Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A212 - Session HC+SS-MoM

Utilization of Theoretical Models, Machine Learning, and Artificial Intelligence for Heterogeneously-Catalyzed Reactions

Moderators: Liney Arnadottir, Oregon State University, Sharani Roy, University of Tennessee Knoxville

8:40am HC+SS-MoM-2 Theoretical Study of Acetic Acid Decomposition on Pd (111) using Density Functional Theory, *Kingsley Chukwu, L Arnadottir,* Oregon State University

Acetic acid decomposition on Pd (111) and the effects of water on the decomposition are good model systems for the study of solvent effects on small oxygenates. Numerous studies have found that solvents influence the selectivity and rate of heterogenous catalytic reactions, so fundamental understanding of how water affects OC-O, C-OH, CO-H, C-H and C-C bond cleavages will give us valuable insight into how water influences selectivity of oxygenates decomposition, further enabling bottom up design of effective catalyst and catalyst system. Here we present density functional theory calculations of the decomposition of acetic acid on Pd (111) and the effects of water on the reaction mechanism. Our results suggest that the most favorable decarboxylation (DCX) and decarbonylation (DCN) mechanisms in vacuum proceed through dehydrogenation of acetic acid (CH_3COOH) to acetate (CH_3COO), followed by dehydrogenation of CH_3COO to CH_2COO. The competition between the most favorable DCN and DCX pathway depends on two endothermic elementary steps, the deoxygenation of CH_2COO to ketene (CH_2CO) and dehydrogenation of the carboxylmethylidene (CH_2COO) to carboxylmethylidyne (CHCOO). Water can affect the different elementary steps by changing the stability of the initial, transition and/or final state or by providing new reaction paths such as through hydrogen shuttling, which can lead to changes in the selectivity of a complex reaction network as presented herein. Here we will discuss how water influences different critical reaction steps and how that effects the overall reaction network.

9:00am HC+SS-MoM-3 Towards a Chemically Accurate Description of Reactions of Molecules with Transition Metal Surfaces, *Geert-Jan Kroes,* Leiden University, Netherlands **INVITED**

Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. Unfortunately, currently no first principles methods can be relied upon to deliver the required accuracy. To solve this problem, in 2009 we came up with a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). This allowed us to reproduce experiments for H_2 reacting on copper surfaces, and to determine barrier heights for H_2-Cu systems, with chemical accuracy. The original procedure used was not extendable to reactions of molecules heavier than H_2 with surfaces, because the metal surface was treated as static. This problem has been solved by combining SRP-DFT with Ab Initio Molecular Dynamics (AIMD). This method was applied to the dissociative chemisorption of methane on a Ni surface, a rate-limiting step in the steam reforming reaction. We were able to reproduce experiments on CHD_3 + Ni(111) with chemical accuracy, and have predicted a value of the reaction barrier height that we claim to be chemically accurate. We have new results for CHD_3 + Pt(111) that are even better, and which show that the SRP density functional for methane interacting with Ni(111) is transferable to methane interacting with another group X metal surface, i.e., Pt(111). Even more interestingly for applications to catalysis, the SRP functional derived for methane reacting with Ni(111) also gives a very accurate description of molecular beam sticking experiments on CHD_3 + Pt(211). Finally, thanks to a collaboration with Jörg Behler (University of Göttingen) we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons, for polyatomic molecules interacting with metals. This has enabled us to compute statistically accurate reaction probabilities for highly activated reactions not open to investigation with AIMD, for which reaction probabilities are less than 0.01.

9:40am HC+SS-MoM-5 The Apparent Activation Energy for Complex Mechanisms: A Simple Relationship via Degrees of Rate Control, *Zhongtian Mao[1][2], C Campbell,* University of Washington

Reactions on surface usually consists of several elementary steps. It is known that the observed reaction kinetics often represents a composite of the contribution from each of these elementary steps. The "rate-determining step" (RDS) assumption is a common approach for dealing with multistep mechanisms, where a single step is assumed to dominate the reaction kinetic behaviors and the kinetic parameters of this RDS (e.g., net rate, activation energy) are good estimation for those of the overall reaction. However, RDS is not a rigorous concept in mathematics and there is no universal definition for RDS. Efforts have been made to clarify the actual physical meaning behind RDS, and the "Degree of Rate Control" (DRC) was raised as a rigorous mathematical approach to quantify to what extent the change of the Gibbs free energy of a species in the reaction scheme can affect the rate of the overall reaction. DRC analysis to reaction kinetics elucidates that there are only rate-determining species with non-negligible DRCs instead of rate-determining steps.

The apparent activation energy E_{app} is determined by fitting the temperature dependence of the reaction rate to the Arrhenius law. It is believed that E_{app} is a direct measurement of energy information in the RDS, which has been challenged by DRC analysis. A general and accurate elaboration of the microscopic origin of E_{app} has not been reported except in cases where there is an analytical rate expression. Here a simple but general mathematical expression of E_{app} in terms of the enthalpies of species in the reaction and their DRCs is derived. To verify the accuracy of this equation, microkinetic modelling of methanol synthesis through CO_2 hydrogenation on Cu-based model catalysts under three different conditions was carried out based on previously-published DFT energetics. On pure Cu(211) at 450 K, there are only one transition state and only one intermediate with non-negligible DRCs, and E_{app} estimated using our equation is within 1 kJ/mol of the true value. When the temperature is raised to 570 K, the surface sites are mostly unoccupied; and, when the model catalyst is promoted by Zn, there are four transition states with non-negligible DRCs, which means the single RDS assumption is not true. In both these complicated cases, the error of the estimated value for E_{app} is still <1 kJ/mol.

10:00am HC+SS-MoM-6 First-Principles Kinetic Monte Carlo Simulation of CO Oxidation on PdO(101): Role of Oxygen Vacancies, *Minkyu Kim, A Asthagiri,* The Ohio State University

CO oxidation on transition metal (TM) oxide surfaces has been widely studied both experimentally and theoretically; however, a healthy debate continues on the coupling between changes in oxide phase and surface reactivity. In this study, we investigated CO oxidation over PdO(101) surface, which has been proposed to be important in Pd oxidation catalysis. In contrast to earlier studies of CO oxidation on TM oxide surfaces, we incorporate neighbor effects of oxygen vacancies on all the elementary surface processes. We employ density functional theory (DFT) to map out the kinetics of 50 elementary surface processes. We find that barriers for elementary steps such as O vacancy, O_2 dissociation, and CO_2 formation can be decreased by 20-40% in the presence of O vacancies, while O_2 desorption is increased by 70%. Using the DFT-derived rate constants, we have developed a lattice-based kinetic Monte Carlo (kMC) framework that can simulate CO oxidation under both ultra-high vacuum (UHV) and reaction conditions.

Initially, the kMC simulations were performed under UHV conditions (low CO partial pressure, no O_2 pressure) as a function of increasing surface temperature. As the CO oxidation proceeds and the surface lattice O atom coverage is depleted, the CO oxidation rate decreases rapidly at 400 K; however, the rate sharply increases at temperatures above 450 K. At 450 K, we find a new complex pathway to CO_2 formation that is activated in the presence of O vacancies and is the source of the increased CO oxidation rate despite the depletion of surface oxygen atoms. These kMC results match UHV isothermal experiments under similar conditions. KMC simulations at steady state conditions of low CO and O_2 pressures (P_{CO}: 5×10^{-9} Torr / P_{O_2}: 1.5×10^{-8} Torr), show that the rate-limiting step is O_2 dissociation and this elementary step requires the presence of adjacent oxygen vacancies to be activated at temperatures below 500 K. Without the addition of O vacancy neighbor effects to the kMC model, the PdO(101) surface would be inactive to CO oxidation because surface oxygens cannot

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**
[2] **Morton S. Traum Award Finalist**

be healed by gaseous O_2. In addition, we will discuss kMC simulations under reaction conditions at varying CO/O_2 partial pressures.

10:40am HC+SS-MoM-8 Accelerating *ab initio* Simulations using Surrogate Machine Learning Models, *Jose A. Garrido Torres*, P Jennings, M Hansen, Stanford University; T Bligaard, SLAC National Accelerator Laboratory

Typically, first-principle calculations are computationally expensive. This problem is usually accentuated when modeling materials due to the large number of atoms involved in the models. Therefore, the development and implementation of robust and fast optimizers have always been a hot topic in this field. The desired algorithms must minimize the number of *ab initio* function calls as much as possible without compromising the accuracy of the simulated properties. Our approach is based on a surrogate machine learning model which allows to substantially reduce the number of function calls in the search of the optimal solution. Here, we present the evidence of the aforementioned acceleration for two of the most commonly encountered optimizations problems in computational catalysis: structural relaxations and transition-state search, such as energy minimization and Nudged Elastic Band (NEB) calculations.

11:00am HC+SS-MoM-9 Integrating Materials Databases and Autonomous Workflows for the Discovery of New Heterogeneous Catalysts, *Kirsten Winther, T Bligaard,* SLAC National Accelerator Laboratory

With the accelerating amount of electronic structure data being generated in materials research, data-driven approaches have a huge potential to guide the discovery of new materials and catalysts. This paradigm relies on the development of sophisticated tools and software for storing, sharing and generating calculational results.

Several open materials databases, including Materials Project and the Open Quantum Materials Database (OQMD), have been successful in making the results of electronic structure calculations openly available, where vast amount of crystalline materials data has been generated. Recently, we developed the Catalysis-Hub.org database platform[1], which is suited to handle the complexity of computational catalysis.

In my talk I will present the Catalysis-Hub platform, which consists of a database for surface reactions containing 105,000+ reaction energies from more than 50 publications, as well as several in-browser apps, such as atomistic machine learning predictions for adsorption energies [2] and generation of crystal [3] and surface-adsorbate geometries[4]. Next, I will discuss how these efforts can be integrated into computational workflows for generating atomic geometries and calculations. This includes how machine learning predictions in an active learning framework can be used for an autonomous exploration of new catalytic materials.

[1] K.T. Winther, M.J. Hofmann, O. Mamun, J. R. Boes, M. Bajdich, T. Bligaard. Scientific Data, Accepted (2019).

[2] M.H. Hansen et al. https://arxiv.org/abs/1904.00904 (2019).

[3] A. Jain, T. Bligaard Phys. Rev. B 98, 214112 (2018).

[4] J.R. Boes, O. Mamun, K. T. Winther and T. Bligaard. JPCA 123, 2281–2285 (2019).

11:20am HC+SS-MoM-10 Knowledge-Based Approaches in Catalysis and Energy Modelling, *Karsten Reuter,* Technical University of Munich, Germany **INVITED**

Reflecting the general data revolution, knowledge-based methods are now also entering theoretical catalysis and energy related research with full might. Automatized workflows and the training of machine learning approaches with first-principles data generate predictive-quality insight into elementary processes and process energetics at undreamed-of pace. Computational screening and data mining allows to explore these data bases for promising materials and extract correlations like structure-property relationships. At present, these efforts are still largely based on highly reductionist models that break down the complex interdependencies of working catalysts and energy conversion systems into a tractable number of so-called descriptors, i.e. microscopic parameters that are believed to govern the macroscopic function. For certain classes of materials like transition metal catalysts, corresponding human-designed models have indeed established trend understanding and spurred a targeted materials design. Future efforts will concentrate on using artificial intelligence also in the actual generation and reinforced improvement of the reductionist models. This is expected to better capture complexities like incomplete understanding or operando changes of interfacial morphology, to provide access to structured and compound materials classes, or ultimately to even fulfill the dream of an inverse (de novo) design from function to structure. In this talk, I will briefly survey these developments, providing examples from our own research, in particular on adsorption energetics at bimetallic catalysts and data mining for the design of organic semiconductors.

Surface Science Division
Room A220-221 - Session SS+HC-MoA

CO2, CO, Water, and Small Molecule Chemistry at Surfaces

Moderators: Donna Chen, University of South Carolina, Omur E. Dagdeviren, Yale University

1:40pm SS+HC-MoA-1 Calculations of the Electrochemical Reduction of CO2 and the Competing Hydrogen Evolution Reaction, *Hannes Jónsson,* University of Iceland, Iceland   **INVITED**
Calculations of electrochemical CO2 reduction to formate, alcohols and hydrocarbons will be presented. The mechanism for the formation of the various products is established, the rate evaluated and comparison made with experimental measurements. The rate of the main side reaction, the hydrogen evolution reaction, is also estimated. The calculations are based on a detailed atomistic model of the electrical double layer (metal slab and water layer) and density functional theory calculations to evaluate not only the free energy of intermediates as a function of applied voltage but also the activation energy for each elementary step, both Heyrovsky and Tafel reactions [1]. Comparison is also made with calculations using an implicit solvation model [2]. A range of close packed metal surfaces are compared, including Cu, Ag, Au, Ni, Fe, Rh, Ir and Pt. The resuls are in remarkably good agreement with the reported experimental measurements. A two parameter descriptor is established that can help identify improved catalysts for CO2 electrochemical reduction.

[1] J. Hussain, H. Jónsson and E. Skúlason, ACS Catalysis 8, 5240 (2018).

[2] M. Van den Bossche, E. Skúlason, C. Rose-Petruck and H. Jónsson, J. Phys. Chem. C 123, 4116 (2019).

2:20pm SS+HC-MoA-3 CO_2 Adsorption on the O-Cu(100) Surface Studied by STM and DFT, *S Tjung, Q Zhang, J Repicky, S Yuk,* The Ohio State University*; X Nie,* Dalian University of Technology*; **Seth Shields,** The Ohio State University; N Santagata,* University of Memphis*; A Asthagiri, J Gupta,* The Ohio State University
Copper oxide catalysts are promising candidates for reducing CO_2 into useful fuels, such as ethanol, but the mechanism remains obscure. Studying the O-Cu(100) surface, which represents the initial transition of the oxidation of copper to copper oxide, and the adsorption process of CO_2 has the potential to elucidate the CO_2 reduction mechanism.

We performed a DFT/STM theoretical and experimental probe of the properties of CO_2 adsorption on the O-Cu(100) surface. The Cu(100) surface was repeatedly sputtered with Ar^+ and annealed at 550°C in an ultra-high vacuum chamber, and subsequent Auger spectroscopy revealed the lack of surface contamination. The O-Cu(100) surface was obtained by exposing the Cu(100) face to 10^{-6} mbar of oxygen for 5 minutes at 300°C. The sample was then cooled and transferred into an attached low temperature (5K) ultra-high vacuum (10^{-11} mbar) STM chamber.

The atomic resolution STM revealed the ($2\sqrt{2}\times \sqrt{2}$) R45°O-Cu(100) reconstruction, in good agreement with the DFT calculations. The reconstruction consists of an O-Cu-O row structure separated by missing Cu rows. Additionally, there are two equivalent domains which result from nucleation along the [001] and [010] directions of the Cu(100). Differential conductance spectroscopy reveals an increase in the work function of the O-Cu(100) surface, and two additional unoccupied states generated by the oxygen atoms, in agreement with the DFT calculations.

CO_2 was adsorbed onto the O-Cu(100) surface via *in situ* dosing in the STM. The CO_2 adsorbed exclusively between two oxygen atoms in the missing row reconstruction, which has the largest predicted adsorption energy. The lack of point defects on the surface indicates that the CO_2 does not dissociate, and the CO_2 molecules are easily disturbed by the tip under all tunneling conditions, which is consistent with the theoretically predicted low diffusion barrier.

This work acknowledges funding from the NSF (1809837).

2:40pm SS+HC-MoA-4 Employing Carbon Monoxide and Carbon Dioxide Plasmas to Improve the Gas Sensing Performance of Tin(IV) Oxide, *Kimberly Hiyoto, E Fisher,* Colorado State University
Metal oxide semiconductors are commonly researched materials for solid-state gas sensors; however, several limitations (i.e., operating temperatures of ≥300 °C and poor selectivity) impede wide-spread commercialization of these devices. Plasma processing offers a desirable alternative route to traditional methods, such as doping, because of the

tunability of treatment parameters and the ability to modify the surface of the material while maintaining bulk properties. Previous work using plasma modification to enhance tin dioxide (SnO_2) gas sensor performance has mainly focused on oxygen or oxygen/argon plasma systems because these systems are thought to etch oxygen from the SnO_2 lattice creating oxygen vacancies that can lead to lower operating temperatures and improved sensor selectivity. Thus, further work needs to be done with other precursor gases to determine an effective strategy for fabricating improved gas sensors.

Here, we present carbon monoxide (CO) and carbon dioxide (CO_2) plasma-treated SnO_2 nanoparticle gas sensors treated at various applied rf powers. After plasma processing, the sensors demonstrate higher response to CO, ethanol, and benzene at lower operating temperatures compared to untreated SnO_2. In addition, the response and recovery behavior of the treated and untreated sensors were also evaluated as a metric for improved performance. To elucidate how plasma modification resulted in these changes, optical emission spectroscopy measured during plasma treatment and material characterization post plasma processing (X-ray photoelectron spectroscopy and X-ray powder diffraction) will also be discussed. All of these data work toward better understanding the relationship between surface chemistry and gas sensing performance, ultimately to develop a targeted approach to designing improved gas sensors.

3:00pm SS+HC-MoA-5 The Role of Steps in the Dissociation of CO_2 on Cu, *Johan Gustafson, B Hagman,* Lund University, Sweden*; A Posada-Borbón, A Schaefer,* Chalmers University of Technology, Sweden*; M Shipilin,* Stockholm University, Sweden*; C Zhang,* Lund University, Sweden*; L Merte,* Malmö University, Sweden*; A Hellman,* Chalmers University of Technology, Sweden*; E Lundgren,* Lund University, Sweden*; H Grönbeck,* Chalmers University of Technology, Sweden   **INVITED**
CO_2 chemistry has received significant attention recently, due to the greenhouse effect of CO_2 emissions and the resulting climate change. CO_2 reduction reactions, such as methanol synthesis and reverse water-gas shift, provide routes for recycling of CO_2 and thus limiting the CO_2 emissions. These reactions are commonly performed over Cu-based catalysts, making the interaction of CO_2 and Cu, on the atomic scale, of importance for a fundamental understanding and the development of new and more efficient catalysts.

We have previously studied the dissociative adsorption of CO_2 on Cu(100) using APXPS and DFT. In summary, exposure of the Cu surface to CO_2 in the mbar range at temperatures above room temperature results in dissociation of CO_2 into CO, that desorbs, and O that stays on the surface. The rate of the increase in O coverage, however, was not consistent with what one would expect from adsorption on the flat Cu(100) surface. Instead, we propose a model where the dissociation happen at atomic steps. The steps were found to both lower the activation barrier for the dissociation and separate the products, such that the probability for recombination is lowered.

As an obvious follow-up of this study, we have studied the dissociative adsorption of CO_2 on Cu(911), which exposes five atoms wide (100) terraces separated by monatomic steps. In contrast to what we expected, the O coverage did not increase significantly faster on this stepped surface. Our preliminary analysis suggests that diffusion of O from one step to another reduces the effect of the steps separating O and CO, but also that the steps facilitate O diffusion to the subsurface region and possibly stabilisation of CO_2 or CO_3 species on the surface.

In this presentation we will report how we conclude that the steps control the dissociation and, especially, the present status of the studies of Cu(911).

4:00pm SS+HC-MoA-8 Surface Temperature Dependence of Methane Dissociation on Ni(997), *Daniel Tinney, E High, L Joseph, A Utz,* Tufts University
Commercial steam reforming reactors operate at temperatures of 1000K or higher, and methane dissociation on the Ni catalyst is generally believed to be the rate-limiting step in this industrially important process. Despite the commercial importance of this reaction, nearly all studies probing the dynamics of methane dissociation have focused on surface temperatures of 600K or lower. Here, we use energy and vibrationally state selected methane molecules in a supersonic molecular beam to quantify the impact of surface temperature on methane activation over a wide range of surface temperatures. Our use of methane molecules with a precisely defined energy highlights provides a clear view of how surface temperature impacts reactivity.

Vibrationally state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Non-statistical, mode-specific, and bond-selective enhancements observed for methane and its isotopologues on transition metal surfaces provide insights into energy flow during reactions. Reactive gas molecules with strictly-defined energy in well-defined energetic coordinates used in state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. For this work, vibrationally state-resolved data was collected via infrared (IR) laser excitation of the anti-symmetric stretch of supersonically-expanded methane (CH_4) gas molecules impinging on a lightly-stepped Ni(997) surface. Measurements on the single crystal were investigated over a broad range of surface temperatures (82 K ≤ T_S ≤ 1000 K) while utilizing varying incident energies (E_i = 20 kJ/mol to >140 kJ/mol). A comparison with prior data on Ni(111) surface reveals the role that steps may play in methane activation.

4:20pm **SS+HC-MoA-9 Promotion and Inhibition of Methane Dissociation by Carbon on Ni Single Crystal Surfaces**, *Arthur Utz, E High, D Tinney,* Tufts University
State-resolved beam-surface scattering measurements, when coupled with molecular beam reactivity modulation measurements, permit real-time measurement of methane dissociation on Ni(111) and Ni(997) surfaces. At surface temperatures above 550K, methyl reaction products dehydrogenate to C atoms, and H atoms recombine and desorb, leaving C atoms behind. At higher surface temperatures, C atoms begin to aggregate on the surface and also absorb into the Ni subsurface region. We monitor how the presence of these C atoms on and beneath the surface impacts methane dissociation probability.

