurface C on Reactivity*, **Eric Dombrowski**, E High, A Utz,* Tufts University

Steam reforming methane over a Ni catalyst is the chief industrial process for H_2 gas production, and activation of methane's C-H bond to form surface-bound CH_3 and H is rate limiting. Conventional and vibrational state-selected molecular beam studies have highlighted the importance of translational (E_{trans}) and vibrational (E_{vib}) energy in promoting this rate limiting step on clean, well-ordered Ni single crystal surfaces. Nearly all of these studies have been performed at low to moderate surface temperatures (T_{surf}< 700K), where carbonaceous reaction products remain bound to the surface throughout the measurement.

Here, we describe experiments that extend these state-resolved measurements to the high surface temperatures typically used in the steam reforming process. Under these conditions,the methyl product promptly dehydrogenates to form surface-bound C and H, and H atoms recombinatively desorb, leaving C on the surface. The remaining carbon can dissolve into the nickel subsurface or bulk during the molecular beam dose, with a T_{surf}-dependent dissolution rate. We measured methane uptake onto, and into, a Ni(111) single crystal *in situ* across a range of surface temperatures from T_{surf} = 680 – 850 K. We varied incident translational energies and incident methane flux, and measured S(θ) for both laser-off and state resolved (v=1, ν_3 antisymmetric C-H stretch) methane. A unique molecular beam reflectivity method allowed us to quantify the initial S_0 as well as S(t) in real time during the dose. Integrating S(t) yielded the integrated amount of C deposited during the dose, (θ) and allowed us to calculate S(θ).

Over the T_{surf} range studied, we observed drastic differences in carbon dissolution during deposition. At T_{surf} = 680K, carbon uptake into the nickel lattice was minimal and about 0.5 ML of C was deposited before the surface became deactivated due to site-blocking. This situation changed dramatically at temperatures above T_{surf} = 750 K. At intermediate temperatures, we observed an induction period prior to the onset of site blocking and surface passivation, and, at T_{surf} = 850 K, deposition of more than 50 ML of C did not completely passivate the surface. Furthermore, we observed that under some conditions, S(θ) *increased* with increasing C concentration beneath the surface. A simple two-step dissolution process that includes T-dependent rate constants for C transport between the surface, subsurface, and bulk qualitatively describes our data. We will also describe our most recent efforts to refine this model to more quantitatively describe our experimental measurements to better understand the role of dissolved C on methane activation.

Surface Science Division
Room 24 - Session SS+HC-FrM

Recent Advances in the Chemistry and Physics of Interfaces

Moderators: Robert Bartynski, Rutgers University, Wei Zhao, University of Washington

8:40am **SS+HC-FrM-2 Enantiospecific Chemistry of Aspartic acid on Copper Surfaces***, **Soham Dutta**,* Carnegie Mellon University*; A Gellman,* Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

Chirality is a geometric property and refers to existence of handedness in any system. While chirality is ubiquitous in nature across all spatial scales, chirality at the molecular level is of special interest given the homochirality of biomolecules such as DNA and the amino acids that are the molecular basis of life. Increasingly, fundamental research is focused on studying chiral molecules adsorbed on surfaces given their applications in enantioselective chemical phenomena such as heterogeneous catalysis. While many examples of 2D chiral assembly of molecules have been studied over the years, fundamental questions about chiral aggregation on surfaces remain unanswered. One such question is whether enantiomers deposited on a surface aggregate into domains containing enantiomers of the same chirality (homochiral) or domains containing both enantiomers (heterochiral).

In this study, we have used a combination of Temperature Programmed Reaction Spectroscopy (TPRS) and isotopic labelling to study the decomposition kinetics and aggregation behavior of aspartic acid (Asp) enantiomers on Cu surfaces. The ionization state of adsorbed Asp monolayer was determined to be anionic using X-ray photoelectron spectroscopy. Next, using isotopic labelling, we have identified Asp decomposition mechanism in greater detail than possible for any comparable size adsorbate on a metal surface. It was found that Asp follows a multi-step decomposition process to form CO_2 and acetonitrile. Then, the first observed enantiospecific decomposition of Asp enantiomers is reported on naturally chiral $Cu(643)^{R\&S}$. Lastly, equilibrium adsorption experiments of Asp enantiomer mixtures on copper surfaces were performed and Asp enantiomers was found to aggregate on the surface. A cluster-adsorption model was developed to quantify the free energy change and equilibrium constants of enantiomer aggregation in 2D for the first time.

The combination of a surface explosion pathway with a naturally chiral catalytic surface leads to high enantiospecificity of Asp decomposition. This non-linear explosive decomposition pathway, coupled with the availability of multiple isotopomers is exploited to quantitatively probe aggregation behavior of aspartic acid with unprecedented detail.