4:40pm **SS+HC-MoA-10 Two-Dimensional Polymorphism as a Result of Non-Equilibrium Self-Assembly**, *Angela Silski[1], J Petersen,* University of Notre Dame*; R Brown,* Clarkson University*; S Kandel,* University of Notre Dame
The challenge in the field of molecular self-assembly is that the outcome of these processes is not easily predicted a priori, rather, results of self-assembly processes are often rationalized after the fact. In this study, a systemic approach to self-assembly is taken; the chemical structure of the starting molecule is iteratively changed (adding, removing or substituting particular functional groups) and the resulting self-assembled structure is observed via scanning tunneling microscopy. The focus of this study is on the functional groups that can form directional interactions (hydrogen- and halogen-bonds). We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with density functional theory providing support for a cyclic structure stabilized by both NH· · ·O and CH· · ·O hydrogen bonds between neighboring molecules. The CH· · ·O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 17 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH···O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. To our surprise, substituting the 6-position with a bromine (6-bromoisatin) which is a position remote to the positions of the hydrogen-bond contacts, does not result in the formation of cyclic pentamers on the surface. A monolayer of 6-bromoisatin consists of almost entirely "zipper" dimer structures. Additionally, the importance of CH···O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak. A mass spectrum of 6-bromoisatin also shows a relatively intense pentamer peak, whereas the other derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen- and halogen-bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

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[1] Morton S. Traum Award Finalist

Energy Transition Focus Topic
Room A212 - Session TL+2D+HC+SS-MoA

Surface Reaction Mechanisms in Energy Conversion (ALL INVITED SESSION)

Moderators: Marie Turano, Loyola University Chicago, Sarah Zaccarine, Colorado School of Mines

1:40pm **TL+2D+HC+SS-MoA-1 Selective Photo-driven Organic Reactions on the Surfaces of Colloidal Quantum Dots**, *Y Jiang, K McClelland, C Rogers, Emily Weiss,* Northwestern University **INVITED**
Colloidal quantum dots present a unique opportunity not only to power chemical reactions with sunlight but to control those chemical reactions through various templating strategies. This talk will explore demonstrations of chemo-, regio-, and stereoselective reactions photocatalyzed by quantum dots.

2:20pm **TL+2D+HC+SS-MoA-3 Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico**, *Charles Sykes,* Tufts University **INVITED**
In this talk I will discuss a new class of metallic alloy catalysts called *Single Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.[1-5] These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between the atomic scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. Over the last five years the concepts derived from our surface science and theoretical calculations have been used to design *Single Atom Alloy* nanoparticle catalysts that can perform industrially relevant reactions at realistic reaction conditions in collaboration with Maria Flytzani-Stephanopoulos at Tufts. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective chemical reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis and Michaelides at UCL that predicts reactivity trends of 16 different *Single Atom Alloy* combinations for important reaction steps like activation of H-H, C-H, N-H, O-H and C=O bonds. This project illustrates that the field of surface science is now at the point where it plays a critical role in the design of new heterogeneous catalysts.

References:

[1] Kyriakou et al. Science **335**, 1209 (2012).

[2] Marcinkowski et al. Nature Materials **12**, 523 (2013).

[3] Lucci et al. Nature Communications **6**, 8550 (2015).

[4] Liu et al. JACS **138**, 6396 (2016).

[5] Marcinkowski et al. Nature Chemistry **10**, 325 (2018).

3:00pm **TL+2D+HC+SS-MoA-5 Understanding Fundamental Energy Conversion Mechanisms: How Surface Science Can Help**, *Ulrike Diebold,* Institute of Applied Physics, TU Wien, Austria **INVITED**
As we move to a more sustainable society, current energy conversion schemes need to be improved and novel ones designed. The relevant charge transfer processes and chemical transformations all occur at interfaces, so insights into fundamental mechanisms are needed to provide a scientific basis for these developments.

Using the frontier tools of surface science, I will discuss how we can directly inspect charge transfer to molecules, investigate the influence of the local environment on the reactivity of active sites, or probe the acidity of individual hydroxyls. Together with first-principles computations such experiments give crisp and clear insights into surface processes. I will also discuss the steps that are necessary to the transfer the knowledge gained from model systems to more complex environments.

4:00pm **TL+2D+HC+SS-MoA-8 Atomically-defined Model Interfaces in Energy-related Catalysis, Electrochemistry, and Photoelectrochemistry**, *Jörg Libuda,* University Erlangen-Nuremberg, Germany **INVITED**
The transformation between chemical energy, solar energy, and electrical energy occurs at interfaces. Therefore, functional interfaces are the key to the development of new materials in energy technology and energy-related catalysis. In our work, we explore model systems, which provide detailed insight into the chemistry and physics at such functional interfaces. Complex, yet atomically-defined model systems are studied

both under 'ideal' surface science conditions and under 'real' conditions, i.e., in contact with gases, liquids, in electrochemical, and in photoelectrochemical environments. We illustrate the approach in three examples from our recent research.[1-5]

First, we consider new noble-metal-efficient catalysts for fuel cell applications.[1] We show that precious noble metals such as Pt can be anchored to nanostructured oxide supports. The resulting materials show very high noble metal efficiency and high stability. Surface science studies on model catalysts provide insight into the functionality of these systems. Electronic metal support interactions modify the reactivity of the catalytic surfaces but also stabilize sub-nanometer-sized Pt nanoparticles against sintering and deactivation.

Secondly, we report on the development of atomically defined model systems for oxide-based electrocatalysts, which can be studied under true operation conditions, i.e., in liquid environments and under potential control. We describe how such model electrodes are prepared by surface science methods and, subsequently, are studied in liquid electrolytes preserving their atomic structure. We investigate the role of particle size effects and identify the origin of metal-support interactions.

In the third part, we scrutinize the role of organic-oxide hybrid interfaces in energy transformation. Particularly fascinating are organic layers of molecular photoswitches, which provide an extremely simple solution for solar energy conversion and storage. We show that it is possible to assemble fully operational solar-energy-storing hybrid interfaces by anchoring tailor-made norbornadiene photoswitches to atomically defined oxides. Interestingly, the activation barrier for energy release in these systems is not affected by the anchoring reaction. Finally, we demonstrate that solar energy storage and release in such systems can also be controlled electrochemically with high reversibility.

[1] A. Bruix, et al., *Angew. Chem. Int. Ed.*, 53, 10525 (2014)

[2] Y. Lykhach, et al., *Nat. Mater.* 15, 284 (2016)

[3] O. Brummel et al., *ChemSusChem* 9, 1424 (2016)

[4] O. Brummel et al., *J. Phys. Chem. Lett.*, 8, 2819 (2017)

[5] F. Faisal et al., *Nat. Mater.*, 17 592 (2018)

4:40pm **TL+2D+HC+SS-MoA-10 Controlling Ultrafast Photochemical Reactions in Photocatalysis**, *Annemarie Huijser,* University of Twente,The Netherlands, The Netherlands **INVITED**
The transition from fossil to renewable energy is one of the most important challenges of our society. Solar devices are widely considered as a highly promising option, as the energy provided by the sun to the earth by far exceeds global needs. We are investigating the use of nanostructured materials for application in solar energy conversion. The overall efficiency relies on the complex interplay of many elementary process, occurring at different time scales and also dependent on the nanostructure. In this presentation I will show how a combination of methods for ultrafast spectroscopy can shed light on the nature of photoinduced processes and provide mechanistic information valuable for the design of novel materials.

Surface Science Division
Room A220-221 - Session SS+2D+HC-TuM

Atom Manipulation and Synthesis/Oxide Surface Reactions & Flash Session

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

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

Real space chemical analysis of two structurally very similar components i.e. regioisomers lies at the heart of heterogeneous catalysis reactions, modern-age electronic devices and various other surface related problems in surface science and nanotechnology. One of the big challenges in surface chemistry is to identify different surface adsorbed molecules and analyze their chemical properties individually. Herein, we report a topological and chemical analysis of two regioisomers, *trans*- and *cis*-tetrakispentafluorophenylporphodilactone (*trans*- and *cis*-H_2F_{20}TPPDL) molecules by high resolution scanning tunneling microscopy (STM), and ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Both isomeric structures are investigated individually on Ag(100) at liquid nitrogen temperature. Following that, we have successfully distinguished these two regioisomeric molecules simultaneously through TERS with an angstrom scale (8 Å) spatial resolution. Also, the two-component organic heterojunction has been characterized at large scale using high resolution two-dimensional (2D) mapping. Combined with time-dependent density functional theory (TDDFT) simulations, we explain the TERS spectral discrepancies for both isomers in the fingerprint region.

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

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

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

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

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

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

References:

[1] L. Gross *et al. Angew. Chem Int. Ed* **57**, 3888(2018)

[2] B. Schuler *et al. Nat. Chem.* **8**, 220 (2016)

[3] N. Pavliček *et al. Nat. Nano.* **12**, 308 (2017)

[4] N. Pavliček *et al. Nat. Chem.* **10**, 853 (2018)

[5] S. Fatayer *et al. Nat. Nano.* **13**, 376 (2018)

[6] S. Fatayer *et al. Phys. Rev. Lett.* **121**, 226101 (2018)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

When the rutile TiO_2(110) and anatase TiO_2(101) surfaces are exposed to atomic hydrogen, NRA shows adsorption of hydrogen on the surfaces with a coverage of about 0.5 monolayer [2]. When the rutile TiO_2(110) surface is exposed to a hydrogen ion beam at 500 eV, on the other hand, NRA reveals a maximum at a depth of about 1 nm extending to ~30 nm with an average concentration of 5.6 at. % and UPS shows an in-gap state (IGS) at ~0.8 eV below the Fermi level with a downward band-bending by 0.5 eV. The IGS intensity is about ten times as large as that of the H-adsorbed surface. Upon annealing at 673 K, the IGS intensity is reduced by about 40 % and H with a coverage of 1.4 monolayer remains in the near-surface region, which suggests stable H occupation of subsurface sites. When the H-ion-irradiated surface is exposed to oxygen molecules, on the hand, the hydrogen distribution remains unchanged although the IGS intensity is substantially reduced. The effect of hydrogen in the near-surface region on the surface electronic state is discussed.

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

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

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

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

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

The growth of crystals from the vapor phase is widely used in many technological applications, ranging from the microfabrication of microprocessors to the development of biological sensors. The dynamics of processes such as the surface diffusion of adatoms are key phenomena governing mass transport and the resulting crystal growth. Atomic exchange with substrate atoms during surface self-diffusion has been inferred from previous field ion microscope(FIM)-based experiments by mapping adatom visitation sites. Here iridium enriched to >93% ^{191}Ir was deposited onto an atomically clean and smooth $Ir(100)$ plane as observed in an atom-probe field ion microscope. Following thermally activated surface self-diffusion the adatom was field desorbed and mass analyzed. Observation of the ^{193}Ir isotope in one-half of the cases demonstrates conclusively that atomic exchange can occur during surface self-diffusion.

Complex Oxides: Fundamental Properties and Applications Focus Topic
Room A220-221 - Session OX+EM+HC+MI+NS+SS+TF-TuA

Complex Oxides: Catalysis, Dielectric Properties and Memory Applications

Moderators: Alexander Demkov, University of Texas at Austin, Jeffry Kelber, University of North Texas

2:20pm OX+EM+HC+MI+NS+SS+TF-TuA-1 Novel Multiferroic and Ferroelectric Ferrite Thin Films, *Peter A. Dowben, C Binek, X Xu,* University of Nebraska-Lincoln **INVITED**
Ferroelectricity and ferromagnetism are foundational to numerous technologies, yet the combination of ferroelectricity and ferromagnetism, namely multiferroicity, may be even more desirable. Multiferroic materials are believed to be a route to voltage controlled spintronic devices. Yet very few single phase materials are known to be ferroelectric and ferromagnetic at the same time, i.e. multiferroic. Even fewer materials are fewer materials are magneto-electric, that is to say materials with magneto-electric coupling, i.e. voltage control of magnetization, but without separate order parameters for magnetism (or antiferromagnetism) and ferroelectricity. This talk will review the electronic structure of the tri-rutile magneto-electric antiferromagnets, like Fe_2TeO_6, as well as rare earth ferrites like $ReFeO_3$ (Re = rare earth) stabilized in the hexagonal phase. Both types of materials are frequently antiferromagnetic, and, in principle, both can exhibit magneto-electric coupling. The surface termination affects the measured spin polarization of the surface and the interface with other materials. This will have a significant influence on the voltage control of magnetization. We have investigated the structural and electronic properties at the surface of these more unusual multiferroic materials using angle-resolved x-ray photoemission spectroscopy (ARXPS), complemented by x-ray diffraction (XRD), x-ray photoemission electron microscopy (X-PEEM), and X-ray circular dichroism. We find that the low local symmetry, especially at surfaces, will split the electronic states, via spin–orbit coupling. In some cases, the result is a net spin polarization at the surface, under electric field cooling. Because of the strongly preferential surface termination of these types of materials, the boundary polarization is roughness insensitive, in some cases making spintronic device applications plausible.

3:00pm OX+EM+HC+MI+NS+SS+TF-TuA-3 Potential Applications and Challenges for Complex Oxides in Advanced Memory and Computing Applications, *Sebastian Engelmann, T Ando, V Narayanan,* IBM T.J. Watson Research Center **INVITED**
As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of redeveloping or optimizing fundamental computing approaches to be more energy efficient. The development of hardware for novel AI systems is no exception. New integration schemes, novel materials, multi-component materials or even nanoscale materials and the ability to integrate all of these approaches together becomes the compounded challenge. Deposition and etch technologies that offer differentiating solutions to these issues therefore need to meet somewhat conflicting demands, such as low damage processing as well as high rate processing beside many other issues.

Novel thin films, thin film laminates and alloys promising unprecedented performance are very interesting candidates to enable such computing paradigm shifts. In particular the class of complex oxides is a very interesting area of research as they offer new phenomena such as ferroelectricity, ferromagnetism or high temperature conductivity. While new phenomena are being discovered, unraveling the fundamental physics behind these properties is a critical element for an industrial exploitation of these properties.

In addition, these new and complex materials are growing the need for the ultimate process solution: atomic layer precision processing. Atomic layer etching is a promising path to answer the processing demands of new devices at the Angstrom scale. Self-limiting reactions, discrete reaction and activation steps or extremely low ion energy plasmas are some of the pathways being pursued for precise material removal control and maintaining the original film performance. Depending on the nature of the material, the etch response may be either too much or not enough chemical modifications of the material. Resulting modifications of the films is an important variable to consider in the readiness of material systems. In

particular synergy to deposition approaches such as atomic layer deposition has been proposed as a solution, but more work is needed.

4:20pm OX+EM+HC+MI+NS+SS+TF-TuA-7 Epitaxial Design of Complex Oxides for Catalysis and Electrocatalysis, *Yingge Du,* Pacific Northwest National Laboratory **INVITED**
Predictive synthesis of highly active and cost-effective catalysts and electrocatalysts for energy conversion and storage is critical for leveraging intermittently available energy sources. Transition metal oxides with perovskite (ABO3) and perovskite-related structures (e.g., Brownmillerite and Ruddlesden-Popper) have been identified as robust catalysts with high oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) activities that rival the performance of noble metals and their compounds. The study of perovskites as epitaxial thin films enables measurement of their intrinsic catalytic activity, deconvolved from the effects of surface roughness and polycrystalline defects (e.g., grain boundaries and edges between facets). In addition, epitaxial growth facilitates accurate control over the composition, crystallographic orientation, and strain in thin films.

In this talk, our recent efforts in the design of epitaxial complex oxides for catalysis and electrocatalysis will be highlighted. Using $LaNiO_3$, a bi-functional electrocatalyst, as an example, I will show how isovalent substitution, alliovalent substitution, and interfacial strain can be used to tune the structural, electronic, and optical properties of the resultant films, and how these observed changes correlate with their (electro)catalytic performance. The use of complex oxide thin films as support or anti-corrosion layers during catalytic reactions will also be discussed.

5:00pm OX+EM+HC+MI+NS+SS+TF-TuA-9 Manipulate the Electronic Structures of Complex (Ni, Co) Oxides by Hole Doping for Oxygen Evolution Reaction, *Kelvin Zhang,* Xiamen University, China
This talk reports a fundmanetal study on the correlation of the composition and electronic structures of complex oxides with their electrocatalytic activity for oxygen evolution reaction (OER). In particular, we modulated the electronic states of complex oxides using hole doping strategy, e.g., Li doped NiO, Sr doped $LaFeO_3$ and Ni doped Co_3O_4. Photoemission spectroscopy and x-ray absorption spectroscopy (XAS) were used to study both the occupied and unoccupied density of states around the Fermi level. The electronic structures determines the adsorption strength of reaction intermediates for OER. Our results reveal two important change in the electronic structures induced by hole doping are crucial for improving OER activity: (1) upshift of the occupied valence band center to enhance the surface absorption; (2) creation of a new hole (unoccupied) state just above the Fermi level to reduces the energy barrier for electron transfer. Our results supplemented with DFT calculations established a direct correlation between the enhancement of activity with electronic structure, providing guideline for design of highly active electrocatalysts.

5:20pm OX+EM+HC+MI+NS+SS+TF-TuA-10 Vanadia/Tungsten Oxide on Anatase TiO2(101): a Model Catalyst Study by STM and XPS, *Tao Xu, J Lauritsen, K Adamsen,* Aarhus University, Denmark*; S Wendt,* iNANO, Aarhus University, Denmark
Nitrogen oxides (NOX) from flue gas are in concern as major sources of air pollution. Increasingly stricter NOX emission control policies (e.g. Euro VI) demand innovation and better performance of NOX reduction technology. The Selective Catalytic Reduction (SCR) of NOX by vanadia supported on anatase titania, with tungsten oxide (WO3) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive RAMAN and infrared spectroscopy studies.

In this work, we use mineral a-TiO2 single crystals exposing the (101) facets as the model surface and deposit V2O5 and WO3 in our ultrahigh vacuum chamber (UHV) chamber by e-beam evaporation in oxygen. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the morphology and oxidation state changes of the model catalyst upon heating and reactant adsorption.

The STM results illustrate the distribution of V2O5 and WO3 on anatase TiO2(101) at the atomic level. It is found that both species are highly dispersed in the sub-monolayer region. For the deposition of surface oxide species, we explored different methods to achieve the highest oxidation state of vanadium (5+) and tungsten (6+). The thermal stability of the as-deposited V2O5 and WO3 are investigated by XPS and STM systematically. We found that when V2O5 and WO3 co-exist on the a- TiO2 surface the

stability of V2O5 is improved. This work provides atomic level understanding on the V2O5/WO3/TiO2 SCR catalyst and new insights into the synergistic interactions between vanadia and tungsten oxide on the a-TiO2 surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA-11 Observation of Memory Effect and Fractal Surface in SrRuO$_3$ Epitaxial Thin Films**, *Ratnakar Palai*, University of Puerto Rico; *H Huhtinen*, University of Turku, Finland

Integration of multifunctional oxide materials (ferroelectrics and multiferroics) into silicon technology is of great technological and scientific interests. The current interest in functional oxides is largely based on engineered epitaxial thin films because of their superior properties compared to the bulk and polycrystalline thin films and their technological applications in dynamic random access memories, magnetic recording, spintronics, and sensors. Most of these applications require bottom and top electrodes to exploit the electronic properties of the functional materials.

SrRuO3 (SRO) has been found to be very useful for electrodes and junctions in microelectronic devices because of its good electrical and thermal conductivities, better surface stability, and high resistance to chemical corrosion, which could minimize interface electrochemical reactions, charge injection in oxide, and other detrimental processes, thus improving retention, fatigue resistance, and imprint. It also has good work function to produce the required large Schottky barrier on most ferroelectric oxide capacitors.

The bulk SRO exhibits several useful properties, such as extraordinary Hall effect, strong magnetocrystalline anisotropy, itinerant ferromagnetism, and spin-glass behavior. Spin-glass materials are currently frontier field of research and the most complex kind of condensed state of matter encountered so far in solid-state physics. Despite of the enormous importance of spin-glass models in neural networks, our knowledge of the underlying mechanistic processes involved is extremely limited. Although memory effect has been reported in bulk SRO, to our knowledge, the behavior is not well understood and there was no such report in thin films.

In this work, we report on the observation of memory effect and strong magnetic anisotropy in extremely smooth 1–3 Å roughness epitaxial (110) and (010) SrRuO3 thin films. The observation of non-zero imaginary susceptibility and frequency dependent cusp at freezing temperatures confirms the spin-glass behavior, which agrees well with the dc magnetization measurement. The origin of memory effect can be attributed to the magnetic frustration and random interaction, which is affected by dynamics of cooling and will be discussed in details.