9:00am **SS+HC-FrM-3 Anchoring Carbon Nanotubes to Solid Supports via Direct Attachment Through the Cage***, **Mackenzie Williams**[1], F Gao,* University of Delaware*; I Ben Dhiab,* Université Pierre et Marie Curie*; A Teplyakov,* University of Delaware

The unique physical, optical, and electronic properties of carbon nanotubes (CNTs) have resulted in their integration into devices for a myriad of applications. For this reason, a great number of studies have focused on the many existing methods of chemical attachment of these structures to various support materials. Carbon nanotubes are typically anchored onto these substrates through additional functional groups, such as carboxylic acids, that are present on the CNT edge or defect sites. This typically results in vertical orientation of the CNTs on the surface and the extra linkages of these functional groups may affect the electronic transfer processes through the structure. This may be desired in some cases; however in others, it is preferable to increase the surface contact between CNT and substrate or to preserve the original electronic structure of the CNTs. To this end, we have focused our efforts on direct attachment of CNTs to surfaces. The work described here finds that these extra functional groups on the CNTs are not the only way through which CNTs can bind covalently to a substrate. In fact, the presence of functional groups is not necessary at all for covalent attachment to the surface to occur. Carbon nanotubes containing no additional functional groups were attached to amine-modified gold and silicon substrates directly through the cage structure, similarly to direct attachment that has been found to occur through other caged structures such as C_{60} buckyballs. Microscopy techniques were used to confirm the presence of CNTs in intimate contact with the surface and X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry were used to investigate the chemistry involved. Through comparison to multiple controls, including carboxylic acid-modified CNTs, it was determined that covalent attachment can occur directly through the cage of the CNT. Density functional theory computational methods were used to predict core level binding energies and to confirm the feasibility of this process.

9:20am **SS+HC-FrM-4 Studying Trends in Aromatic Adsorption on Fe{110} using Density Functional Theory Calculations***, **Bianca Provost**,* University of Cambridge, UK*; M Ho, T Hughes,* Schlumberger Gould Research, UK*; J Goodman, S Jenkins,* University of Cambridge, UK

Aromatic adsorption on metal surfaces plays a key role in many fields including heterogeneous catalysis, electrochemical devices, photovoltaics, corrosion protection and chemical sensing. Benzene and to a lesser extent larger aromatic systems have been studied on a variety of metal surfaces both computationally and experimentally.[1-3] However, one metal surface which has received very little attention for aromatic adsorption is iron. Experimental UHV adsorption studies carried out on iron surfaces are complicated by the metal's reactivity and strong tendency to passivate, which result in significant difficulty obtaining a high purity metal surface. Still, iron is deserving of study as it is the major component of steel and catalyses important industrial reactions such as the Fischer-Tropsch and Haber processes. A computational study of the surface chemistry of aromatic molecules on iron will provide novel insight on these systems as well as a level of detail which would not be afforded using experimental techniques.

We have carried out a density functional theory (DFT) study of benzene, naphthalene and quinolinium adsorption on the most stable and therefore predominantly exposed surface facet of a bcc iron crystal, Fe{110}. All identified stable adsorption sites are presented and the most energetically favourable sites are compared across all three studied adsorbate-surface systems. To support the energetic and geometric results of our study, charge density differences, residual spin densities, density of states (DOS) and work function changes have also been calculated and analysed. Finally, we have studied the effect of van der Waals corrected DFT on binding site energetics and geometries. Such corrections have been shown to provide results in better agreement with experiment for aromatic adsorption on certain metal surfaces.[1]

[1] Carrasco, J., Liu, W., Michaelides, A., Tkatchenko, A. *J. Chem. Phys.* **2014**, 140, 084704

[2] Jenkins, S. J. *Proc. R. Soc. A* **2009**, 465(2110), 2949-2976

[3] Netzer, F. P. *Langmuir* **1991**, 7(11), 2544-2547

9:40am **SS+HC-FrM-5 Surface Heterogeneity and Inhomogeneous Broadening of Vibrational Line Profiles***, S Taj, D Baird, A Rosu-Finsen, **Martin McCoustra**,* Heriot-Watt University, UK

The surface heterogeneity of amorphous silica (aSiO2) has been probed using coverage dependent temperature programmed desorption (TPD) of a simple probe molecule, carbon monoxide (CO). As a proof-of-principle, the resulting distribution of interaction energies is the foundation from which an environmentally broadened vibrational line profile synthesis has been undertaken. These simulations are compared with measured line profiles recorded at 0.1 $cm^{-}1$ resolution using reflection–absorption infrared spectroscopy (RAIRS). Additional demonstrations of this methodology on solid water and methanol surfaces will be reported.