6:00pm **OX+EM+HC+MI+NS+SS+TF-TuA-12 *In situ* Auger Electron Spectroscopy of Complex Oxide Thin Film Surfaces Grown by Pulsed Laser Deposition**, *Thomas Orvis*, M Surendran, Y Liu, A Cunniff, J Ravichandran, University of Southern California

Complex oxides can enhance the functionality of electronic and photonic devices by supplementing them with interesting properties such as ferroelectricity, superconductivity, and magnetoresistivity. Furthermore, low dimensionality in these materials can result in additional useful properties, inspiring the continued study of complex oxides in thin film form. However, the deposition of these materials is typically governed by notoriously complex growth mechanisms, revealing the need for *in situ* probes to observe and understand their precise nature. To this end, we report the *in situ* observation of chemical composition of complex oxide thin film surfaces with Auger electron microscopy during growth by pulsed laser deposition. Our implementation of real-time monitoring techniques for complex oxide thin films sheds an important light on the intricacies of the relationships between processing conditions and resulting composition.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A213 - Session HC+2D+SS-WeM

Exotic Nanostructured Surfaces for Heterogeneously-Catalyzed Reactions

Moderators: Ashleigh Baber, James Madison University, Erin Iski, University of Tulsa

8:20am HC+2D+SS-WeM-2 Selective Alkane Chemistry on IrO$_2$(110) Surfaces, *Aravind Asthagiri, M Kim,* The Ohio State University; *J Weaver,* University of Florida

Selective conversion of alkanes to higher value species using heterogeneous catalysts is of great interest with the increasing availability of light alkanes from shale fracking. We have used a combination of temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) to demonstrate that the stoichiometric terminated IrO$_2$(110) surface can activate methane and ethane below room temperatures, and furthermore, that this surface can be selective towards ethane dehydrogenation to ethylene. For ethane, DFT shows that adsorption and initial C-H bond cleavage to surface bound C$_2$H$_4$* is facile and the selectivity step occurs between further C-H bond breaking leading to complete oxidation versus ethylene desorption. The reactivity of this surface is mediated by the presence of undercoordinated Ir (Ir$_{cus}$) and adjacent bridge O atoms (O$_{br}$). Using the combination of TPRS and DFT we find that pre-hydrogenating the IrO$_2$(110) surface results in the formation of HO$_{br}$ sites that increases the selectivity towards ethylene by increasing the barrier to C-H bond cleavage for C$_2$H$_4$* and decreasing the desorption energy of C$_2$H$_4$*. We will discuss efforts to use DFT and microkinetic modeling to explore doping strategies of both the Ir$_{cus}$ and O$_{br}$ sites to promote selectivity towards ethylene formation.

8:40am HC+2D+SS-WeM-3 Design of Nanostructured Catalysts for Better Performance, *Francisco Zaera,* University of California, Riverside **INVITED**

One of the major challenges in heterogeneous catalysis is the preparation of highly selective and robust catalysts. The goal is to be able to synthesize solids with stable surfaces containing a large number of specific surface sites designed for the promotion of a particular reaction. New synergies between surface-science studies and novel nanosynthesis methodology promise to afford new ways to design such highly selective catalysts in a controlled way. In this presentation we will provide a progress report on a couple of projects ongoing in our laboratory based on this approach. Platinum-based catalysts have been prepared for the selective trans-to-cis conversion of olefins, with a design based on early surface-science work with model surfaces and quantum mechanical calculations that indicated a particular preference for (111) facets in promoting the formation of the cis isomers. We are currently extending this research by using the concept of "single-site catalysis" with Pt-Cu bimetallics for the selective hydrogenation of unsaturated aldehydes. In a second example, new metal@TiO$_2$ yolk-shell nanomaterials conceived for both regular and photo-induced catalytic applications have been used to promote CO oxidation at cryogenic temperatures and to suggest that in photocatalysis the role of the metal may not be to scavenge the excited electrons produced in the semiconductor upon absorption of light, as commonly believed, but rather to promote the recombination of the adsorbed atomic hydrogen initially produced by reduction of H$^+$ on the surface of that semiconductor. New mixed-oxide surfaces are being designed using atomic layer deposition (ALD) as well.

9:20am HC+2D+SS-WeM-5 Characterization of a Pd/Ag(111) Single Atom Alloy Surface Using CO as a Probing Molecule for H$_2$ Dissociation, *Mark Muir, M Trenary,* University of Illinois at Chicago

Tuning catalysts for selective hydrogenation reactions is ultimately determined by the nature of the active site for H$_2$ dissociation and the adsorption of atomic hydrogen on the surface. Several single atom alloys (SAAs) consisting of small amounts of Pd deposited onto surfaces of metals that do not activate H$_2$ dissociation, such as Cu(111) and Au(111), have been previously studied. In the present study, we characterize Pd/Ag(111), a possible new single atom alloy surface using reflection absorption infrared spectroscopy (RAIRS) of adsorbed CO as a probe. From 0.01 to 0.04 ML Pd/Ag(111), a v(CO) stretching peak was seen at 2050 cm^{-1} corresponding to CO adsorbed on palladium atoms at the on-top site, indicating a single atom alloy surface. By increasing the palladium coverage

to approximately 0.05 ML and above, a second v(CO) stretching peak was seen at 1950 cm^{-1} corresponding to CO adsorbed on a palladium bridge site, indicating palladium dimer formation. The surface palladium coverage was determined using temperature programmed desorption (TPD) of CO and Auger electron spectroscopy (AES). By annealing these surfaces to 500 K, the palladium atoms diffuse into the subsurface, and a v(CO) stretching peak at 2150 cm^{-1} (CO adsorbed on silver atoms) is greatly enhanced in intensity due to subsurface palladium. The subsurface to surface palladium ratios on the single atom alloy surfaces were varied from capped Ag/Pd/Ag(111), to a 50:50 ratio, to approximately a 60:40 ratio. The ability of subsurface palladium on the Pd/Ag(111) SAA surfaces to facilitate hydrogen dissociation was explored using H$_2$ and D$_2$ TPD.

9:40am HC+2D+SS-WeM-6 Propyne Hydrogenation over a Pd/Cu(111) Single Atom Alloy Catalyst Studied with Infrared Spectroscopy, *Mohammed Abdel-Rahman, M Trenary,* University of Illinois at Chicago

The hydrogenation of propyne (C$_3$H$_4$) to propylene (C$_3$H$_6$) using a Pd/Cu(111) single atom alloy (SAA) has been studied using polarization dependent-reflection absorption infrared spectroscopy. This method allows for simultaneous monitoring of reactants and products in the gas-phase and species adsorbed on the surface during the reaction. The results were compared with the hydrogenation of propyne using Pd-free Cu(111) as well as previous studies on Pd/Cu SAA alumina-supported metal catalysts. Propylene production first occurs at 383 K as indicated by the presence of an infrared peak at 912 cm^{-1}, which is a uniquely characteristic of gas-phase propylene. The presence of propyne oligomers on the surface is indicated by a dramatic increase in the peak intensity at 2968 cm^{-1} at temperatures above 400 K. The progression of the peaks at 912 and 3322 cm^{-1} was used to calculate the rate of production of propylene and the rate of consumption of propyne, respectively. This reaction rate was used to determine a turnover frequency (TOF) for the reaction on the Pd/Cu SAA catalyst.

11:00am HC+2D+SS-WeM-10 "Single-Atom" Catalysis: How Structure Influences Reactivity, *Gareth S. Parkinson,* TU Wien, Austria **INVITED**

The field of „single-atom" catalysis (SAC) [1-2] emerged as the ultimate limit of attempts to minimize the amount of prescious metal used in heterogeneous catalysis. Over time, it has become clear that metal adatoms behave differently to supported nanoparticles [3-4], primarily because they form chemical bonds with the support and become charged. In this sense, SAC systems resemble the mononuclear coordination complexes used in homogeneous catalysis, and there is much excitement that SAC could achieve similar levels of selectivity, and even heterogenize problematic reactions currently performed in solution. It is important to note, however, that homogeneous catalysts are designed for purpose based on well-understood structure-function relationships, but the complexity of real SAC systems means that the structure of the active site is difficult to determine, never mind design. In this talk, I will describe how we are using precisely-defined model supports [5] to unravel the fundamentals of SAC. I will show a selection of our latest results in this area, including scanning probe microscopy, x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) data to show how the local structure of Ir$_1$/Fe$_3$O$_4$(001) and Rh$_1$/Fe$_3$O$_4$(001) single atom catalysts changes based on preparation and adsorption of reactants, and how the structures obtained can be rationalised by analogy to Ir(I) and Ir(IV) complexes, respectively. If time permits, I will also show that CO oxidation activity in the Pt$_1$/Fe$_3$O$_4$(001) system is promoted by water.

[1] Qiao, B., et al., Single-atom catalysis of CO oxidation using Pt1/FeOx. Nature Chemistry **3** (2011) 634-41.

[2] Liu, J., Catalysis by supported single metal atoms. ACS Catalysis **7** (2016) 34-59.

[3] Gates, B.C., et al., Atomically dispersed supported metal catalysts: perspectives and suggestions for future research. Catalysis Science & Technology **7** (2017) 4259-4275.

[4] Parkinson GS, Catalysis Letters 149 (2019), 1137-1146

[5] Bliem, R., et al., Subsurface cation vacancy stabilization of the magnetite (001) surface. Science, 346 (2014) 1215-8.

11:40am HC+2D+SS-WeM-12 Oxidation Reactions on Rh(111), *Marie Turano, G Hildebrandt,* Loyola University Chicago; *R Farber,* The University of Chicago; *D Killelea,* Loyola University Chicago

The uptake and subsequent surface structures of oxygen on transition metal surfaces reveal much about the reactivity of the metal catalyst. On clean Rh(111) at room temperatures in ultra high vacuum (UHV), oxygen molecules (O$_2$) readily dissociate into two adsorbed oxygen atoms,

asymptotically approaching a saturation coverage of 0.5 monolayers (ML, 1 ML= 1.5×10^{15} O atoms cm^{-2}). However, exposing Rh(111) to gas-phase oxygen atoms (atomic oxygen, AO) generated by thermally cracking molecular oxygen over a hot Ir filament, allows for higher oxygen coverages. In addition, oxygen not only adsorbs to the surface, but it may also penetrate into the subsurface region of the crystal. After atomic oxygen exposures at elevated temperatures, the Rh(111) surface is covered in a combination of oxides, adsorbed surface oxygen, and subsurface oxygen (O_{sub}). The coexistence of a variety of structures allows for the determination of which species is reactive to the oxidation of carbon monoxide (CO) on highly oxidized Rh(111) surfaces. Using scanning tunneling microscopy (STM), we have determined that CO oxidation occurs mainly at the interface between the metallic and oxidic surface phases on Rh(111) where the O_{sub}, upon emergence from the bulk, replenishes the surface oxygen. Once O_{sub} is depleted, CO consumes the oxide and the surface quickly degrades into the (2×2)-O+CO adlayer.

12:00pm **HC+2D+SS-WeM-13 Adsorption and Motion of Atomic Oxygen on the Surface and Subsurface of Ag(111) and Ag(110)**, *S Isbill, C Mize, L Crosby, Sharani Roy*, University of Tennessee Knoxville

Silver surfaces act as important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards understanding the mechanism of heterogeneous catalytic oxidation by silver, the role of subsurface oxygen in such catalysis has yet to be elucidated. Subsurface oxygen is adsorbed just beneath the surface of the metal and is believed to play an important role in surface reconstruction and oxidation catalysis. In the present study, density functional theory (DFT) was used to study the interactions of atomic oxygen with the surface and subsurface of the Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption of atomic oxygen at different coverages and examine its effects on the structural and catalytic properties of silver. Our study of O/Ag(111) showed that adsorption of atomic oxygen was strong at low coverage but became weaker with an increase in coverage, much more so for surface oxygen than for subsurface oxygen. Therefore, at higher and industrially relevant oxygen coverages, oxygen preferred to bind to the subsurface than to the surface. In contrast, atomic oxygen bound more strongly to the surface than to the subsurface at all studied coverages. Based on the results from DFT, we constructed analytic models for adsorption in O/Ag(111) and O/Ag(110) as well as performed kinetic Monte Carlo simulations to explain the differences in coverage dependence of surface adsorption versus subsurface adsorption on the two surfaces. The results provide qualitative insight on why surface and subsurface oxygen might have qualitatively different effects on the electronic, geometric, and catalytic properties of silver.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+OX+SS-WeA

Metal-Support Interactions Driving Heterogeneously-Catalyzed Reactions

Moderators: Aravind Asthagiri, The Ohio State University, Jason Weaver, University of Florida

2:20pm **HC+OX+SS-WeA-1 Yittria-stabilized Zirconia (YSZ) Supports for Low Temperature Ammonia Synthesis**, *Z Zhang, S Livingston,* Colorado School of Mines*; L Fitzgerald,* University College Dublin*; D Way,* **Colin Wolden**, Colorado School of Mines

The use of renewable hydrogen for distributed synthesis of ammonia requires the development of efficient catalysts and processes that operate under mild conditions. Here we introduce yittria stabilized zirconia (YSZ) as a more active Ru catalyst support for NH_3 synthesis than traditionally used supports such as Al_2O_3. The addition of Cs promoter increased rates an order of magnitude higher by reducing the apparent activation energy from 103 kJ/mol to 65 kJ/mol. The rate enhancement is largely insensitive to the amount of promoter addition, with Cs outperforming Ba and K by a factor of 2. At 400°C under 1.0 MPa, the synthesis rate was comparable with that of most active oxide-supported Ru catalysts. The rate becomes inhibited by H_2 absorption at low temperature (< 350°C), but the use of lower H_2:N_2 ratios enables the rate to remain comparable to what is observed in stoichiometric mixtures at temperatures > 400°C. A detailed microkinetic model was developed that successfully captures the observed behavior, revealing that adsorption is coverage dependent. These results provide insight and direction into developing alternatives to Haber-Bosch for distributed synthesis of green ammonia.

2:40pm **HC+OX+SS-WeA-2 Operando PTRF-XAFS Technique for 3D Structure Determination of Active Metal Sites on a Model Catalyst Surface under Working Conditions**, *Satoru Takakusagi, L Bang, D Kido, Y Sato, K Asakura,* Hokkaido University, Japan

Polarization-dependent total reflection fluorescence (PTRF)-XAFS is a powerful technique which can determine 3D structure of highly dispersed metal species on a single-crystal surface by measuring polarization-dependent XAFS of the metal species. To obtain atomic-level understanding of metal/oxide-support interaction in heterogeneous catalysis, we have determined the precise 3D structures of single metal atoms and metal clusters deposited on single-crystal oxide surfaces such as $TiO_2(110)$ and $Al_2O_3(0001)$ by UHV PTRF-XAFS apparatus.[1]

Recently we have constructed a new apparatus which enables us to measure PTRF-XAFS of active metal species dispersed on a single-crystal oxide surface under working condition. A compact vacuum chamber which works both as PTRF-XAFS cell and batch-type reactor was designed and constructed. The sample can be transferred without exposure to air from another UHV chamber where the sample preparation (ion sputtering, annealing and metal deposition) and its surface characterization (LEED, XPS) are carried out. The sample in the compact chamber can be heated at high temperatures (< 700 °C) in the presence of reactant gases (typically 10~100 Pa), which makes the operando PTRF-XAFS measurements possible. Thus 3D structure-activity relationship of the active metal species on an oxide surface in heterogeneous catalysis can be obtained. We will show the details of the operando PTRF-XAFS technique and its application to CO oxidation on a $Pt/Al_2O_3(0001)$ surface.

(References)

[1] S. Takakusagi et al., *Chem. Rec.* **18** (2018) 1*, J. Phys. Chem. C* **120** (2016) 15785, *Top. Catal.* **56**(2013*)* 1477, *Phys. Chem. Chem. Phys.* **15**(2013*)* 14080.

3:00pm **HC+OX+SS-WeA-3 Understanding and Tuning Catalytic Materials Using Nanocrystal Precursors**, *Matteo Cargnello,* Stanford University **INVITED**

Catalytic processes are central to the goal of a sustainable future. A promising approach in developing catalytic materials is represented by the design of catalytic sites based on the knowledge of reaction mechanisms and structure-property relationships and aided by computation, and in the precise synthesis of these sites at the atomic and molecular level. The materials-pressure gap, however, still hinders the full realization of this strategy. Nanocrystal precursors, with tunable active sites and compositions, can help bridge this gap. The goal of this talk is to show how

this approach can provide not only fundamental understanding of catalytic reactions, but also represents a way to precisely engineer catalytic sites and metal-support interactions to produce efficient catalysts that are active, stable and selective for several important catalytic transformations. Examples of the use of these building blocks as supported systems or in combination with hybrid organic materials will be shown, both to understand trends in methane and CO2 activation, and in the preparation of optimized catalytic systems combining multiple active phases. In all these examples, important efforts to obtain useful structure-property relationships will be highlighted, with this knowledge used to prepare more efficient catalysts for sustainable production of fuels and chemicals.

4:20pm **HC+OX+SS-WeA-7 CO_2 Hydrogenation on Supported Zirconium Oxide Clusters**, *Yilin Ma*[1], Stony Brook University*; M White,* Brookhaven National Laboratory

In this work, zirconium atoms and zirconium oxide clusters are deposited onto metal/metal oxide surfaces as model "inverse" catalysts for the study of CO_2 hydrogenation. The control over the stoichiometry of clusters and the oxidation state of the metal centers enables the study of atomic level details such as identification of active sites, interfacial electron transfer and the role of sulfur vacancies. Recent AP-XPS, AP-IR and STM results of supported zirconium oxide on $Cu_2O/Cu(111)$ surface will be presented. Reactivity studies over $Zr/Cu_2O/Cu(111)$ show that the formation of CO_2^- (ad)and $HCOO^-$ can be seen on regions with the presence of Zr on Cu_2O surface during the reaction condition(CO_2/H_2=1, total pressure=0.5torr), however CO_2 only binds weakly on bare $Cu_2O/Cu(111)$ surface. Moreover, the change of zirconium oxidation state indicates the adsorption of CO_2 happens on metal or metal-support interface, where the zirconium gets oxidized when exposing to CO_2. Some DFT studies of above systems will also be shown, including the electronic structures of clusters, binding sites of CO_2 molecules, etc.

4:40pm **HC+OX+SS-WeA-8 Tuning Surface Hydrophobicity to Enhance Reaction Rate of the Lewis Acid Zeolite Nano Sn Beta for Alcohol Ring Opening of Epoxides**, *Nicholas Brunelli, A Spanos, A Parulkar, N Deshpande,* The Ohio State University

Ring opening epoxides produces compounds that are valuable in the production of fine chemicals and pharmaceuticals. Recent work[1]has demonstrated that the bulky reactants typically involved in fine chemical synthesis benefit from reducing the length scale of the materials to produce nano-zeolites (nano-Sn-Beta), which requires using a custom-synthesized structure directing agent in hydroxide conditions. While the nanozeolites can achieve higher overall conversion than Sn-Beta synthesized using fluoride conditions, the initial reaction rate is higher for Sn-Beta that tends to be hydrophobic compared to nano-Sn-Beta that is demonstrated to be hydrophilic. These results suggest that the alcohol ring opening reaction is sensitive to the reaction environment. The surface of nano-Sn-Beta can be treated to reduce the amount of defects and correspondingly increase the hydrophobicity. Interestingly, the treatment of nano-Sn-Beta materials more than doubles the observed reaction rate. Overall, this demonstrates a valuable method to tune the reaction environment that could be widely applicable to many chemical reactions.

References

(1) Parulkar, A.; Spanos, A. P.; Deshpande, N.; Brunelli, N. A. Synthesis and catalytic testing of Lewis acidic nano zeolite Beta for epoxide ring opening with alcohols. *Applied Catalysis A: General,* **2019**, *577*, 28–34.

5:00pm **HC+OX+SS-WeA-9 Understanding Metal-Metal and Metal-Support Interactions in Bimetallic Catalysts**, *Donna Chen,* Univeristy of South Carolina*; S Farzandh, D Shakya, A Brandt, T Maddumapatabandi,* University of South Carolina **INVITED**

Bimetallic catalysts are known to exhibit superior properties compared to their individual pure metal components, but in many cases the nature of these improved properties is not well understood. The main goal of this work is to understand how oxidation states, metal-support interactions, and metal-metal interactions in supported bimetallic clusters can be used to control catalytic activity. Specific catalytic reactions investigated are the water gas shift reaction (WGS)on Pt-Re and selective hydrogenation of unsaturated aldehydes on Pt-Sn. Model catalyst surfaces are prepared via vapor-deposition of metal clusters on single-crystal oxide and carbon supports. These surfaces are fully characterized by a variety ultrahigh vacuum (UHV) surface science techniques and their activities are studied in a microreactor (P~ 1 atm) coupled to the UHV chamber. Scanning tunneling

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

microscopy investigations indicate that exclusively bimetallic clusters can be prepared by sequential deposition of metals. For the WGS reaction, the active site is determined to be Pt with subsurface Re, while Re oxide does not play a role. Density functional theory studies show that the presence of subsurface Re decreases the adsorption energy of CO on Pt, thus preventing Pt active sites from being poisoned by CO. WGS activity increases with increasing perimeter for Pt/TiO$_2$ clusters, and the turnover frequency is also lower in the absence of the TiO$_2$ support. For hydrogenation on furfural, the Pt-Sn alloy surface exhibits high selectivity to furfuryl alcohol compared to pure Pt, whereas furan and tetrahydrofuran are the main products on Pt.