10:20am **SS+HC-FrM-7 Ab-Initio Study of Low Index Surface Planes of γ-Al2O3 and their Interface with Pt**, ***Kofi Oware Sarfo***, *A Clauser, Z McClure, M Santala,* Oregon State University*; L Árnadóttir,* Oregon State University

Metal/metal oxide interfaces are important because of their substantial impact on the composite properties of materials in a vast range of scientific and technological applications. Historically, metal oxides have been used as thermal barriers to protect metals from thermal degeneration in high temperature environments. Metal/oxide interfaces are important in applications such as protective coatings for metal medical implants, in electronic devices, and in heterogeneous catalysis mostly as catalyst support. γ-Al2O3 is a common catalyst support due to its high surface area, which enables fine dispersal of metal catalysts, such as Pt, Pd, Ru, and Rh. The structure and metal/metal oxide interactions at the interface of these materials can significantly impact the electronic and mechanical properties of the catalyst and the support. In this work, we combine theoretical and experimental approaches to study the nature of the metal/metal oxide interface between γ-Al2O3 and Pt. The theoretical approach utilized density functional theory (DFT) to study the structure and atomistic

---

[1] **National Student Award Finalist**

interactions at the interface. To determine the effect of the environment on the stability of different surface termination, we calculate the surface energy of three different low index planes and possible terminations of γ-Al2O3 as a function of partial pressures of oxygen at the experimental fabrication temperature (1100K). The (100) surface plane of γ-Al2O3 was found to be most stable and the (111) surface plane had the highest surface energy corresponding to lowest stability due to its highly polar structure. The stoichiometric terminations were found to be the most stable for the (100) and (110) planes at all partial pressures of oxygen, while the most stable termination of the (111) plane transitions from the stoichiometric surface to an oxygen rich surface termination at higher partial pressures of oxygen. This provides the basis for the experimental study of the atomic structure of the interface between γ-Al2O3 and Pt nanoparticles.

11:00am **SS+HC-FrM-9 Ambient STM Study of Sequentially Adsorbed Octanethiol and Biphenylthiol Monolayers on Au(111)***, **Gaby Avila-Bront**,* College of the Holy Cross

The mixed monolayers of biphenyl-4-thiol (BPT) and octanethiol (OT) are studied at the molecular level using

scanning tunneling microscopy (STM) in ambient conditions and X-ray photoelectron spectroscopy (XPS) on

Au(111). The effect of both the sequence of deposition, and the concentration of the BPT solution used is

investigated. We observe signs of coexisting domains in the form of disordered patches surrounding flat patches

when a 100 µM solution of BPT is used. This observation holds for both OT being deposited first, and BPT being

deposited first. The most clear formation of coexisting domains occurs when an OT monolayer is immersed in a

100 µM solution of BPT. The XP spectra reveal a shift in the C 1s signal of the monolayers that is unique to what

films are deposited on the surface. These data demonstrate the importance characterizing mixed self-assembled

monolayers that form final monolayer structures unique to each mixture.

11:20am **SS+HC-FrM-10 Molecule Assembly Structure and Tilt Geometry Evaluation of 5,6,7-Trithiapentacene-13-one (TTPO) / Pentacene-Quinone on Au(111) with NC-AFM***, A Larson,* University of New Hampshire*; P Zahl,* Brookhaven National Laboratory*; **Karsten Pohl**,* University of New Hampshire

Using non-contact atomic force microscopy (NC-AFM) the 3D molecular structure, tilt and assembly details of a new pentacene-based organic semiconductor, 5,6,7-trithiapentacene-13-one (TTPO) adsorbed on Au(111) were determined. 3D AFM force maps of individually resolved molecular orbitals were acquired to visualize the complete adsorption structure.

Robust, thermally stable, and highly inert to photo-oxidation, TTPO is a very promising organic semiconductor. Simple to synthesize and purify, TTPO readily crystallizes and is indefinitely stable against degradation in acid-free solution. TTPO has a high molar absorptivity, optical and electrochemical HOMO−LUMO gaps of 1.90 and 1.71 eV, respectively. Melting in air from 386−388°C without decomposition, TTPO can be thermally evaporated to produce highly uniform thin films. TTPO has the potential to be used in thin-film electronic devices that require operation over a wide range of temperatures such as transistors, switches, sensors, and solar cells. When adsorbed on a gold electrode, initial scanning tunneling microscopy (STM) experiments and first-principle computation reveal a novel 3-D angular assembly of the TTPO molecules, with the long axis of the molecule parallel to the gold surface, distinctive from any previously observed pentacene and pentacene derivative assemblies. Structures assembled are angularly dependent on TTPO molecular interactions, while commensurate with the underlying gold substrate, allowing for potential tailoring of pi-molecular orbital overlap through tilt-angle control. Understanding of the structure of these novel organic-metallic interfaces will guide nanoscale modifications for improved electrical transport and energy-conversion efficiency in future devices.

Single molecule STM images are input for DFT calculations to model the most-probable adsorption structure, in particular the molecular tilt-angle. NC-AFM, in contrast, is potentially the only technique capable of directly resolving the 3D angular arrangement of the individual adsorbed molecule. Indeed, by evaluating consecutively acquired constant height force maps, we were able to directly measure the 3D structure and tilt of small TTPO and Pentacene-Quinone byproduct assemblies on Au (111). Using GXSM-3, a new constant height mode “fuzzy-regulation” with current based compliance setting was used to scan a wider range of height’s otherwise not possible without losing the CO terminated tip molecule. Comparing 3D AFM force maps with a mechanical probe particle based simulation the molecule tilt was evaluated to 11±1°.

Author Index

Bold page numbers indicate presenter

Author Index