Surface Science Division
Room A220-221 - Session SS+AS+HC+OX-WeA

Reactions at Alloy Surfaces and Single Atom Catalysis

Moderators: Erin Iski, University of Tulsa, Bruce E. Koel, Princeton University

2:20pm **SS+AS+HC+OX-WeA-1 Correlating Structure and Function for Nanoparticle Catalysts**, *Graeme Henkelman,* University of Texas at Austin **INVITED**

Metal nanoparticles of only 100-200 atoms are synthesized using a dendrimer encapsulation technique to facilitate a direct comparison with density functional theory (DFT) calculations in terms of both structure and catalytic function. Structural characterization is done using electron microscopy, x-ray scattering, and electrochemical methods. Combining these tools with DFT calculations is found to improve the quality of the structural models. DFT is also successfully used to predict trends between structure and composition of the nanoparticles and their catalytic function for reactions including the reduction of oxygen and selective hydrogenation. This investigation demonstrates some remarkable properties of the nanoparticles, including facile structural rearrangements and nanoscale tuning parameters which can be used to optimize catalytic rates. In this presentation I will focus on a pair of random alloy bimetallic nanoparticles which have complete different trends in hydrogenation activity as a function of composition. Pd/Au is found to be tunable as a function of composition whereas Pt/Au is not. The reason behind these different behaviors will be discussed.

3:00pm **SS+AS+HC+OX-WeA-3 Surface Reactivity of PtAg and PdAg: From Single-Atom Alloys to Supported Nanoparticles**, *Dipna Patel*[1][2], Tufts University*; C O'Connor, R Madix, C Friend,* Harvard University*; E Sykes,* Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt and Pd are catalytically active towards hydrogenation, they are often costly, and can suffer from poisoning by CO and coke. Previously, Ag based catalysts have been modified by alloying Pt or Pd for applications in highly selective heterogeneous catalysis. This has shown promise for catalyst design since Ag is cheaper and more resilient to poisoning. It is well known that ensemble size can dramatically change the catalytic pathway, however the atomic-scale structure of PtAg and PdAg alloys and their relation to catalytic activity is still unknown. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of Pt deposited on Ag(111) as a function of alloying temperature. At low temperatures, intermixing of PtAg 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. STM characterization of the surface structure of PdAg alloys reveals the formation of large Pd islands on Ag(111). Using STM, we investigated H$_2$ activation on active Pd sites and spillover on to Ag(111). The characterization of PtAg and PdAg surface alloys enables us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and to inform catalyst design that optimizes catalytic selectivity.

3:20pm **SS+AS+HC+OX-WeA-4 Single-site Catalysts by Metal-ligand Complexation at Surfaces: From Model Systems in Vacuum to High-pressure Catalysis on Oxide Supports**, *Steven L. Tait,* Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination networks at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. Studies of model systems in ultra-high vacuum allow for detailed characterization of the structure and chemistry of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands and found activity toward dioxygen activation with a high degree of selectivity compared to vanadium nanoparticles. Reaction with O$_2$ causes an increase in V oxidation state from V^{II} to V^{IV}, resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface [1]. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. New results extend these chemical studies to more complex systems that include bimetallic sites and redox isomer systems [2-3], which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble quasi-square planar metal-organic complexes on high surface area powdered oxides under ambient conditions through a modified wet-impregnation method. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly [4-5]. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts. They also show excellent activity for hydrogenation in flow reactor experiment.

1. Tempas, Morris, Wisman, *et al.*, *Chem. Sci.*, **9**, 1674-1685 (2018). DOI: 10.1039/C7SC04752E

2. Tempas, Skomski, Cook, *et al.*, *Chem. Eur. J.*, **24**, 15852–15858 (2018). DOI: 10.1002/chem.201802943

3. Morris, Huerfano, Wang, *et al.*, *Chem. Eur. J.*, **25**, 5565-5573 (2019). DOI: 10.1002/chem.201900002

4. Chen, Sterbinsky, and Tait, *J. Catal.*, **365**, 303-312 (2018). DOI: 10.1016/j.jcat.2018.07.004

5. Chen, Ali, Sterbinsky, *et al.*, *ChemCatChem*, *in press* (2019).DOI: 10.1002/cctc.201900530

4:20pm **SS+AS+HC+OX-WeA-7 Controlling the Local Coordination and Reactivity of Oxide-supported Atomically Dispersed Pt-group Species**, *Phillip Christopher,* University of California at Santa Barbara **INVITED**

The synthesis of oxide supported Pt-group catalysts typically produces metal particles with dimensions of a few nanometers. Recent work has shown that Pt-group species can co-exist as nanoparticles and single atoms, and that careful synthetic approaches can produce exclusively single atoms. Interest in the reactivity of supported isolated Pt-group metal atoms stems from the maximized metal utilization efficiency, unique reactivity or selectivity, connection to organometallic catalysis, and the potential for making well-defined active sites. It has proven challenging to characterize the intrinsic catalytic activity of these dispersed active sites on oxide supports at a level that relates local electronic and geometric structure to function. The difficulty arises from their atomic dispersion, heterogeneity in the local coordination of active sites on most catalysts (i.e. isolated species sit at different sites on the support), dynamic changes in local coordination under reactive environments, and often the low loading of metal that is required to achieve site isolation.

In this talk I will describe a synthetic approach to produce isolated Pt-group atoms that exhibit uniformity in their bonding environment on an oxide support and show how a combination of microscopy, spectroscopy and theory can be used to describe the local coordination of these species. Then I will describe two different approaches to control the local environment of Pt-group atoms: (1) through varied pre-treatment that tunes the local coordination and oxidation state of the single atom, and (2) through the site selective deposition of single atoms near well-defined acid sites on oxide supports. Detailed characterization by a combination of

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spectroscopy and microscopy is used to develop structure-function relationships for these well-defined single atom active sites in the context of CO oxidation, methanol carbonylation and ethylene hydroformylation. This work highlights the ability to tune the local environment of single Pt-group atom active sites on oxide supports in analogous ways to the engineering of organometallic catalysts.

5:00pm SS+AS+HC+OX-WeA-9 Coordination Defines Reactivity of a Model Single-atom Catalyst: Ir$_1$/Fe$_3$O$_4$(001), *Zdenek Jakub*[1], *J Hulva, M Meier, U Diebold, G Parkinson,* TU Wien, Austria

The development of single-atom catalysts (SACs) was originally motivated by saving of the precious metal, but an equally intriguing characteristic of the ideal SAC is potentially high selectivity due to the high number of identical active sites. The coordination of the active metal center is known to play a crucial role in homogeneous catalysis, and in this talk, I will demonstrate that similar effects can be observed on a model single atom catalyst: Ir$_1$/Fe$_3$O$_4$(001). Using scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), temperature programmed desorption (TPD), x-ray photoemission spectroscopy (XPS) and DFT calculations, I will show that the coordination of single Ir$_1$ adatoms can vary depending on preparation, and that the local environment has dramatic consequences for the ability of the catalyst to adsorb CO. As deposited at room temperature, Ir atoms take 2-fold coordination to the surface oxygen atoms. Upon annealing, they incorporate into the first surface layer (5-fold coordinated Ir$_1$), and then into the first subsurface layer (6-fold coordinated Ir$_1$). The 2-fold adatoms can form both monocarbonyls and dicarbonyls, but the 5-fold Ir only binds a single CO. The structures are understood by analogy to square planar Ir(I) and octahedral Ir(III) complexes, respectively. The 6-fold Ir is coodinatively saturated, and thus deactivated for CO adsorption. These results show that control of the local coordination environment is critical to design so-called single-atom catalysts, and that incorporation into the support can be as critical a deactivation mechanism as thermal sintering.

5:20pm SS+AS+HC+OX-WeA-10 Capturing the Early Stages of Oxidation on Low-Index Ni and Ni-Cr Surfaces, *William H. Blades, P Reinke,* University of Virginia

The early stages of oxidation and corrosion of alloys control the structure and development of the oxide layer and therefore decisively influence its protective function. To this end, we have studied thenanoscale evolution of surface oxides prior to the formation of a complete layer. The oxidation of Ni(100), Ni(111), and Ni-Cr(100), Ni-Cr(111) surfaces was captured by sequential oxidization and measured with scanning tunneling microscopy/spectroscopy (STM/STS). The early-stage oxidation, and the influence of alloy composition and crystallographic orientation on surface reactivity, was studied by comparing pure Ni(100/111) and Ni-Cr(100/111) surfaces. Alloy thin films (8-18 wt.% Cr) were prepared on MgO(100/111) and exposed to oxygen up to 400 L at 773 K. Under these conditions, oxide nucleation is predicated by the development of oxygen adlayers on both the pure Ni(100/111) surfaces. The formation of a c(2x2)-O chemisorbed phase on the Ni(100) surface causes the step edges to facet into {100} segments, kinetically limiting NiO growth. However, no such faceting is observed on the Ni(111) surface and the nucleation and growth of NiO begins after only 300 L of O$_2$. Our experiments demonstrate that the addition of small amounts of Cr completely change the oxidation pathways. On the Ni-Cr(100) surface, the nucleation and growth of NiO initiates along the step edges, forming low-angle NiO wedges with a NiO-Ni(7x8) superstructure. Terrace oxide growth commences with the nucleation of small oxide particles, driven by the presence of Cr, which grow into large oxide nodules after further oxidation. NiO growth extends into the terraces and takes a NiO-Ni(6x7) cube-on-cube interfacial relationship. Several novel surface reconstructions are observed and are tentatively attributed to Cr(100)-O reconstructions, suggesting surface segregation and phase separation of BCC Cr. Similarly, nano-sized oxide particles nucleate on the Ni-Cr(111) terrace and step edges, while single atomic NiO rows extend across the surface. Oxide nodules, similar to those found on the Ni-Cr(100) surface are observed and grow laterally along the terraces. Each of these aforementioned surface oxides present unique electronic signatures, and STS maps are used to quantify the spatial variations in their density of states and band gaps. The electronic heterogeneity of the surface underscores that the use a homogenous electric field to capture oxidation kinetics at the alloy-oxide interface should be revisited.

5:40pm SS+AS+HC+OX-WeA-11 Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous Ag$_{0.03}$Au$_{0.97}$, *Matthijs van Spronsen,* Lawrence Berkeley National Laboratory*; B Zugic,* Harvard University*; M Salmeron,* Lawrence Berkeley National Laboratory*; C Friend,* Harvard University

Activating pretreatments can be used to tune both surface composition and surface structure of bimetallic alloy catalysts. Careful selection of both gas mixtures and reaction temperatures can lead to surfaces that are able to achieve optimum selectivity and activity under steady-state reaction conditions. The activation-induced changes in material properties of a nanoporous (np) Ag$_{0.03}$Au$_{0.97}$ alloy and their subsequent evolution under steady-state conditions for CH$_3$OH oxidation are presented. Initial activation by oxidation in O$_3$ at 423 K leads to the formation of AgO and Au$_2$O$_3$ driving a strong Ag enrichment in the near-surface region, based on ambient-pressure X-ray photoelectron spectroscopy (AP XPS) and extended X-ray absorption fine structure (EXAFS) analysis. Exposing this oxidized np Ag$_{0.03}$Au$_{0.97}$ to the O$_2$/CH$_3$OH reaction mixture reduces both Ag and Au oxides and results in a surface alloy locally highly enriched in Ag. Both the oxides and the highly Ag enriched alloy unselectively oxidize methanol to CO$_2$. However, at the reaction temperature of 423 K, the Ag slowly realloys with Au. Although decreasing, the composition remains enriched in Ag in the top few nanometers under steady-state conditions. The Ag content in the surface is 29 at.% in steady state and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO, leading locally to Ag-rich alloys, were observed with environmental transmission electron microscopy (E TEM). These local Ag-rich AgAu alloy regions are critical for initiation of the catalytic cycle through O$_2$ dissociation. Calculations based on density-functional theory (DFT) indicate that the O on the surface assist in stabilizing the Ag. Moreover, an essential factor for retaining this local enrichment in Ag is the modest reaction temperature of 423 K. At higher temperatures, bulk diffusion induces sintering and redistribution of the Ag, leading to a loss of activity. These findings demonstrate that material properties determining catalytic activity are *dynamic* and that metastable (kinetically trapped) forms of the material may be responsible for catalysis. Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

6:00pm SS+AS+HC+OX-WeA-12 Reduction and Oxidation of Transition Metal Oxides: From Tailoring the Surface and Interface Properties to the New Crystalline Phases Formation, *Dominik Wrana,* Jagiellonian University, Poland*; C Rodenbücher,* Forschungszentrum Jülich GmbH, Germany*; K Cieślik, B Jany,* Jagiellonian University, Poland*; K Szot,* Forschungszentrum Jülich GmbH, Germany*; F Krok,* Jagiellonian University, Poland

In the recent years transition metal oxides have attracted tremendous interest, mostly due to the manifold real applications, ranging from (photo)catalysis, through memristive and neuromorphic device development, to energy storage and production. A specific quality which makes them so versatile is the ease by which their electronic and structural properties can be controlled by changing a cation's reduction state.

In this presentation we will present an overview of the impact that thermal reduction and oxidation have on the surface properties, which enable a precise control over the valence state of prototypical binary and ternary oxide representatives: TiO$_2$ and SrTiO$_3$. We will focus on the preparation methods under regular UHV conditions and upon additionally reduced oxygen partial pressure.

Reduction of both crystals results in the formation of oxygen vacancies and therefore d-electrons, which leads to changes in the work function and a corresponding rise in electrical conductivity, which could be tuned over many orders of magnitude [1]. A newly developed SPM-based technique, combining LC-AFM and KPFM, allows both measurements to probe the same area of the reduced TiO$_2$(110) surface [2], helping understanding of the nanoscale resistive switching . Besides the change in electrical properties, the surface structure evolves towards nonstoichiometric reconstructions [1], due to the increased oxygen deficiency. Surprisingly, not only is oxygen flow possible during UHV annealing of the oxide crystal, but also incongruent cation sublimation can be triggered, as demonstrated for the perovskite oxides like SrTiO$_3$ [3]. Extremely low oxygen partial pressure (ELOP), achieved by the use of an oxygen-getter, initiates SrTiO$_3$ crystal decomposition and the formation of stable monocrystalline cubic TiO nanowires with a c(4x4) reconstructed surface [4]. Such bottom-up

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growth of conductive TiO nanostructures could be an alternative to other costly methods, resulting in the creation of the TiO/SrTiO$_3$ interface, with a sharp transition between Ti^{2+} and Ti^{4+} states, proven by atomically-resolved electron microscopy. This oxide heterostructure provides an interesting metal/insulator junction with a 0.6 eV work function difference [5], opening many new possibilities for (photo)catalysis and aiding in the search for exotic interface states.

[1] Wrana, D. et al. (2018) *Applied Surface Science*, *432*, 46-52.

[2] Rodenbücher, C. et al. (2018) *APL Materials*, *6*(6), 066105.

[3] Rodenbücher, C. et al. (2017) *physica status solidi (RRL)–Rapid Research Letters*, *11*(9), 1700222.

[4] Wrana, D. et al. (2019) *Nanoscale*, *11*(1), 89-97.

[5] Wrana, D. et al. (2019) Beilstein Arch., 201912.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A213 - Session HC+2D+SS-ThM

Nanoscale Surface Structure in Heterogeneously-Catalyzed Reactions

Moderators: Rebecca Fushimi, Idaho National Laboratory, Eric High, Tufts University

8:20am **HC+2D+SS-ThM-2 Low-temperature Investigation of Propylene on TiO₂/Au(111)**, *M Gillum, M DePonte, J Wilke, E Maxwell, V Lam, D Schlosser, **Ashleigh Baber**, James Madison University*
The partial oxidation of propylene creates industrially important feedstocks that are used in a multitude of chemical fields ranging from textiles to cosmetics to air sanitation. One avenue of research on propylene oxidation is being conducted using metal/oxide model catalysts, as they have shown an affinity for high selectivity oxidation reactions. To gain a comprehensive understanding of olefin intermolecular and surface interactions, temperature programmed desorption (TPD) studies were conducted using Au(111)–based model catalysts with different surface preparations. Using TPD, we were able to identify the specific adsorption sites of propylene on a TiO₂/Au(111) model catalyst, differentiating between the TiO₂ nanoparticles, the Au-TiO₂ interface, and the gold surface. Desorption kinetics propylene were studied on pristine and titania–modified Au(111) surfaces. Desorption products were monitored using quadrupole mass spectrometry and the surface morphology was analyzed using ex-situ atomic force microscopy. The presence of titania was confirmed via X-ray photoelectron spectroscopy. By understanding the characteristic behaviors with combined experimental techniques, active sites and reaction pathways for partial olefin oxidation over Au–based catalysts may be identified.

8:40am **HC+2D+SS-ThM-3 Structure and Reactivity of Supported Oxide and Metal Nanoparticles**, *Geoff Thornton,* University College London, UK **INVITED**
Heterogenous catalysts typically consist of metal nanoparticles on an oxide support. Model experiments involving nanoparticle growth on single crystalline oxide have been successfully employed to understand aspects of the nucleation, structure and reactivity. This contributes to catalysis design programs. Many subtleties continue to emerge, some of which will be discussed in this talk. For instance, low temperature STM experiments have allowed direct imaging of CO overlayers formed on the Pd nanoparticles themselves supported on TiO₂. The results show that the nanoparticles grow like a carpet over substrate step-edges, giving rise to a curved top facet that changes the adsorption behavior. Au nanoparticles supported by TiO₂ have been the subject of much work since the discovery by Haruta that Au is a low temperature oxidation catalyst. Despite this earlier work there has been no definitive evidence for the binding site or the direction of charge transfer associated with gold atoms and nanoparticles on the model substrate TiO₂(110). We show with STM that single Au atoms are in indeed bound to oxygen vacancies on the substrate, with dimers similarly anchored. Associated DFT calculations suggest electron transfer from bridging O vacancies to Au. XPEEM in conjunction with STM have also been used to probe the electronic character of Au nanoparticles as a function of particle size and coverage. Pt and related metals on CeO₂/ZrO₂ are used for CO oxidation in autocats. The accepted mechanism is that the oxide supplies oxygen to the metal to react with CO, with the oxide being directly reoxidized. In XPEEM studies of a model inverse catalyst we show that the reoxidation can also involve the metal.

9:20am **HC+2D+SS-ThM-5 Catalysis by Well-defined Oxide Nanostructures: From Atomic-scale Properties to Rational Design**, *Fan Yang,* Dalian Institute of Chemical Physics, China
The catalytic properties of nano-oxides are increasingly recognized and currently explored for a wide range of applications. However, the nature of the active sites of these nano-oxides, as well as their catalytic chemistry, remain poorly understood, because of the difficulties to access these surface/interfacial sites at the atomic level. Using molecular beam epitaxy, we construct well-defined oxide nanostructures (NSs) on planar metal or oxide surfaces, which serve as the model systems for understanding the catalytic chemistry of the metal-oxide interface and nano-oxides. In this talk, we report our recent progress in the studies of low temperature CO oxidation and CO disproportionation reaction, using supported FeO and CeOₓ NSs as the model catalysts. Overall, we wish to demonstrate that the control over supported oxide NSs could enable a wide range of catalytic properties for the rational design of highly efficient catalysts.

9:40am **HC+2D+SS-ThM-6 Structural and Chemical Effects of Cesium on the Cu(111) and CuₓO/Cu(111) Surface**, *Rebecca Hamlyn[1],* Stony Brook University*; M Mahapatra,* Brookhaven National Laboratory*; I Orozco,* Stony Brook University*; M White, S Senanayake, J Rodriguez,* Brookhaven National Laboratory
Surface additives, particularly those of alkali metals, are commonly used for promotion of catalytic processes. These processes include carbon oxide reactions such as the water-gas shift and methanol synthesis over Cu-based catalysts. Both reactions are known to be promoted by Cs doping. Partially oxidized Cu is also understood to have a critical role in the activity of the aforementioned processes, as strictly metallic copper will not survive under redox conditions. In an effort to better understand how small additions of alkalis such as Cs act as promoters, we have carried out model studies of cesium over a metallic and oxidized copper surface using scanning tunneling microscopy and x-ray photoelectron spectroscopy. We find that the oxide structure assists in anchoring Cs over the weaker electrostatic interactions with the bare copper surface, allowing for room temperature imaging. Furthermore, with higher coverages or elevated temperature, cesium induces formation of a new ordered structure. This work provides a molecular-scale understanding of the cesiated surface, and serves as a basis for insight toward its mechanism of action in conversion of relevant gases (H₂O, CO, CO₂).

11:00am **HC+2D+SS-ThM-10 Mythbusting: From Single Crystals in UHV to Catalytic Reactors**, *Robert Madix,* Harvard University **INVITED**
For decades it has been an objective of surface science studies of chemical reactivity to make a direct connection to heterogeneous catalysis. Over these years the difficulties encountered in connecting these two areas of research gave rise to the dismissal of this possibility by the catalysis community and the invention of such shorthand terms as "pressure gap" and "materials gap" to express this view. Usually overlooked is also the fact that catalytic reactions are conducted at much higher temperatures than the related studies on single crystal surfaces, so a "temperature gap" also exists. In fact, these regimes of reactivity are directly linked by fundamental knowledge of the identity and rate constants for the operative elementary steps comprising the catalytic cycle under catalytic conditions. Further, for many catalytic materials, its state can be defined by the reaction conditions themselves in quaisi-thermodynamic terms. Connection between the reactivity observed on the single crystals with that on the catalyst surface is possible by the use of a transient pressure method which is conducted over the actual catalyst material under Knudsen flow conditions. Recently we have demonstrated this historically elusive connection between UHV-based studies and catalytic performance for the catalytic oxygen-assisted synthesis of methyl formate from methanol over a nanoporous gold catalyst. The connection is entirely based on the kinetics and mechanism determined on single crystal gold surfaces. A brief history of this development will be discussed and the specifics of how this bridge was built examined.

11:40am **HC+2D+SS-ThM-12 Cooperativity Between Pd and AgOₓ Phases on Ag(111)**, *V Mehar, M Yu, Jason Weaver,* University of Florida
Metals dispersed on a reactive metal-oxide have potential to effect selective catalysis through cooperative interactions between the co-existing metal and metal-oxide phases. In this talk, I will discuss our recent investigations of the structure and reactivity of oxidized Ag(111) as well as Pd/AgOₓ surfaces that are generated by depositing metallic Pd onto a single-layer AgOₓ structure in ultrahigh vacuum (UHV). Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) show that the oxidation of Ag(111) with atomic oxygen mainly produces a single-layer AgOₓ phase with a p(4 x 5r3) structure as well as smaller amounts of p(4 x 4) and c(3 x 5r3) structures during the initial stages of oxidation. Surface infrared spectroscopy and temperature programmed reaction spectroscopy (TPRS) demonstrate that the single-layer AgOₓ structures are nearly unreactive and bind CO negligibly at temperatures down to ~100 K. In contrast, we find that CO adsorbs and oxidizes efficiently on Pd islands during TPRS, even when the AgOₓ phase is the only oxidant source. STM further demonstrates that the metallic Pd islands induce partial reduction of the AgOₓ support structure at 300 K. We find that the Pd/AgOₓ surfaces continue to exhibit high CO oxidation activity with increasing Pd coverage up to nearly 2 ML (monolayer), suggesting that oxygen transfer from the

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[1] **Heterogeneous Catalysis Graduate Student Presentation Award Finalist**

AgO$_x$ phase occurs at both the interior and perimeter of Pd islands. Our results reveal a cooperative mechanism for CO oxidation on Pd/AgO$_x$ surfaces wherein O-atoms from the AgO$_x$ support phase migrate onto metallic Pd islands and react with adsorbed CO to produce CO$_2$. These findings illustrate that oxygen transport across metal/metal-oxide interfaces can be highly efficient when the oxygen chemical potential is lower on the initial metal phase (Pd) compared with the metal-oxide (AgO$_x$) support.

12:00pm HC+2D+SS-ThM-13 Migration Across Metal/Metal Oxide Interfaces: Enhancing the Reactivity of Ag Oxide with H$_2$ by the Presence of Pd/Pd Oxide, *Christopher O'Connor[1], M van Spronsen, E Muramoto, T Egle, R Madix, C Friend,* Harvard University

An important factor in exploiting bifunctionality in dilute alloy catalysts is surface migration across interfaces separating the dissimilar materials. Herein, we demonstrate the transfer of hydrogen atoms from islands of Pd oxide onto a surrounding O/Ag(111) surface using ambient pressure X-ray photoelectron spectroscopy (APXPS) and scanning tunneling microscopy (STM). These Pd oxide islands enhance the rate of reduction of Ag oxide by more than four orders of magnitude compared to pure oxidized Ag(111). The increase in the rate of reduction of Ag oxide by H$_2$ is attributed to H$_2$ activation on Pd/Pd oxide followed by migration (spillover) to Ag/Ag oxide and rapid reaction thereafter. The oxidation and subsequent reduction processes induce significant structural changes of the catalyst surface. We further establish that the transfer of hydrogen atoms occurs from islands of metallic Pd onto a surrounding Ag(111) surface using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed reaction spectroscopy (TPRS). For the metallic PdAg system, hydrogen spillover is shown to be a kinetically limited process that can be controlled by temperature, pressure of H$_2$ and surface concentration of Pd. The highest efficiency for the amount of hydrogen spillover per surface Pd occurs for a dilute concentration of Pd in Ag. This study establishes that the migration of intermediates across interfaces can occur for oxidized PdAg alloy surfaces and specifically that hydrogen atom migration has a significant effect on the catalytic activity of this type of binary material.

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic
Room A124-125 - Session LS+HC+SS-ThM

Frontiers of Time-resolved Techniques for Energy & Catalysis Highlight Session

Moderator: Jessica McChesney, Argonne National Laboratory

11:00am LS+HC+SS-ThM-10 How to Probe Solid/Liquid Interfaces using Standing-wave Photoemission?, *Slavomir Nemsak,* Lawrence Berkeley National Laboratory*; H Bluhm,* Fritz Haber Institute, Germany*; C Fadley,* University of California, Davis

A great efforts have been made in the development of *in-situ* and *operando* experimental methods in the last two decades, with ambient pressure photoelectron spectroscopy being one of the most profound examples [1]. In combination with advanced techniques, such as standing wave excitation, an unprecedented depth resolution across operating interfaces can be obtained, providing valuable information on processes governing interfacial behavior.

With the excellent depth selectivity and sensitivity to chemistry and electrostatic gradients, standing wave ambient pressure photoelectron spectroscopy is exploited to probe two different solid/liquid interfaces relevant to energy research, electrochemistry, and atmospheric and environmental science [2,3]. Liquid layers are prepared either by water adsorption in a saturated vapor ambiance or using a so-called meniscus method, in which the sample is pulled out of a liquid reservoir leaving a thin liquid film on the sample's surface. The latter experimental configuration allows also for the *operando* electrochemistry [4]. The outlook and future developments of the technique will be also discussed.

[1] D.E. Starr et al., *Chem. Soc. Rev.***42**, 5833 (2013).

[2] S. Nemšák et al., *Nat. Comm.***5**, 5441 (2014).

[3] O. Karslıoğlu et al., *Faraday Discuss.***180**, 35 (2015).

[4] S. Axnanda et al., *Sci. Rep.***5**, 9788 (2015).

11:20am LS+HC+SS-ThM-11 *In situ* Spectroscopy of Synthesis of Next-Generation Cathodes for Batteries*, Feng Wang,* Brookhaven National Laboratory

There has been considerable interest in developing low-cost, high-energy electrodes for batteries. However, synthesizing materials with the desired phases and properties has proven difficult due to the complexity of the reactions involved in chemical synthesis. Additional challenge comes from the fact that synthesis is often undertaken under conditions and, hence, the process is hard to be predicted by theoretical computations. probing of synthesis reactions allows for identification of intermediates and determination of thermodynamic/kinetic parameters governing kinetic reaction pathways, thereby enabling synthetic design of materials with desired structure and properties. In this presentation, we will report our recent results from technique development and application to *in situ* probing and synthetic control of local structural ordering and stoichiometry during synthesis of next-generation cathode materials for lithium-ion batteries. Findings from this study, along with its implication to designing viable cathodes for practical use in batteries, will be discussed.

11:40am LS+HC+SS-ThM-12 Structural Heterogeneity and Dynamics of 2D Materials Studied by Full-field X-ray Diffraction Microscopy and Ultrafast Surface X-ray Diffraction*, Haidan Wen,* Argonne National Laboratory
INVITED

Transition metal dichalcogenides (TMD) at the two-dimensional (2D) limit have sparked great interests in both fundamental physics and devices applications. Surfaces and interfaces play an important role in t he most common setting, i.e., a monolayer crystal on a substrate, for studying 2D phenomena and device applications. However, the structural characterization with atomic accuracy in this form has been a challenge because the crystal size is usually small and transmission electron microscopy is difficult to apply. In this talk, we show microscopic insights of structural properties can be obtained in the space or time domain using newly developed multimodal full-field x-ray imaging and ultrafast surface x-ray scattering. In the first example, we demonstrate full-field x-ray diffraction imaging of a monolayer 2D material at the Advanced Photon Source. The structural variation across a TMD monolayer or heterostructure is spatially correlated with the electronic properties characterized by the *in-situ* photoluminescence measurements. The correlation reveals mesoscale structure-property relationship in TMDs. In the second example, we report the first femtosecond surface X-ray diffraction using the free-electron laser at Linac Coherent Light Source to quantify the ultrafast structural dynamics of monolayer WSe2 crystals supported on a substrate. We found the absorbed optical photon energy is preferably coupled to the in-plane lattice vibrations within one picosecond whereas the out-of-plane lattice vibration amplitude remains unchanged during the first ten picoseconds. The observed nonequilibrium anisotropic structural dynamics agrees with first-principles modeling in both real and momentum space, marking the distinct structural dynamics of monolayer crystals from their bulk counterparts.

Surface Science Division
Room A220-221 - Session SS+AS+HC+TL-ThM

Surface Science of Energy Conversion and Storage

Moderators: Steven L. Tait, Indiana University, Francisco Zaera, University of California, Riverside

8:00am SS+AS+HC+TL-ThM-1 Chemical and Electrochemical Stability of Perovskite Oxide Surfaces in Energy Conversion: Mechanisms and Improvements*, Bilge Yildiz,* Massachusetts Institute of Technology **INVITED**

A broad range of highly active doped ternary oxides, including perovskites, are desirable materials in electrochemical energy conversion, catalysis and information processing applications. At elevated temperatures related to synthesis or operation, however, the structure and chemistry of their surfaces can deviate from the bulk. This can give rise to large variations in the kinetics of reactions taking place at their surfaces, including oxygen reduction, oxygen evolution, and splitting of H$_2$O and CO$_2$. In particular, aliovalent dopants introduced for improving the electronic and ionic conductivity enrich and phase separate at the surface perovskite oxides. This gives rise to detrimental effects on surface reaction kinetics in energy conversion devices such as fuel cells, electrolyzers and thermochemical

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H_2O and CO_2 splitting. This talk will have three parts. First, the mechanisms behind such near-surface chemical evolution will be discussed. Second, the dependence of surface chemistry on environmental conditions, including temperature, gas composition, electrochemical potential and crystal orientation will be described. Third, modifications of the surface chemistry that improve electrochemical stability and activity, designed based on the governing mechanisms, will be presented. Guidelines for enabling high performance perovskite oxides in energy conversion technologies will be presented.

8:40am SS+AS+HC+TL-ThM-3 Mechanism of Oxygen Reduction Reaction on Nitrogen-doped Carbon Catalysts, *Junji Nakamura,* University of Tsukuba, Japan

Nitrogen-doped carbon materials are expected to be non-Pt catalysts for 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) has been 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. Recently we have reported model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule and acridine (Ac)molecule)[2]. The DA molecules form a two-dimensional ordered structure along the direction of the HOPG substrate by self-organization. Adsorbed DA on the HOPG surface shows high ORR activity in terms of specific activity per pyridinic nitrogen and is comparable to that of pyridinic-nitrogen-doped carbon catalysts. We study the mechanism of ORR taking place on the DA/HOPG model catalyst. In acidic reaction conditions, pyridinic nitrogen is protonated to pyridinium nitrogen (NH+) species. It is suggested that the adsorption of oxygen take place on a carbon atom in a DA molecule upon reduction of the NH+ species. Generally, the reduction of NH+ is difficult to proceed thermodynamically at higher potentials above 0 V vs RHE. However, in the presence of oxygen, the reduction of NH+ is possible by an energy gain due to simultaneous adsorption of oxygen. The supplied electron goes to pai system as SOMO electron upon reduction, which is responsible for the adsorption of oxygen. That is, the role of pyridinic nitrogen is to provide SOMO electron upon reduction of NH+ species.

References

Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J, (2016). Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science*, 351, 361-365.

Shibuya R, Kondo T, Nakamura J, (2018). Bottom-up design of nitrogen-containing carbon catalysts for the oxygen reduction reaction. *ChemCatChem* doi.org/10.1002/cctc.201701928

9:00am SS+AS+HC+TL-ThM-4 Copper Corrosion Inhibition Investigated on the Molecular Scale Using APXPS, *Bo-Hong Liu,* Lawrence Berkeley National Laboratory*; O Karslıoğlu,* Lawrence Berkeley Nationa lLaboratory*; M Salmeron, S Nemšák,* Lawrence Berkeley National Laboratory*; H Bluhm,* Fritz Haber Institute of the Max Planck Society, Germany

Copper has been used in a wide variety of applications. Though relatively inert, it corrodes when in contact with aqueous solutions/water vapor and corroding agents such as chlorine.[1] Benzotriazole (BTA) is a commonly used corrosion inhibitor to protect copper surfaces. A consensus regarding the mechanism of corrosion protection is that BTA complexes with surface copper atoms, resulting in a Cu(I)-BTA protective polymer layer.[2] UHV-based surface science studies clarified the structure of the BTA layer on copper single crystal surfaces at low dosage, as demonstrated by a very recent study combining DFT and spectroscopic techniques;[3] however, the effect of environmental factors could not be well addressed by this approach. Here, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) study of the influence of water vapor and chlorine on well-defined Cu surfaces. To capture the material complexity of the corrosion phenomenon, we study copper single crystals as well as polycrystalline foils of metallic copper, cuprous oxide and cupric oxide. In this presentation, we will show that the water uptake of copper surfaces under humid condition is strongly influenced by the presence of a BTA layer. Also, a BTA layer blocks chlorine uptake in some conditions. Based on these experimental results, factors that influence the BTA inhibitory effect on copper corrosion are identified.

1. Atlas, D.; Coombs, J.; Zajicek, O. T., THE CORROSION OF COPPER BY CHLORINATED DRINKING WATERS. *Water Research* **1982,***16* (5), 693-698.

2. Finsgar, M.; Milosev, I., Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. *Corrosion Science* **2010,***52* (9), 2737-2749.

3. Gattinoni, C.; Tsaousis, P.; Euaruksakul, C.; Price, R.; Duncan, D. A.; Pascal, T.; Prendergast, D.; Held, G.; Michaelides, A., Adsorption Behavior of Organic Molecules: A Study of Benzotriazole on Cu(111) with Spectroscopic and Theoretical Methods. *Langmuir* **2019,***35* (4), 882-893.

9:20am SS+AS+HC+TL-ThM-5 Analysis and Deliberate Modification of Electrochemical Interfaces, *Esther Takeuchi, K Takeuchi, A Marschilok,* Stony Brook University   **INVITED**

Interfaces in electrochemical energy storage systems are critical in the transport of electrons and ions and are significant factors in electrochemical function, yet remain a challenge to fully understand. In lithium based systems, the interfaces or interphases often form spontaneously due to reactions of the active materials and the electrolytes. The interfaces formed due to these spontaneous reactions may prove beneficial as they provide needed protection inhibiting further and continuous reaction. However, the characteristics of the interface may also contribute to decreased ion transport and the accompanying increased effective resistance.

Conversion-type materials for next generation lithium ion systems are appealing due to the opportunity for multiple electron transfer within one metal center. However, implementation of conversion materials has been hindered by the phase transformations occurring during cycling as well as formation of a resistive solid electrolyte interphase (SEI). This presentation will explore the effective implementation of combinations of characterization techniques including the use of *ex-situ* and *operando* methods to provide insight into the formation, composition and deliberate modification of the SEI.

11:00am SS+AS+HC+TL-ThM-10 An Investigation on Active Sites of La₂O₃ Catalyst for OCM Reaction: A Combined Study of *in situ* **XRD, XPS and Online MS,** *Yong Yang, C Guan, E Vovk, Z Liu, X Zhou, J Liu, Y Pang,* ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C_2 products (ethane and ethylene). Previous results suggested that the bulk structure change of the La_2O_3 catalyst was related to the performance of the reaction. In this work, a designed *in situ* XRD-MS coupled characterization setup coupled with online MS instrument are used for measuring both the reaction products and the bulk structure of the catalyst in real time and under simulated industrial conditions. This allows for the more detailed study in order to relate information from of bulk structure change vs. CO_2 related treatment and quantitative analysis of the reaction products, thus for a further connection and understanding of the conversion rate of CH_4 and the selectivity of C_2. The work presented focused on online characterization of the OCM reaction on La_2O_3 catalyst, covering different parameters including: 1. La_2O_3 pretreatment under different CO_2 concentrations, 2. Consecutive OCM reactions, comparing the behavior of a clean surface La_2O_3 catalyst with a La_2O_3 catalyst after OCM, 3. OCM performed after La_2O_3 has undergone pretreatment with pure CO_2. Results indicate that carbonates formation on La2O3 is two step, surface carbonates formation at below 500°C and bulk formation at 500-700°C. *In situ* TPD performed in a high pressure gas cell (HPGC) and XPS measurement results confirm the above.

The results showed that bulk CO_3^{2-} formation under CO_2 exposure, results in higher light-off temperature of CO_2 and C_2 than the clean surface during OCM reaction. There is carbonate formation on commercial La_2O_3 during OCM reaction and CO_2 desorption after OCM reaction by in situ XRD-MS, and it influences the light-off temperature of CO_2 and C_2 up to 65°C higher than the clean surface. It is proposed that CO_3^{2-} may perform as a catalyst poison in this reaction. This result provides an important insight of the active site for OCM reaction. Based on this result, a brief XPS study of the carbonate free sample surface, which may be only preppared from the HPGC vacuum connected further reveals an oxide feature related with methane activation. Additional DFT calculations based upon the experimental data indicates a carbonation mechanism which occurs in the subsurface, which in turn could be related to La_2O_3 activity.

11:20am SS+AS+HC+TL-ThM-11 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers, *J Phillips, K Boyd, I Baljak, L Harville, Erin Iski,* University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated

with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an applied external potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Furthermore, by shifting from a nonpolar to polar side chain, island area also increased. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

11:40am **SS+AS+HC+TL-ThM-12 Deposition and Structure of MoO₃ Clusters on Anatase TiO₂ (101)**, *Nassar Doudin, Z Dohnálek,* Pacific Northwest National Laboratory

Oxide clusters supported on metal oxide substrates are of great interest due to their importance in heterogeneous catalysis [1]. The nature and strength of the interactions between the metal oxide clusters and the support materials not only govern their structure and stability but also control the energetics of elementary steps that are critical for the overall activity [1]. Understanding the nature of the interactions is therefore important to tailor the supported metal oxide cluster systems to achieve the desired reactivity and selectivity. Here, we present a scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study of the monodispersed MoO_3 clusters deposited by the sublimation of MoO_3 powder on anatase TiO_2(101) surface at 300 K. After the deposition, the STM images of the lowest concentration of MoO_3 show that the clusters initially migrate over the surface and preferentially anchor at step edges before they start to aggregate on the terraces. Interestingly, the aggregates are mostly composed of three adjacent clusters, with a small concentration of monomers and dimers. Further exposures to MoO_3 increase the cluster coverage until a fully saturated over-layer is created with each clusters being are centered on top of the Ti sites. The adsorbed clusters appear as bright protrusions, with an apparent cluster height of approximately 1.5 Å and diameter of about 8.5 Å. Since the cyclic $(MoO_3)_3$ trimers are known to be a dominant gas phase species resulting from the sublimation of MoO_3 [1], we propose that each cluster on the surface is a trimer. Annealing to 550 K results in a better-order of the $(MoO_3)_3$ layer, but further annealing to 650 K leads to three-dimensional clusters. The XPS results indicate that the $Mo(3d_{5/2})$ binding energy in as-deposited $(MoO_3)_3$ is characteristic of Mo^{6+}, and the oxidation state of Mo remains (+6) upon heating to 600 K. As such, this system may offers great promise as an ideal platform for reactivity studies on well-defined supported model transition-metal oxide catalysts.

[1] Zdenek Dohnálek et al. Royal Society of Chemistry 43, 7664–7680 (2014).

12:00pm **SS+AS+HC+TL-ThM-13 Ionic Conducting Nanostructures Tailored on Porous Mixed Conduction Composite Electrodes for Enhancement of Oxygen Reduction Reaction**, *Jong-Eun Hong, D Joh, S Kim, H Ishfaq,* Korea Institute of Energy Research, Republic of Korea*; C Jung, J Park,* DGIST, Republic of Korea*; S Lee, H Kim, T Lim, S Park, R Song,* Korea Institute of Energy Research, Republic of Korea*; K Lee,* DGIST, Republic of Korea

With decrease in the operation temperature of solid oxide fuel cells, the oxygen reduction reaction (ORR) in the cathodes, which is sluggish, plays an important role in improving the electrochemical performance. Much effort has given to facilitate the ORR by the applications of cathode surface modification using active catalysts, nano-particle cathodes, and advanced cathode materials. In particular, the cathode surface modification with a reactive electro-catalyst has been appeared to increase the electrode reactivity and thus to decrease the polarization resistance to the oxygen reduction reaction. Infiltration of electro-catalysts has been widely utilized to tailor the cathode microstructures as it is a facile method. In this study, one-step infiltration using an in-situ sol–gel process was applied to modify porous mixed conducting composite cathodes, and the impact of surface microstructure tailoring on the electrochemical performances was investigated. The precursors of Sm- and Nd-doped ceria (SNDC), whose ionic conductivity is even higher than that of Gd-doped CeO_2 (GDC), were infiltrated into the cathode by using an ultrasonic spray nozzle to produce fine and uniform droplets. The infiltrated samples then experienced an in-situ heat-treatment after repeating the ultrasonic spraying and drying processes and were submitted for electrochemical measurements. The detailed results on the microstructure evolution and electrochemical properties of the specimens prepared using the ultrasonic spraying infiltration are presented, and the elucidation of the results are discussed.

2D Materials
Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications
Moderator: Mark Edmonds, Monash University, Australia

2:20pm 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-1 Molecular Layers on Nanoporous Gold Electrodes, *Elizabeth Landis,* College of the Holy Cross
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials, *Paul Brown,* American Society for Engineering Education*; S Fischer, J Kołacz, C Spillmann, D Gunlycke,* U.S. Naval Research Laboratory
Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?, *Vladimir Korolkov,* Oxford Instruments-Asylum Research*; S Chulkov, M Watkins,* University of Lincoln, UK*; P Beton,* The University of Nottingham, UK
Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces[1,2] and bulk polymers[3].

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model[4] to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

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[1]Korolkov et al., Nat. Chem., 2017

[2]Korolkov et al., Nat. Comm., 2017

[3]Korolkov et al., Nat. Comm., 2019

[4]Hapala et al., Phys. Rev. B 90, 085421

3:20pm 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds, *Jangyup Son,* University of Illinois at Urbana-Champaign*; N Buzov,* University of California at Santa Barbara*; S Chen,* University of Illinois at Urbana-Champaign*; D Sung,* Sejong University, Republic of Korea*; H Ryu,* Seoul National University, Republic of Korea*; J Kwon,* Yonsei University, Republic of Korea*; S Kim, J Xu,* University of Illinois at Urbana-Champaign*; S Hong,* Sejong University, Republic of Korea*; W King,* University of Illinois at Urbana-Champaign*; G Lee,* Seoul National University, Republic of Korea*; A van der Zande,* University of Illinois at Urbana-Champaign
Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF$_2$) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:00pm 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-6 Functionalization of MoS$_2$ with Halogens, *G Copetti,* IF-UFRGS, Brazil*; E Nunes,* IQ-UFRGS, Brazil*; G Soares,* IF-UFRGS, Brazil*; Cláudio Radtke,* IQ-UFRGS, Brazil
Transition metal dichalcogenides (TMDs) with lamellar structures similar to that of graphite have received significant attention because some of them are semiconductors with sizable bandgaps and are naturally abundant. This offers opportunities for fundamental and technological research in a variety of fields including catalysis, energy storage, sensing, and electronic devices. In order to TMDs fulfill their potential, a precise control i) of surface functionalization and ii) of the number of stacked TMD monolayers are mandatory. Surface functionalization was shown to play a key role in

tuning photoluminescence properties of MoS_2, formation of controllable and low defect density dielectric/MoS_2 interfaces obtained by atomic layer deposition, and etching of MoS_2 layers. Halogenation is one of the most promising functionalization techniques of TMDs. MoS_2 etching with atomic layer control was already achieved by chlorine adsorption associated with Ar^+ sputtering. Moreover, doping techniques to tune the conductivity and photoemission properties of MoS_2 are essential. Previous works have already shown that incorporation of F-containing species in MoS_2 leads to doping, as well as other interesting properties such as tunable ferromagnetic ordering. In this work, we performed first principal calculations with the density functional theory (DFT) to gain insight into the effect of MoS_2 exposure to halogens. Results evidenced different reactivities while comparing F and Cl, as well as MoS_2 surfaces with variable amounts of defects. These results were explored experimentally. Bulk exfoliated MoS_2 as well as CVD-grown monolayer MoS_2 samples were used. Chlorination was achieved by irradiating the samples with UV light in Cl_2 flux. Prior to chlorination, sputtering of the MoS_2 with Ar ions is performed to induce S removal. X-ray Photoemission Spectroscopy measurements and Rutherford Backscattering Spectrometry showed that S vacancies play a fundamental role in the chlorination process, with vacancy concentration dictating the balance between etching of the MoS_2 layer and Cl incorporation. Fluorination was performed by exposing the samples to pulses of XeF_2. Different degrees of fluorination are achieved by varying exposure time. S is removed and F is incorporated without any loss of Mo. Chemical displacement on the Mo 3d and S 2p XPS peaks was observed after both halogenations processes. These results can clarify the mechanisms of Cl and F incorporation. Finally, the halogenation techniques proposed can be simple and useful methods to adapt the MoS_{---2} properties for future applications.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study***, *Tao Jiang*, D Le, T Rahman, University of Central Florida
Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO_2 towards ethanol formation, in the reaction pathway of which thecrucial step for forming C_2 bond, i.e. reaction of adsorbed species CH_3* and CO* to form CH_3CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS_2 functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH_3* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C_2 species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya,A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS_2 activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers**, *Woo-Kyung Lee*, J Pietron, D Kidwell, J Robinson, C McGann, S Mulvaney, U.S. Naval Research Laboratory
A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the

electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is 6.2×10^4 $\Omega \cdot cm$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA).We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-9 Sensor for Breath and Skin Diagnostics**, *Pelagia I Gouma,* The Ohio State University
Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-10 Symmetry Controlled Ddsorption of Diodobenzene on MoS_2**, *Zahra Hooshmand,* University of Central Florida; *P Evans, P Dowben,* University of Nebraska - Lincoln; *T Rahman,* University of Central Florida
In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS_2(0001). The intensity ratio of iodine to molybdenum measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS_2(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS_2, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS_2(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS_2 and 2D-MoS_2 Catalysts**, *Mihai Vaida,* University of Central Florida
Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H_2 molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS_2 and MoS_2. Crystalline 2D-TaS_2 and 2D-MoS_2 with surface area of 1 cm^2 are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling

microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS_2 occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS_2, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C_2H_2).

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A213 - Session HC+SS+TL-ThA

Reaction Pathways and Addressing Challenges for Energy Production in the 21st Century & Heterogeneous Catalysis Graduate Student Award Presentation

Moderators: Sanjaya Senanayake, Brookhaven National Laboratory, Arthur Utz, Tufts University

2:20pm **HC+SS+TL-ThA-1 High Resolution XPS to Identify C_xH_y Surface Species on a Cobalt Model Catalyst: New Experimental Evidence for the Importance of Alkylidynes as Growth Intermediates in Fischer-Trospch Synthesis**, *Kees-Jan Weststrate,* Syngaschem BV, Netherlands*; D Sharma, D Garcia Rodriguez, M Gleeson,* DIFFER, Eindhoven University, The Netherlands, Netherlands*; H Fredriksson, H Niemantsverdriet,* Syngaschem BV, Netherlands

Supported cobalt catalysts find their most widespread application in low temperature Fischer-Tropsch synthesis (FTS), a process in which C-C bond forming reactions produce long chain saturated hydrocarbon chains from synthesis gas, a mixture of CO and H_2. The versatile FTS process may very well continue to play a role in future energy scenarios: synthesis gas can be derived from any carbon-containing source, e.g. biomass or even CO_2 may be used. These renewable carbon sources offer a sustainable alternative to replace petroleum as the principal feedstock of chemicals and liquid transportation fuels.

The FTS reaction mechanism can be ranked among the most complex in the chemical industry. CO and H_2 are converted into long chain hydrocarbons in a sequence of bond-breaking and bond-making steps that are catalyzed by metals such as cobalt, ruthenium and iron (the latter is active in the carbide form). As the steady state concentration of chain growth intermediates is below the detection limits of in-situ spectroscopies simplified model studies are needed to elucidate the mechanism by which long hydrocarbon chains grow on the cobalt catalyst surface. Since chains grow on a surface that is packed with CO, it is of crucial importance to consider how CO spectators influence the reactivity of hydrocarbon adsorbates. We use a Co(0001) single crystal surface as a model system to study how C_2H_x adsorbates react on a cobalt surface, both in ultrahigh vacuum (~10^{-10} -10^{-7} mbar) as well as at near-ambient pressure (~0.1 mbar). By using the high resolution available of x-ray photoemission spectroscopy at the SuperESCA beamline of ELETTRA (Trieste, Italy), and the unique opportunity to combine these qualities with measurements at near-ambient pressure at the HIPPIE beamline of MAX IV (Lund, Sweden), we were able to elucidate the reaction mechanism by which carbon-carbon bonds form on a cobalt surface. We find that CO's presence is of essential importance: It promotes hydrogenation of acetylene, HC≡CH [the most stable C_2H_{xad} without CO] to ethylidyne, ≡C-CH_3, a facile reaction that occurs around 250 K. Ethylidyne dimerization around 310 K produces 2-butyne (H_3C-C≡C-CH_3), a strongly bound alkyne adsorbate that hydrogenates to 2-butene (g) above 400 K. Extrapolated to FTS, the findings speak in favour of the alkylidyne chain growth mechanism: long chain alkylidynes (≡C-R), stabilized by the presence of CO spectators, react with a methylidyne (≡CH_{ad}) monomer to produce a 1-alkyne (R-C-CH) adsorbate. Partial hydrogenation of the 1-alkyne product is promoted by CO_{ad} and produces the alkylidyne species needed for the next CH insertion step.

2:40pm **HC+SS+TL-ThA-2 Beam Reflectivity Measurements of Carbon Dissolution on Nickel Single Crystal Catalysts**, *Eric High*, *D Tinney, A Utz,* Tufts University

The interaction of carbon with metal catalysts is of significant interest. In methane steam reforming, the build-up of carbon in the nickel subsurface

leads to a gradual reduction in reactivity on the surface and ultimately results in deactivation of the metal catalyst. Additionally, the initial dissolution and subsequent reemergence of carbon from the subsurface are key steps in the growth of well-ordered graphene on nickel substrates via chemical vapor deposition (CVD). Researchers have previously used Auger and X-ray photoelectron spectroscopy to investigate the dynamics of carbon dissolution into nickel surfaces. We instead employ beam reflectivity measurements to monitor the process of carbon diffusion into the nickel subsurface in real-time. We will present data collected via exposure of a Ni(997) single crystal to supersonically expanded CH_4 molecules at surface temperatures above 600 K. We observe significant changes in the reaction profile by increasing surface temperature as the rate of dissolution approaches the reactive flux of the high energy gas molecules. We use these results to further develop kinetic models for methane reactivity as a function of surface coverage as well as carbon diffusion into the stepped nickel crystal. The major parameters from these models include the site-blocking coverage and its subsequent dependence on surface temperature as well as an updated measure of the barrier to diffusion for the C/Ni system.

3:00pm **HC+SS+TL-ThA-3 Fundamental Research Opportunities to Advance Energy Technologies**, *Bruce Garrett,* Department of Energy **INVITED**

The U. S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) supports fundamental research in chemical and materials sciences to provide the foundations for new energy technologies and to support DOE missions in energy, environment, and national security. This presentation will discuss opportunities for fundamental research to impact DOE's energy mission "to catalyze the timely, material, and efficient transformation of the nation's energy system and secure U.S. leadership in energy technologies" with a focus on the way we generate, store and use energy nationally. I will provide an overview of BES strategic planning over the past decade that identified priority research directions for advancing energy applications, highlight key scientific advances in these areas, and discuss some future opportunities for modern science, particularly studies of interfacial processes, to accelerate the transformation of the U. S. energy portfolio.

4:00pm **HC+SS+TL-ThA-6 Oxidation and Redox-Mediated Transformation of a Tb2O3 Thin Film from the Cubic Fluorite to Bixbyite Structure**, *Christopher Lee, J Weaver,* University of Florida

The terbium oxides, a member of the rare earth oxide family, exhibit favorable properties in selective oxidation catalysis due to the high mobility of oxygen stored and released within the lattice. Of particular note is the ease of structural rearrangement into highly stable, well-ordered intermediates between the Tb_2O_3 and TbO_2 stoichiometries in addition to a continuum of nonstoichiometric states. As opposed to ceria, which stabilizes strongly in the CeO_2 stoichiometry, thin film terbia is very stable in the Tb_2O_3 stoichiometry and can exist in an oxygen deficient cubic fluorite arrangement (CF-Tb_2O_3) as well as the bixbyite structure (c-Tb_2O_3).

We discovered a redox-mediated mechanism for the transformation of thin film CF-Tb_2O_3(111)/Pt(111) to c-Tb_2O_3(111)/Pt(111) in ultrahigh vacuum (UHV). Low energy electron diffraction (LEED) and temperature programmed desorption (TPD) shows that repeated oxidation and thermal reduction to 1000 K transforms an oxygen deficient cubic fluorite Tb_2O_3(111) thin film to the well-defined bixbyite, or c-Tb_2O_3(111) structure. In addition, TPD measurements show the development of several distinct O_2 desorption peaks arising from the oxidation of c-Tb_2O_3 domains to the stoichiometrically-invariant ι-Tb_7O_{12} and δ-$Tb_{11}O_{20}$ phases and demonstrates the more facile oxidation of c-Tb_2O_3 relative to CF-Tb_2O_3. We present evidence that nucleation and growth of c-Tb_2O_3 domains occurs at the buried TbO_x/CF-Tb_2O_3 interface, and that conversion of the interfacial CF-Tb_2O_3 to bixbyite takes place mainly during thermal reduction of TbO_x above ~900 K and causes newly-formed c-Tb_2O_3 to advance deeper into the film. The avoidance of low Tb oxidation states may facilitate the CF to bixbyite transformation via this redox-mechanism.

Further oxidation of a well-ordered c-Tb_2O_3 film provides evidence of the sequential phase stabilization of ι-Tb_7O_{12}, δ-$Tb_{11}O_{20}$, and α-TbO_{2-x} stoichiometric structures along with lower temperature peaks corresponding with more weakly-bound surface oxygen. Oxidation at temperatures between 300-500 K reveals an apparent Arrhenius activation barrier of ~7.4 kJ/mol for the initial conversion of c-Tb_2O_3 to ι-Tb_7O_{12}. Furthermore, oxidation at 100 K creates an additional oxygen species stable at lower temperatures that has a much more pronounced effect on oxidation of the film surface over the bulk of the film . The ability to control

the surface termination of the TbO$_x$(111) thin films along with selectively creating surface bound oxygen species provides the structural basis necessary to clarify the partial oxidation mechanisms associated with terbia-based catalysis.

4:20pm HC+SS+TL-ThA-7 Discrimination of Surface Storage and Mechanistic Pathways Using Dynamic Pulse Response Experiments, *Y Wang, M Kunz,* Idaho National Laboratory; *G Yablonsky,* Washington University in Saint Louis; *Rebecca Fushimi,* Idaho National Laboratory

Pulse response experiments in a pure diffusion reactor significantly increase the number of gas/solid collisions for probing kinetic interactions but maintain straightforward transport modeling by avoiding gas phase dynamics. Using inverse-diffusion methods [1] the millisecond time-dependence of the reaction rate can be calculated as it responds to the forced concentration dynamic. More importantly, in this experiment the gas and surface concentrations are decoupled and their influence on the transformation rates of reactants and products can be studied.

Vacuum pulse response studies of ammonia decomposition on polycrystalline Fe, Co and a CoFe bimetallic preparation were conducted to investigate the microkinetic features that lead to very distinct global performance [2]. We present dynamic atomic accumulation; a new measure used to characterize the ability of a complex surface to regulate adsorbed species. We find Fe can support hydrogenated species with a longer surface lifetime that either CoFe or Co. From the time-dependence of the rate we find Co can support two mechanistic pathways for H$_2$ production. The quantitative rate, gas and surface concentration data of microkinetic reaction steps explain why materials with cobalt perform better at a global level.

1. Redekop, E.A., et al., *The Y-Procedure methodology for the interpretation of transient kinetic data: Analysis of irreversible adsorption.* Chem. Eng. Sci., 2011. **66**(24): p. 6441-6452.

2. Wang, Y., et al., *Transient Kinetic Experiments within the High Conversion Domain: The Case of Ammonia Decomposition.* Catalysts, 2019. **9**(1): p. 104.

4:40pm HC+SS+TL-ThA-8 Nuclearity Effects in Supported Zinc and Gallium Catalysts for Alkane Dehydrogenation, *Susannah Scott,* University of California at Santa Barbara **INVITED**

The selective dehydrogenation of alkanes to alkenes is an important process in the valorization of shale gas liquids and in the production of on-demand olefins. Ga- and Zn-modified aluminosilicates have been extensively studied as catalysts for these reactions. In the presence of Brønsted acid sites (BAS), the olefins undergo subsequent aromatization to more valuable BTX. The nuclearity of the metal active sites, the proximity between the metal sites and the BAS, and the nature of the support, may influence the catalytic activity but detailed structure-property relationships are difficult to ascertain in conventional catalysts with many types of sites. The reactions of GaMe$_3$ and ZnMe$_2$ with the hydroxyl-terminated surfaces of dehydrated silica and alumina, as well as with the internal and external surfaces of H-ZSM-5, are particularly simple. They generate methane and isolated dimethylgallium and methylzinc sites. K-edge X-ray absorption spectra, analyzed via inspection of the wavelet transform EXAFS (WT-EXAFS) and curvefitting of the Fourier transform EXAFS (FT-EXAFS), reveal that the silica and zeolite materials contain dinuclear grafted sites, regardless of the thermal pretreatment of the support, while alumina gives dispersed mononuclear grafted sites. Differences in reactivity and stability appear to originate in these structural variations.

5:20pm HC+SS+TL-ThA-10 Fundamental Insights into Hydrocarbon Conversion Mechanisms in Lewis and Brønsted Acid Zeolites using Temporal Analysis of Products, *Hari Thirumalai[1], J Rimer, L Grabow,* University of Houston

The surge in natural gas production has incentivized the search for processes that can utilize methane and light olefin derivatives in the manufacture of useful products such as benzene, toluene and xylene (BTX). These are important commodity chemicals that are used as fuel additives and as raw materials in the synthesis of specialty chemicals. Industrial demand is met through processes such as the synthesis of BTX through dehydroaromatization of light olefins or through alkylation of aromatics, typically with the use of zeolites as catalysts. Complex reaction mechanisms determined by the presence of a hydrocarbon pool dominate hydrocarbon chemistry and are challenging to study. These challenges hinder the in-depth understanding of the role of the catalyst and its eventual design for tailored applications.[1]

In this work, we use the transient kinetics technique, temporal analysis of products (TAP), to probe hydrocarbon conversion and upgrade in the transient regime of reaction. TAP experiments help probe the intrinsic kinetics of reactant conversion in a well-defined Knudsen transport regime under high-vacuum conditions. We studied the dehydroaromatization of ethylene and the methylation of toluene as case-studies for hydrocarbon conversion reactions. The precise control of reactant molecules entering the reactor and responses recorded by a high-resolution mass spectrometer at the reactor outlet in the dehydroaromatization of ethylene suggest that a Lewis acid such as Ag$^+$ or Ga^{3+} in the zeolite accelerate the retention of long lived carbonaceous species in the zeolite, thus attaining the autocatalytic arene cycle more rapidly. Pulse responses provide qualitative evidence that olefins are strongly bound to the metal-exchanged zeolite samples with delayed desorption, enhancing the rate of hydrocarbon conversion and carbon retention. Finally, experiments investigating the methylation of toluene to xylene provide valuable information on competitive binding of reactants to the zeolite acid sites and the ensuing primary reactions that drive the reaction.

Overall, our experiments under semi-idealized conditions help provide insight into the crucial primary reactions that initiate the hydrocarbon pool mechanism, thus elucidating the role of extra-framework species such as Ag$^+$ or Ga^{3+} and their synergy with the Brønsted acid sites in hydrocarbon conversion. The fundamental understanding gained from these experiments will be crucial in deciphering the role of the different zeolitic active sites in model hydrocarbon conversion reactions.

References

1. Hsieh, M. F., Zhou, Y., Thirumalai, H., Grabow, L. C., & Rimer, J. D. ChemCatChem, (2017), 9(9), 1675-1682.

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic
Room A210 - Session LS+AC+HC+SS-ThA

Emerging Methods with New Coherent Light Sources

Moderator: Germán Rafael Castro, Spanich CRG BM25-SpLine Beamline at the ESRF

4:00pm LS+AC+HC+SS-ThA-6 Resolving X-ray Based Spectroscopies in the Sub-nanometer Regime: Enabling Atomic Scale Insights into CO Adsorption on Thin Film Surfaces, *Heath Kersell, B Eren, C Wu,* Lawrence Berkeley National Laboratory; *I Waluyo, A Hunt,* Brookhaven National Laboratory; *G Somorjai, M Salmeron,* Lawrence Berkeley National Laboratory

X-ray based spectroscopies routinely yield detailed elemental, chemical, electronic, and magnetic information on a wide array of physically and chemically diverse samples. However, the spatial resolution of these techniques is limited, frequently by the size of the X-ray spot. Conversely, certain structural probes readily resolve sample topography with nanoscale- or even atomic-resolution. The union of X-ray based spectroscopies with nanoscale structural probes enables the acquisition of spectroscopic information at unprecedented length scales. We will demonstrate the combination of X-ray based spectroscopies (e.g. X-ray photoelectron spectroscopy {XPS}) with scanning tunneling microscopy (STM), and its application to CO adsorption and oxidation on model catalyst surfaces.

CO adsorption on various crystal surfaces plays a critical role in numerous chemical processes, including for example CO oxidation, the water gas shift reaction, and methanol oxidation. CO oxidation is widely used as a prototype reaction for studies of fundamental catalytic phenomena and is crucial in exhaust gas processing for automobiles and stationary CO sources. Recent studies demonstrate strikingly high activity for CO oxidation by Pt nanoparticles supported on cobalt oxide (CoO$_x$) as compared to either of the constituent materials. In the further development of these catalysts, a deeper understanding of the active sites and their deactivation is crucial. Using a combination of *operando* high pressure STM (HP-STM) and ambient pressure XPS (AP-XPS), we investigate the nature of catalytically active sites for CO oxidation on CoO-Pt catalysts at CO and O$_2$ pressures up to 130 mTorr. Our experiments showed very different behavior for the lattice oxygen (O$_{lat--}$) in CoO between fully oxidized and sub-stoichiometric cobalt oxides. At RT, fully oxidized Co films adsorbed CO in the form of stable surface carbonate species, poisoning the reaction until reaching higher temperatures where they decomposed. On sub-stoichiometric CoO$_x$ the CO oxidation reaction proceeded at RT,

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

reducing the oxide to the metallic state. We discuss these results in the context of structural transformations observed *in-situ-* via HP-STM, and demonstrate the behavior of surface sites under relevant gas mixtures.

As an outlook, we will discuss various *in-situ* multi-modal approaches which enhance the spatial resolution of X-ray based spectroscopies toward the nano- or even single atom scales. Such a union of spectroscopic and structural probes will provide a more accurate and complete picture of operating devices in the near future.

4:20pm **LS+AC+HC+SS-ThA-7 Imaging with XPS: Advanced Characterization for Advanced Materials and Devices**, *Tatyana Bendikov, H Kaslasi, E Sanders, E Joselevich, D Cahen,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS), as a surface sensitive technique with the sensitivity down to single atomic layer, provides unique information about elemental composition and chemical and electronic states of elements in the material. For some research goals, however, this knowledge is not sufficient as it does not provide the entire information required for a comprehensive characterization of the investigated system. In addition to the basic functions of standard XPS, our instrument is equipped with advanced capabilities such as XPS imaging, which is particularly valuable in the analysis of patterned or inhomogeneus specimens. Following image acquisition, specific areas can thus be chosen and small spot XP spectra acquired at sites of particular interest. This information is useful in the characterization of patterned surfaces or inhomogeneous samples with surface features between several to hundreds of micrometers.

We present here two examples where XPS imaging is successfully used providing crucial information for understanding the investigated systems.

In the first example bunches of GaN nanowires (50-100 nm each) randomly spread on Si substrate were monitored with XPS imaging. Then, focusing on the GaN bunch itself, small area XP spectra were obtained. This allowed to get precise top surface composition of the bunches significantly consuming the analysis time.

In the second example variations in chemical composition though dimensions of the $Cs_xMa_{1-x}PbBr_3$ (MA = CH_3NH_3)

crystal were studied using XPS imaging. Significant changes in the N/Cs ratio, depending on the distance from the crystal edge/center, were observed on the top surface. Variations in the N/Cs and Pb/(N+Cs) ratios were also observed along the crystal bulk.

4:40pm **LS+AC+HC+SS-ThA-8 Time-Resolved Photoemission with Free-Electron Lasers**, *Kai Rossnagel,* CAU Kiel / DESY, Germany **INVITED**
Photoelectron spectroscopy is an essential analytical tool for learning about the properties and workings of quantum materials and functional interfaces, in which electrons are the main actors. In practice, photoelectron spectroscopy is a toolbox comprising three major techniques, where the momentum selectivity and atomic-site specificity of valence and core electron emissions are exploited, respectively: Angle-resolved photoelectron spectroscopy (ARPES) is the most powerful imaging technique for the energy-momentum space of the active electrons near the Fermi level, while x-ray photoelectron spectroscopy (XPS) is a universal tool for chemical analysis and x-ray photoelectron diffraction (XPD) an established surface structural probe. A dream is to combine all three techniques into a single experiment, make it complete by adding spin and femtosecond time resolution, and thus be able to shoot femto-stroboscopic movies of intertwined electronic, magnetic, chemical, and geometric structure dynamics and gain previously unachievable, direct "in operando" insight into dynamic structure-function relationships of materials and interfaces. Here, we aim to realize this dream by combining the soft x-ray SASE3 free-electron-laser (FEL) beam at the European XFEL with the most advanced photoelectron detection scheme currently available: the time-of-flight momentum microscope with efficient 3D energy-momentum detection and 2D spin filtering. The status of the project and of FEL-based photoelectron spectroscopy in general will be presented.

5:20pm **LS+AC+HC+SS-ThA-10 Ultrafast Magnetization Dynamics on the Nanoscale**, *Bastian Pfau,* Max Born Institute, Germany **INVITED**
Nanometer-scale spin configurations are attractive as information entities for spintronic applications to realize nonvolatile and energy-efficient data storage and processing. In recent years, this research field was stimulated by the discovery that the spin can be effectively manipulated using ultra-short light pulses exciting suitably designed magnetic materials. Scattering and imaging methods based on sources delivering ultra-short x-ray pulses

are particularly successful in revealing the magnetization dynamics on the relevant time and length scales. I will present research results on optically induced demagnetization and formation of nanoscale magnetic domains and skyrmions in Co-based multilayer systems. We investigate these processes using small-angle scattering signals or direct imaging via holography with femtosecond x-ray pulses delivered by free-electron laser sources. These methods additionally allow to address the influence of lateral nanoscale inhomogeneity and to work with laterally localized or structured excitation.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room Union Station AB - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Poster Session

HC-ThP-1 The Role of Boron in Supported Platinum Dry Reforming Catalysts, *Carly Byron, S Bai, A Teplyakov,* University of Delaware

Dry reforming of methane (DRM) has been proposed as an alternative to coal or natural gas production of synthesis gas, and the process has been optimized with various metal catalysts to enhance catalytic activity and reduce surface carbon contamination. In this work, boron was paired with platinum, a highly active DRM catalyst, on a silica support material, and surface characterization techniques were used to determine how the presence of boron affected the metal catalyst and the catalytic performance. X-ray photoelectron spectroscopy (XPS) revealed the existence of trigonal (BO_3 structures) and tetrahedral (BO_4 structures) B-containing surface species, which agreed with solid-state ^{11}B NMR results. Density functional theory (DFT) calculations were performed to determine the thermodynamically stable configuration of the B/SiO_2 species, as well as the most favorable species for platinum adsorption. Tetrahedrally coordinated boron was found to be the most favorable species for platinum adsorption. A butane dehydrogenation reaction was utilized to produce fully deactivated $Pt/B/SiO_2$ catalysts samples for further analysis. After complete catalyst deactivation, ^{11}B NMR combined with theoretically-predicted isotropic chemical shifts calculated by Amsterdam Density Functional (ADF) revealed that, in addition to BO_3 and BO_4 fragments, a boron-carbon surface species had been formed during butane dehydrogenation, but this was only observed on catalysts containing platinum. From this observation, it has been concluded that platinum causes carbon contamination during this reaction, but it is mitigated by the presence of boron.

HC-ThP-2 Spectroscopic Characterization of Ethylidyne formed from Acetylene on Pd(111), *Ravi Ranjan, M Trenary,* University of Illinois at Chicago

The surface species formed following the adsorption and hydrogenation of acetylene (C_2H_2) on Pd(111) in the temperature range of 90-450 K are identified and characterized. The techniques used to detect the species are reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). Acetylene was adsorbed at low temperature and then heated to 300 K where it converts to ethylidyne (CCH_3), which is identified by its $\delta(CH_3)$ bending mode at 1327 cm^{-1}. The reaction mechanism for this conversion is quite complex; in the literature there are discrepancies in the identification of the intermediates with both vinyl ($CHCH_2$) and vinylidene (CCH_2) having been proposed. The experimental data available to date favors the formation of vinylidene as an intermediate in the conversion of acetylene to ethylidyne (CCH_3). Evidence for vinylidene is seen in the appearance of its bending mode ($\delta(HCH)$) at 1425 cm^{-1}. The possible mechanism of ethylidyne (CCH_3) formation is through isomerization of acetylene to vinylidene (CCH_2) followed by hydrogenation of vinylidene. In the temperature range of 400 to 450 K, C_2H_2 decomposes and forms a C_xH_y species as verified by TPD spectra showing an H_2 peak at 440 K following C_2H_2 adsorption at low temperature. The low energy electron diffraction (LEED) pattern of acetylene adsorbed at 95 K gives rise to a ($\sqrt{3}\times\sqrt{3}$)R30° pattern. The experimental result is also supported by quantum mechanical computational calculations based on density functional theory.

HC-ThP-3 XPS, TOF-SIMS, and AES Analysis of Fresh and Aged Alumina-Supported Silver Catalysts, *John Newman, D Carr, D Paul, L Swartz,* Physical Electronics*; M Di Mare, W Suchanek,* Scientific Design Company, Inc.

Alumina supported silver catalysts have been used for decades for the direct oxidative conversion of ethylene to ethylene oxide. Ethylene oxide is used in many cleaning and sterilizing products; however, its major industrial application is in the production of ethylene glycol used in the generation of antifreeze, polyesters, liquid coolants and solvents. Global production of ethylene oxide is estimated to grow to 28 million metric tons in 2019 at an estimated market value of over $48 billion (1, 2).

Due to the huge size of this market, incremental improvements in the efficiency and longevity of the catalyst can be very beneficial. Many companies continuously explore ways in which to improve the various aspects of the catalyst system – the physical and chemical properties of the catalyst, the preparation technology, and the reaction conditions.

In this investigation, three surface sensitive (outermost ≤ 5 nm) techniques, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), and Auger Electron Spectroscopy (AES) were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. XPS provided insights into the overall surface concentrations of the elements present as well as chemical state changes that occurred during aging. TOF-SIMS was used to detect and spatially locate elements at concentrations often too low to detect with XPS or AES, and AES high magnification elemental mapping and small area spectroscopy were used to study the localized elemental changes that occurred between fresh and aged catalyst samples. Information gained from these experiments provides valuable insights on the physical and chemical transformations taking place during aging of the catalyst. This information can then be used to suggest further modifications to improve the performance of the catalyst system.

References

1. PR Newswire, *Global Ethylene Oxide Market Report 2018 - Forecast to 2023: The Growing Demand for PET Bottles from the Packaging Industry*, Nov 26, 2018

2. Business Wire, *Global Ethylene Oxide Market Report By Application*, April 24, 2018

HC-ThP-4 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) and Pd/Cu(111) Single Atom Alloy Surfaces under Ambient Pressure Conditions, *Arephin Islam, M Trenary,* University of Illinois at Chicago

Copper catalysts are used in the water gas shift reaction to convert mixtures of carbon monoxide and water to hydrogen and carbon dioxide. Conversely, the reverse water gas shift reaction utilizes carbon dioxide as a resource. Related to the reverse water gas shift reaction is the synthesis of methanol from carbon dioxide and hydrogen. The mechanisms of these reactions involve several possible surface intermediates, each of which should be identifiable by their vibrational spectra. We have used reflection absorption infrared spectroscopy (RAIRS) to study these reactions under ambient pressures in the range of 0.1 to 150 Torr. In the presence of ambient pressures of carbon dioxide, a peak is observed at 1295 cm^{-1}, which is assigned to the symmetric stretch of an adsorbed CO_2 molecule that is bent through its interaction with the surface. Upon addition of $H_2(g)$ at 300 K, the spectra change and new peaks due to surface species appear. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be detected with RAIRS.

HC-ThP-5 Morphology of an Oxide Formed on Au(111) at High Temperatures under Ambient Pressure Conditions, *Jordon Baker, H Kaleem, E Maxwell, A Baber,* James Madison University

The deactivation of heterogeneous catalysts occurs via several mechanisms such as poisoning, coking, and sintering, among others. In order to maintain the high chemical reactivity of heterogeneous catalysts, the process for catalyst deactivation must be well understood and avoided. The effect of high temperature annealing cycles on the morphology of TiO_2/Au(111) model catalysts has been studied. When modified with TiO_2 nanoparticles, the morphology of the model catalyst can vary based on differences in the annealing cycle parameters. Atomic force microscopy (AFM) was used to image the morphology of the surface before and after annealing TiO_2/Au(111) to 1000 K. TiO_2 nanoparticles sintered and Au(111) step edges smoothed, but surprisingly a new surface feature was observed with AFM under ambient conditions, resembling mixed metal oxides formed under UHV conditions. X-ray photoelectron spectroscopy was used to characterize the surface species remaining after the high temperature exposure. The stabilization of a mixed metal oxide on Au(111) has not previously been observed, and future work will investigate the chemical reactivity of these materials.

HC-ThP-6 Machine-Learning Enabled Search for The Next-Generation Catalyst for Hydrogen Evolution Reaction, *Sichen Wei, S Baek, K Reyes, F Yao,* University at Buffalo

As a zero-emission, eco-friendly fuel, hydrogen gas can be generated via electrochemical (EC) water splitting. Achieving high-efficiency water splitting requires the use of a catalyst to minimize the overpotential to drive the hydrogen evolution reaction (HER). Noble metals such as

platinum (Pt) can provide an excellent catalytic activity for HER but are too expensive and scarce for broad applications. Therefore, the development of active HER catalysts made from low-cost materials constitutes a crucial challenge in the utilization of hydrogen energy.

Earth-abundant transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2), have been discovered recently, which exhibit good activity and stability for electrocatalytic reactions. In order to fully explore the untapped potential of MoS_2, the synthesis recipe for MoS_2 needs to be optimized. Such an optimization process needs scientists to search through a combinatorically large space of experimental parameters, which will be time-consuming and costly if using conventional trial-and-error approaches.

In this report, MoS_2 HER catalytic activity optimization is performed by examining different combinations of synthesis parameters during the hydrothermal process. To investigate the structure-activity relationship, scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy and various electrochemical characterizations have been conducted. A strong correlation between hydrothermal conditions and HER performance matrix has been observed. In order to accelerate the search for the best synthesis recipe, machine-learning (ML) techniques have been introduced to help identify the optimal parameter combinations for producing MoS_2. The hydrothermal parameters with the corresponding onset potentials and Tafel slopes are adopted as prior knowledge and are incorporated into the Bayesian Optimization model. The model will be able to guide the wet chemical synthesis of MoS_2 and yield the most effective HER catalyst eventually.

HC-ThP-7 Intermolecular Interactions of Small Alcohols on Au(111), *Eric Maxwell, J Baker, H Kaleem, A Baber,* James Madison University

Metal oxide nanoparticles supported on Au(111) are active catalysts for the oxidation of small alcohols to form industrially significant products and intermediates such as aldehydes. In a systematic study to better understand the adsorption behavior of these small alcohols, coverage studies of methanol, ethanol, and 1-propanol have been conducted on Au(111) using ultrahigh vacuum temperature-programmed desorption (TPD). These three alcohols molecularly adsorb to distinct terrace, step edge, kink, and multilayer sites, for which desorption energies are calculated by Redhead's peak maximum method. The use of complete analysis as a more accurate method for the calculation of desorption energies is also explored for the case of methanol. TPD experiments and subsequent analysis uniquely allow for the investigation of both adsorbate-surface interactions and adsorbate-adsorbate intermolecular interactions. This provides a more robust understanding of surface phenomena and affords valuable data for modelling and predicting the adsorption behavior of small alcohols on Au(111)-based catalysts. It is shown that, for all adsorption sites, desorption energy is directly proportional to carbon chain length. However, the rate at which desorption energy increases varies distinctly between adsorption sites. This study indicates that the role of intermolecular interactions in the adsorption behavior of small alcohols varies between adsorption sites, and can be predicted for other small alcohols.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room A213 - Session HC+SS-FrM

Catalysis at Complex Interfaces

Moderators: Elizabeth Landis, College of the Holy Cros, Fan Yang, Dalian Institute of Chemical Physics, China

8:20am **HC+SS-FrM-1 Pd Nanoparticles on Alumina Nanofibers by Electrospinning for Heterogeneous Catalysis**, *Miguel Angel Rodriguez Olguin*, M Enes da Silva, J Faria, A Susarrey Arce, H Gardeniers, University of Twente, Netherlands

The pressing transition from unsustainable fossil fuels to a sustainable economy based on renewables with minimal chemical waste is one of the grand challenges for the twenty-first century. To mitigate these challenges, it is crucial that improved synthetic catalytic methods are developed, that increase conversion and selectivity of existing chemical transformation processes. For example, *alumina* is a widely used catalyst support owing to its excellent thermal stability and inherent chemical acidity. Technologies like three-way catalytic converters rely on well-defined alumina-based structured monoliths of about hundred of micrometers to millimeters dimensions without spatial control on the allocation of the metal catalyst. The latter is considered essential to derive at more stable catalysts, it may prevent sintering for instance. Additive manufacturing of catalyst materials can pave the path to control the distribution of catalytic nanoparticles, and mass transport modulation by optimized 3-dimensional support designs. In this work, we present co-axial electrospinning to control the distribution of Pd nanoparticles (Pd NPs) over synthetic fibrous-like Al_2O_3 structures. First, our approach involved several synthetic routes for the fine tuning of the Al_2O_3 fibers by varying the formulation of $Al(NO_3)_3 \bullet 9H_2O$, $Al(OH)_3$, $C_{14}H_{27}AlO_5$ precursors and Al_2O_3 nanoparticles additives. Thermal stability and chemical properties of the nanofibers have been tested. The Al_2O_3 fibers morphology is visualized with Scanning Electron Microscopy (SEM), and the fiber diameter is estimated between 81 nm to 107 nm depending on aluminum precursor. Furthermore, X-ray Diffraction (XRD) is utilized to confirm the crystalline phase of the Al_2O_3 used as support. Second, the Al_2O_3 that performs best in terms of morphology, crystallinity, surface area and acidity is loaded with Pd NPs. The location of Pd NPs is varied by tuning the Pd concentration of the precursor suspension. Finally, the Al_2O_3-Pd fibrous catalyst is tested by chemisorbing CO species. CO chemisorption in liquid phase is performed with *in-situ* Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR). Further, liquid phase catalytic reactions will be explored.

8:40am **HC+SS-FrM-2 Multi-Layered TiO₂ Nanofibrous Structures Decorated with Catalytic Nanoparticles for Photoelectrocatalytic Applications**, *Cristian Deenen*, C Eyövge, A Susarrey-Arce, H Gardeniers, University of Twente, Netherlands

Electrospinning is a technique to fabricate nanofibers by applying a high potential between a nozzle and a collector. As a solution is pumped through the nozzle, a jet is ejected from the nozzle that solidifies as it moves towards the collector, resulting in nanofiber deposition on the collector.

A drawback in conventional electrospinning setups consisting of a singular electrified nozzle is the difficulty in depositing multiple material combinations due to the time and labor required to either manually replace the nozzle or to flush the fluidic elements of the electrospinning setup. A novel multi-nozzle approach will be demonstrated to reduce the time required for the switching of precursor materials from minutes to seconds. The proposed concept opens up new possibilities for the fabrication of complex devices with a variety of material formulations, such as alternating functional layers of interest to the fields of catalysis, electrochemistry and photovoltaics.

Mounting multiple nozzles on a rotating disc allows the inactive nozzles to be rotated out-of-plane, away from the electric field between the active nozzle and the collector, which at the same time reduces the risks of dripping from the inactive nozzles. Combining this concept with appropriate control of electrical voltages and fluidic flow through the different nozzles, allows the engineering of a flexible platform for fast and reliable manufacturing of multi-component materials using electrospinning. In this work, we will demonstrate the instrumental concept and apply it to the fabrication of catalytic layers composed of TiO2, decorated with three different metal catalyst nanoparticles (Au, Pd, Pt)

which function in concert for light harvesting and efficient hydrogen production during photoelectrocatalysis.

9:00am **HC+SS-FrM-3 Water Oxidation Reaction in Natural Photosynthesis**, *Junko Yano*, Lawrence Berkeley National Laboratory **INVITED**

Many of the catalytic reactions in inorganic systems and natural enzymes involve multiple electrons, and proceed through several intermediate steps. For example, photosynthetic water oxidation in nature is catalyzed by the metal center that consists of oxo-bridged four Mn and one Ca atoms, which is located in multi-subunit membrane protein, Photosystem II (PSII). This is one of the most important, life-sustaining chemical processes occurring in the biosphere. The oxygen-evolving complex (OEC) in PSII, which contains the heteronuclear Mn_4CaO_5 cluster, catalyses the reaction

$2H_2O \rightarrow O_2 + 4e- + 4H+$
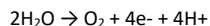
that couples the four-electron oxidation of water with the one-electron photochemistry occurring at the PSII reaction center. The OEC cycles through five intermediate S-states (S_0 to S_4) that corresponds to the abstraction of four successive electrons from the OEC (Fig. 1). Once four oxidizing equivalents are accumulated (S_4-state), a spontaneous reaction occurs that results in the release of O_2 and the formation of the S_0-state.

Recently, the development of X-ray Free Electron Lasers (XFELs) has opened up opportunities for studying the dynamics of biological systems. Intense XFEL pulses enable us to apply both X-ray diffraction and X-ray spectroscopic techniques to dilute systems or small protein crystals. By taking advantage of ultra-bright femtosecond X-ray pulses, one can also collect the data under functional conditions of temperature and pressure, in a time-resolved manner, after initiating reactions, and follow the chemical dynamics during catalytic reactions and electron transfer. Such an approach is particularly beneficial for biological materials and aqueous solution samples that are susceptible to X-ray radiation damage.

We have developed spectroscopy and diffraction techniques necessary to fully utilize the capability of the XFEL x-rays for a wide-variety of metalloenzymes, like Photosystem II, and to study their chemistry under functional conditions. One of such methods is simultaneous data collection for x-ray crystallography and x-ray spectroscopy, to look at overall structural changes of proteins and chemical changes at metal catalytic sites. We have used the above techniques to study the water oxidation reaction of Photosystem II, in which the Mn_4CaO_5 cluster catalyzes the reaction. The current status of this research and the mechanistic understanding of the water oxidation reaction based on the X-ray techniques is presented.

9:40am **HC+SS-FrM-5 Synthesis and Characterization of Carbon-supported PdCu Nanoparticles for the Water Electrolysis in Acid Medium**, *Jonder Morais*, D Lima, M Castegnaro, M Alves, Universidade Federal do Rio Grande do Sul, Brazil

Hydrogen is an important option for an energetic vector due to its high energy density, high heat of combustion and it can be produced in different ways, such as water electrolysis, which is a clean and efficient process. It generates pure H_2 and the required energy for the process can be obtained from renewable sources. However, it is essential to find efficient catalytic materials to be applied as the electrodes for the water electrolysis that usually involves the use of noble metals. An important alternative to lower the production costs for the electrode material is the development of bimetallic nanoparticles supported on amorphous conducting carbon. Recently, a catalyst composed by carbon-suported bimetallic PdCu alloy nanoparticles presented significant activity in the oxygen oxidation reaction [1]. In this sense, PdCu based electrocatalysts were synthesized accordingly and the morphology, composition and structure of PdCu nanoparticles were characterized by TEM, EDS and XRD, respectively. Cathodes were prepared by the brushing technique with the electrocatalyst [2] and tested in the hydrogen evolution reaction (HER) employing 0.5 M H_2SO_4 aqueous sol ution as the electrolyte. Cyclic voltammetry, chronoamperometry and Tafel analysis were carried out to evaluate the stability, reaction mechanism determination and efficiency of HER. Moreover, XPS measurements were performed on the PdCu cathodes before and after the electrochemical measurements in order to monitor the modifications on the electronic structure of the electrocatalyst. Cyclic voltammetry analysis of the cathode showed that the system rapidly becomes highly stable. Tafel analysis indicated that for this system, the mechanism of the reaction is that of Volmer-Heyrovsky, where the H+ desorption is the determining step. The reaction exchange current density of HER for PdCu was around 0.8 mA cm^{-2}, in the equilibrium potential of -270 mV_{SCE}. Moreover, the current density observed in the chronoamperometry analyzes at -2 V_{SCE} was around

340 mA cm^{-2}. XPS analysis showed a significant change in the copper structure after the hydrogen evolution reaction, indicating that it assumed a more metallic character after the reaction. The obtained results indicate that the PdCu carbon-supported bimetallic nanoparticles are a very promising electrocatalysts and should be further studied.

[1] M. V. Castegnaro, J. Morais et al, *Langmuir* 33 (2017) 2734-2743

[2] D. W. Lima, E. M. A. Martini et al, *J. Int. J. Hydrogen Energy* 42 (2017) 5676-5683

10:00am HC+SS-FrM-6 Nanoscale Spectromicroscopy and Chemical Activity of Bilayer Silicate Films on Pd(100) and Pd(111), *Samuel Tenney, C Eads,* Brookhaven National Laboratory; *L Mark,* University of Colorado at Boulder; *V Lee,* University of North Texas; *M Wang,* Brookhaven National Laboratory; *J Medlin,* University of Colorado at Boulder; *J Kelber,* University of North Texas; *D Stacchiola,* Brookhaven National Laboratory

In this talk we present the first reported photothermal infrard (PTIR) spectra and hyperspectral images of ultrathin bilayer silicate films with a spatial resolution better than 10nm and compare this with traditional infrared reflection absorption spectroscopy (IRRAS) of the same surface. The growth of the ultrathin bilayer silicates on Pd(100) and Pd(111) surfaces was observed in real-time with an in-situ low energy electron microscope (LEEM) capable of selected area low energy electron diffraction (μ-LEED). The samples were further probed with ambient pressure X-ray photoelectron spectroscopy (AP-XPS), temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). The chemical activity and enhanced selectivity of these model silicate/Pd catalysts will be discussed.

10:20am HC+SS-FrM-7 Formation and Properties of Mirror Twin Grain Boundary Networks in Molybdenum Dichalcogenides, *Matthias Batzill,* University of South Florida **INVITED**

Edges, defects, and dopants in 2D transition metal dichalcogenides have been shown to give rise to special chemical, electronic, and magnetic properties in these materials. To utilize the potential of these modifications a detailed understanding of their controlled formation and atomic scale properties is needed. In this talk we present our studies on the controlled formation of metallic mirror twin grain boundaries (MTBs) in MoSe$_2$ [1] or MoTe$_2$ [2] by incorporation of excess Mo into the lattice. Very high density of MTB networks can be obtained in MoTe$_2$ that effectively metallizes the material and thus may act as a metallic contact patch [3]. Such line defects may also increase electrocatalytic properties for hydrogen evolution reactions [4]. On a more fundamental level, we show that these 1D metallic grain boundaries host one dimensional electron gas and we present the first angle resolved photoemission (ARPES) studies of such line defects. These studies show evidence for the presence of Tomonaga-Luttinger Liquid behavior of 1D electron systems [5]. Finally, we show that other transition metals may also be incorporated into MoTe$_2$ and the incorporation of vanadium induces room temperature ferromagnetic ordering and thus is an example of a 2D dilute ferromagnetic semiconductor [6].

[1] Y Ma, S Kolekar, H Coy Diaz, J Aprojanz, I Miccoli, C Tegenkamp, M Batzill. Metallic Twin Grain Boundaries Embedded in MoSe$_2$ Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* 11, 5130-5139 (2017)

[2] HC Diaz, Y Ma, R Chaghi, M Batzill. High density of (pseudo) periodic twin-grain boundaries in molecular beam epitaxy-grown van der Waals heterostructure: MoTe$_2$/MoS$_2$. *Appl. Phys. Lett.* 108, 191606 (2016)

[3] PM Coelho, HP Komsa, H Coy Diaz, Y Ma, AV Krasheninnikov, M Batzill. Post-Synthesis Modifications of Two-Dimensional MoSe2 or MoTe2 by Incorporation of Excess Metal Atoms into the Crystal Structure. *ACS Nano* 12, 3975-3984 (2018).

[4] T Kosmala, H Coy Diaz, HP Komsa, Y Ma, AV Krasheninnikov, M Batzill, S Agnoli. Metallic Twin Boundaries Boost the Hydrogen Evolution Reaction on the Basal Plane of Molybdenum Selenotellurides. *Adv. Energy Mat.*, 1800031 (2018).

[5] Y Ma, et al. Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe2 grain boundary. *Nature Commun.* 8, 14231 (2017).

[6] PM Coelho, et al. Room temperature ferromagnetism in MoTe2 by post-growth incorporation of vanadium impurities. *Adv. Electr. Mat.* in press.

11:00am HC+SS-FrM-9 Selectable Catalytic Reduction of Carbon Dioxide to Formic Acid or Methanol over Defect Hexagonal Boron Nitride*, *K Chagoya, T Jiang, D Nash, D Le,* **Talat S. Rahman**, *R Blair,* University of Central Florida

Finding effective heterogeneous catalysts, consisting of abundant elements, for the hydrogenation of waste gas carbon dioxide into value added molecules is a challenging task for global energy and sustainability solutions. In a closely coupled computational and experimental effort, we find that vacancies induced in defect-laden hexagonal boron nitride (*dh*-BN) can effectively activate the CO$_2$ molecule for hydrogenation. Computationally, we demonstrate that activation occurs through back-donation to the π* orbitals of CO$_2$ from frontier orbitals (defect state) of the *h-BN* sheet localized near a nitrogen vacancy (V$_N$). Subsequent hydrogenation to formic acid (HCOOH) and methanol (CH$_3$OH) occurs through vacancy facilitated co-adsorption of hydrogen and CO$_2$. More importantly, we find that *dh*-BN is a temperature-driven switchable catalyst with formic acid formation observable at reaction temperatures above 160 ˚C and pressures of 583 kPa, while methanol formation was observed at lower temperatures (as low as 20 ˚C), which are in great agreement with thermodynamics and kinetics of our calculated reaction pathways.

Surface Science Division
Room A220-221 - Session SS+HC+PS-FrM

Planetary, Ambient, and Operando Environments

Moderators: Catherine Dukes, University of Virginia, Petra Reinke, University of Virginia

8:20am SS+HC+PS-FrM-1 Seeing is Believing: Atomic-scale Imaging of Catalysts under Reaction Conditions, *Irene Groot,* Leiden University, The Netherlands, Netherlands **INVITED**

The atomic-scale structure of a catalyst under reaction conditions determines its activity, selectivity, and stability. Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra)high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra)high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts in situ under industrially relevant conditions.

In this talk, I will give an overview of the in situ imaging techniques we use to study the structure of model catalysts under industrial conditions of atmospheric pressures and elevated temperatures. We have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance. Furthermore, we use other in situ imaging techniques such as transmission electron microscopy, surface X-ray diffraction, and optical microscopy, all combined with mass spectrometry.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. Results for reactions such as NO oxidation and hydrodesulfurization will be discussed.

9:00am SS+HC+PS-FrM-3 *Operando* NAP-XPS and NAP-STM Investigation of CO Oxidation on CoO Nanoislands on Noble Metal Surfaces, *Jonathan Rodríguez-Fernández, Z Sun, E Rattigan,* Aarhus University, Denmark; *C Martín, E Carrasco,* IMDEA Nanoscience, Spain; *E Pellegrin, C Escudero,* ALBA Synchrotron Light Source, Spain; *D Ecija,* IMDEA Nanoscience, Spain; *J Lauritsen,* Aarhus University, Denmark

Nanostructured cobalt oxides (CoOx) have proven to be interesting low temperature oxidation catalysts, for example for preferential oxidation

(PROX) of carbon monoxide (CO). CoOx has been identified as one of the most active materials for CO oxidation showing activity down to temperatures as low as -80^0C^1. However, the pure oxide catalyst seems to be strongly poisoned by water. Some studies indicate that combining CoOx with gold synergistically improves the catalytic performance and poisoning resistance[2-3], but an understanding of this metal-oxide effect is lacking. To obtain an atomic scale understanding of the improved catalytic performance of combined Au-CoOx catalysts we have designed a model system where cobalt oxide nanoparticles are synthesized on an Au single crystal surface by physical vapor deposition in an oxygen environment [4-5].

Here, we significantly advance the mechanistic understanding of cobalt oxide nanocatalysts for CO oxidation by studying the surface chemistry of the model catalyst under *operando* conditions. We use powerful near ambient pressure techniques such as scanning tunneling microscopy (NAP-STM) and synchrotron X-ray photoelectron spectroscopy (NAP-XPS) to study CoO_x nanoislands on Au(111) at mbar pressure in a CO/O_2 gas mixture. From STM results, we find that the structure of the ~20nm wide monolayer cobalt oxide nanoislands is static during exposure to a mixture of CO and O_2 gases at a pressure of 1.5 mbar. Under these conditions at room temperature, the nanoislands seem to exhibit activity towards CO oxidation, and we can detect CO, CO_2 surface species by NAP-STM experiments and by analysis of the corresponding O1s and C1s core level NAP-XPS spectra. In addition, we study the morphological evolution by NAP-STM and the reactivity of the CoO nanoislands from RT to 300^0C under *operando* conditions. At around 200^0C, CO_2 is found in gas phase and decreasing at the surface. Furthermore, to observe the influence of the substrate, we repeated the CoO nanoislands on Pt(111), obtaining similar reactivity results.

References:

1. Xie, X., et al., Nature 458 (2009): 746-749.

2. Cunningham, D. A. H., et al., Catal. Lett. 25 (1994): 257-264.

3. Liu, Y., et al., J. Catal. 309 (2014): 408-418.

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

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

9:20am SS+HC+PS-FrM-4 Reaction of 2-Propanol on SnO$_2$(110) Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy, *J Diulus, R Addou, Gregory Herman,* Oregon State University

Tin dioxide (SnO_2) has a wide range of applications, including gas sensors, transparent conductors, and oxidation catalysts. The surface chemistries for each of these applications can be strongly influenced by the surface structure and cation oxidation states. The oxidation of volatile organic compounds (VOC) has recently been demonstrated using SnO_2, where 2-propanol was used as the probe molecule. More recently it was observed that the surface Sn^{2+}/Sn^{4+} ratio strongly influenced the activity of carbon monoxide oxidation. In this study, we have used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to characterize the surface chemistry of 2-propanol on well-defined SnO_2(110) surfaces. We have prepared stoichiometric and reduced surfaces which were characterized with both AP-XPS and low energy electron diffraction. AP-XPS was performed on these surfaces for 2-propanol pressures up to 1 mbar, various 2-propanol/O_2 ratios, and a range of temperatures. These studies allowed us to evaluate the chemical states of 2-propanol on the SnO_2(110) surface under a wide range of experimental conditions. The effect of surface preparation, 2-propanol/O_2 ratios, and sample temperature was evaluated using AP-XPS and mass spectrometry. Using valence-band spectra, we have found that the surface was reduced from Sn^{4+} to Sn^{2+} when the sample was heated in 2-propanol and that the main reaction product in the gas phase was acetone. This suggests that the reaction occurs through a mechanism where bridging oxygens are hydroxylated upon adsorption of 2-propanol. These bridging hydroxyl groups can react and result in water desorption. This process leads to the reduction of the SnO_2(110) surface. We have found that the low temperature AP-XPS spectra (300-400 K) was nearly identical for 2-propanol and 2-propanol/O_2 mixtures. After running the reactions at higher temperatures we found that the surface remained oxidized. Several oxidation products were also observed in the gas phase. Based on the experimental results we find that the surface was inactive for the oxidation of 2-propanol for temperatures below 500 K. With 2-propanol/O_2 mixtures the reactivity increased substantially at lower temperatures. Furthermore, we propose that in 2-propanol/O_2 mixtures the reaction occurs through a Mars–van Krevelen mechanism.

9:40am SS+HC+PS-FrM-5 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages, *Daniel Killelea, M Turano,* Loyola University Chicago*; R Farber, K Gibson, S Sibener,* The University of Chicago*; W Walkosz,* Lake Forest College*; R Rosenberg,* Argonne National Laboratory

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O_{sub}); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O_{sub} into the selvedge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O_2. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of O_{sub} and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O_{sub} is present. This enhanced reactivity is located at the interface between the less reactive RhO_2 oxide and O-covered metallic Rh. These results reveal the conditions under which O_{sub} is formed and stable, and show that O_{sub} also leads to enhanced reactivity of oxidized metal surfaces.

10:00am SS+HC+PS-FrM-6 Molecular Processes on Icy Surfaces in the Interstellar Medium and the Outer Solar System, *Edith Fayolle, R Hodyss, P Johnson,* Jet Propulsion Laboratory, California Institute of Technology*; K Oberg,* Harvard University*; J Fillion, M Bertin,* Sorbonne Université **INVITED**
Molecular ices have been observed in various planetary and astrophysical environments: from patches in permanently shadowed regions on Mercury and the Moon, to the ice crust of outer Solar System bodies, and onto dust grains in prestellar cores, protostellar envelopes, and protoplanetary disks. Interstellar and planetary ices are mostly composed of H_2O, and more volatile molecules, e.g. N_2, CO, CH_4, CO_2, H_2S, SO_2, NH_3, held together as a solid through van Der Waals forces and dipole-dipole interactions, such as hydrogen bonding. They are found as mixtures or pure layers and display crystalline or amorphous structures.

Understanding ice formation, sublimation, and composition is crucial to interpret both gas phase and solid state observations, constrain the physical conditions encountered in space, and test for the likely chemical inheritance from star-forming environments to planetary systems. Vacuum and cryogenic techniques are used to reproduce astrophysical conditions and grow ice analogues. Analytical techniques, including IR- UV- spectroscopy, mass spectrometry, and microgravimetry, are employed to measure fundamental parameters such as desorption, diffusion energies, and reactions products & rates in the solid phase.

In this talk, I will show several examples of astrochemical experiments relevant to icy environments. The fundamental parameters derived from these experiments are further used as inputs for astrochemical models simulating the formation and evolution of ices on various bodies. In some cases, these experiments can directly explain recent observations, for e.g., the unexpected variety of molecules detected in lunar cold traps by the Lunar Crater Observation and Sensing Satellite mission or the location of snowlines in protostellar and protoplanetary environments probed by radio-interferometers like the Atacama Large Millimeter Array.

10:40am **SS+HC+PS-FrM-8 Bilayer Silicates as Models for Space-weather-mediated Water-cycling Processes at the Interface of Airless Bodies**, *B Dhar*, **William E. Kaden**, University of Central Florida

Following recent observations indicating the presence of water and/or hydroxyl groups inhomogeneously distributed across the surface of the moon, many groups have worked to put forwarded feasible models necessary to rationalize both effects. From those models, there seems to be reasonable agreement that a solar-wind mediated, H^+ implantation-based mechanism is responsible for initial hydration/hydroxylation at the lunar surface. How and why the OH-group concentration varies with both latitude and longitude, however, remains debated in the literature. A recently reported kinetics model provided a plausible temperature-dependent recombinative desorption/dissociative readsorption pathway, which accurately predicts observed systematic trends in the concentration of OH groups as a function of latitude when also accounting for daily oscillations in photon and proton flux vs. latitude over long periods of time. Key to the postulated OH-group migration pathway is the presence of mineral surfaces with atypically low barriers to recombinative water desorption; something that varies with both surface composition/structure and OH group concentration. To account for the effects of the average lunar mineralogical surface composition, the author's simply modeled the moon as a homogenous distribution of simple binary oxides present at concentrations corresponding those associated with each of the corresponding metals.

In the work presented in this this talk, we have used recently developed recipes allowing for the growth of extremely well-defined, atomically-planar, and crystalline silicate sheets to serve as tailor-designed anologues of mineralogically relevant structures containing deliberately varied surface sites expected to be present at the surface of the moon and elsewhere. More specifically, we have grown and fully characterized two bilayer films; one consisting of pure silica (SiO_2) and the other present as a two-dimensional alumino-silicate ($Al_{0.33}Si_{0.67}O_2$). Using temperature programmed desorption, we have then characterized differences in the OH-silicate interactions as a function of one deliberately varied surface-site's coordination, and then link our observations to help provide a more nuanced insight into how and why water may evolve and cycle into and out of the surface of airless bodies in the presence of the solar wind.

11:00am **SS+HC+PS-FrM-9 Unraveling the Evolution of the Solid-Electrolyte Interphase Layer at Li-Metal Anodes**, *Venkateshkumar Prabhakaran, S Roy, G Johnson,* Pacific Northwest National Laboratory, Joint Center for Energy Storage Research*; M Engelhard, V Shutthanandan, A Martinez, S Thevuthasan,* Pacific Northwest National Laboratory*; K Mueller, V Murugesan,* Pacific Northwest National Laboratory, Joint Center for Energy Storage Research

Chemical transformations of electrolyte constituents (such as solvent and solvated electroactive ions) at the Li-metal electrode determine the evolution of the solid-electrolyte interphase (SEI). The ability to rationally design an SEI layer that will provide efficient charge transfer processes will improve the performance of Li-batteries. The main challenge is to unravel the complex set of interfacial reactions that occur during charge transfer processes and subsequently delineate the pathways of various decomposition reactions and phase formation. Herein, we report progress in understanding such complex interfaces using bottom-up assembly of solvated cations and bare anions of selected composition on Li-metal anodes. Soft landing of mass-selected ions, a versatile approach to surface modification, is ideally suited for building the interface with selected electroactive ions which will help unravel the complexity associated with the multitude of interfacial processes occurring during evolution of the SEI layer.[1,2] Ion soft landing combined with operando infrared reflection-absorption spectroscopy (IRRAS) and in-situ x-ray photoelectron spectroscopy (XPS) were used to characterize the decomposition of counter anions and solvent molecules on bare Li metal surfaces. Specifically, we soft-landed isolated electrolyte anions (*e.g.,* bis(trifluoromethane)sulfonimide, $TFSI^-$, polysulfides, S_x^-) and solvated Li solvent cluster cations (e.g. Li-$(dimethoxyethane)_x$) on bare Li metal surfaces without their corresponding counter ions, and monitored their spontaneous decomposition using IRRAS and XPS. Our in-situ multimodal measurements captured the spectroscopic signatures of reaction pathways of the electrolyte anions and solvent molecules on the reactive Li surface. We will discuss the evolution of the SEI layer based on multimodal spectroscopic analysis of electrochemical interfaces prepared using the ion soft landing approach. In particular, the chemical signatures of transient species that evolve during decomposition at well-defined interfaces will be discussed.

References:

1. Johnson, G. E.; Hu, Q.; Laskin, J., Soft landing of complex molecules on surfaces. *Annual Review of Analytical Chemistry* **2011,***4*, 83-104.

2. Prabhakaran, V.; Johnson, G. E.; Wang, B.; Laskin, J., *In situ* solid-state electrochemistry of mass-selected ions at well-defined electrode–electrolyte interfaces. *Proceedings of the National Academy of Sciences* **2016,***113*, 13324-13329.

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