

Surface Science Division

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

Dynamical Processes at Surfaces

Moderator: Gareth Parkinson, TU Wien

8:20am SS+HC+MI-MoM-1 Light Induced Single-Molecule Dynamics at Surfaces, *Wilson Ho*, University of California, Irvine **INVITED**

Inhomogeneity of different length scales is one of the fundamental characters of matter that has its origin in the spatial variations of the charge and mass distributions. While many changes in nature and in the laboratory can be observed with the naked eyes, ultimately the interactions that lead to these changes occur at the atomic scale. In addition, heterogeneity influences the time scale that transformations occur at different locations, and the average time may differ significantly from the local times. The desire to understand and control changes in the charge and mass distributions would require experimental tools that possess simultaneous spatial and temporal resolutions to reveal the heterogeneity. This joint Å-fs resolution can be achieved by the combination of a femtosecond laser with a low temperature scanning tunneling microscope (fs-STM) that probes chemical transformations of single molecules. These experiments demonstrate the fs-STM approach in probing the effects of heterogeneity in space and time on the chemical dynamics in single molecules.

9:00am SS+HC+MI-MoM-3 Probing the Effects of Surface Structure on the Dissociative Chemisorption of Methane, *Eric High¹, D Tinney, A Utz*, Tufts University

Vibrational state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Insights into energy flow during reaction obtained from observations of non-statistical mode-specific and bond-selective enhancements observed for methane and its isotopologues on transition metal surfaces are one example. By providing reactive gas-molecules with precisely defined energy in well-defined energetic coordinates, state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. In this work, we will present vibrational state-resolved data collected via IR laser excitation of the antisymmetric stretch of supersonically expanded CH₄ gas molecules incident on a Ni(997) surface. We will focus on measurements investigating both the low and high incident energy regimes on this lightly stepped single crystal at a wide range of surface temperatures (T_s = 120 K to 1000 K). We will explore the possibility of benchmarking site-specific reaction barriers for dissociative chemisorption with molecules near the energy threshold for reaction. For higher energy molecular beams incident on higher surface temperatures, we will report on how the presence of steps on the Ni(997) surface modifies the kinetics of surface-bound C diffusion into the Ni subsurface and bulk and how this process impacts subsequent methane reactivity on this surface.

9:20am SS+HC+MI-MoM-4 Adsorption and Diffusion of NH₃ on Anatase-TiO₂ (101), *Kræn Christoffer Adamsen, S Koust, E Kolsbjerg, B Hammer, S Wendt, J Lauritsen*, Aarhus University, Denmark

Fundamental understanding of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on VO_x/TiO₂ based catalysts, and adsorption of ammonia on such oxides is therefore of great importance for fundamental understanding of NO_x-removal and SCR catalysis. Here we present a fundamental study of the static and dynamic behaviour of ammonia on anatase-TiO₂ (101), the predominant facet on anatase-TiO₂ nanoparticles. High resolution Scanning Tunneling Microscopy (STM) of static adsorbed ammonia molecules at room temperature, indicates a strong binding to the surface. Through synchrotron radiation XPS ammonia was found to adsorb molecularly. The strong binding of ammonia was further quantified by Temperature Programmed Desorption (TPD) which also shows a highly coverage dependent binding energy, indicating molecular repulsion. All experimental obtained results are in accordance with a proposed theoretically calculated DFT-model of ammonia absorption.

Next, single ammonia molecule diffusion measured utilizing the high-speed Aarhus STM, show diffusibility to all neighbouring sites. Molecular repulsion also show a clear effect on static structures, where nearest

neighbouring site occupation is rarely observed. Statistical analysis of intermolecular coordination supplied repulsion energies, which agree with observed values in TPD spectra and theory. For diffusion, we conclude that molecular repulsion increases the diffusibility for higher coordinated ammonia molecules. However when two ammonia occupy two nearest neighbour sites, they have the possibility of diffusing through a rolling effect, where ammonia can move more easily in one direction, this phenomena has also been seen for water on other oxide surfaces. Our analysis thus shows a surprisingly complex diffusion behaviour of NH₃ on anatase TiO₂(101), which however resembles water dimer diffusion of water dimers on Rutile-TiO₂ (110).

9:40am SS+HC+MI-MoM-5 Non-equilibrium Growth of Metastable Clusters as a Means of Controlling Supramolecular Structure., *Ryan Brown*, Clarkson University; *A Kandel*, University of Notre Dame

This poster will review the use of non-equilibrium growth conditions to produce supramolecular structures not easily accessible using traditional self-assembly approaches. Specifically, the formation of cyclic, hydrogen-bonded clusters at the vacuum-solid interface following the direct injection of a solution into a high vacuum chamber gives insight into the utility of employing non-equilibrium growth conditions for producing supramolecular structures with metastable configurations. When deposited in a rapidly evaporating droplet, hydrogen bonding small molecules can form clusters with 5-fold symmetry if the correct combination of hydrogen bonding groups are present. These features persist at room temperature, but evolve into more complex structures upon mild annealing. Initial studies of this phenomenon in ferrocenecarboxylic acid, 1,1'-ferrocenedicarboxylic acid, indole carboxylic acid, and isatin will be discussed. Finally, future systems and directions of study will be discussed.

10:00am SS+HC+MI-MoM-6 Ultrafast Dynamics of Reaction Pathways on Metal Surfaces, *Jerry LaRue*, Chapman University

Important chemical processes often occur on the femtosecond timescale, requiring the use of femtosecond excitation and probing techniques to study them. Optical femtosecond laser pulses are a convenient method of initiating catalytically important reactions on metal surfaces, such as CO hydrogenation and CO oxidation, on the femtosecond timescale. Using femtosecond x-ray pulses from free electron lasers (FEL), we have selectively probed the bond making and breaking processes of these reactions using O and C k-edge x-ray absorption and emission spectroscopies to obtain time-resolved electronic structure maps. These electronic structure maps reveal the time evolution of different surface species along the reaction pathway, providing new insights into the reaction dynamics on metal catalysis. This talk will highlight past and recent results in reaction dynamics on metal surfaces as investigated using femtosecond x-ray pulses and supported through density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations. Specific systems include CO desorption CO oxidation, and CO hydrogenation on ruthenium.

10:40am SS+HC+MI-MoM-8 Designer Solids via Multi-Heteroepitaxy: Layer-by-Layer Deposition of Molecular Frameworks on Solid Substrates, *Christof Wöll*, Karlsruhe Institute of Technology, Germany **INVITED**

Realizing molecular "Designer Solids" by programmed assembly of building units taken from libraries is a very appealing objective. Recently metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical [1,2], photoelectro-chemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [8]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical [9] and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Furthermore, we will discuss further applications realized by loading MOFs with nanoparticles or quantum dots.

References:

¹ Morton S. Traum Award Finalist

Monday Morning, October 22, 2018

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11:20am **SS+HC+MI-MoM-10 Isotope Enrichment via Non-Equilibrium Differential Condensation and Reflection using Supersonic Beam Gas-Surface Scattering**, *Jacob Graham, A McMillan, K Nihill, S Sibener*, University of Chicago

Isotopically enriched materials have a variety of uses including chemical labeling, energy, medicine, and quantum computing. To stimulate the further development of these applications, modern, efficient isotope enrichment methods are needed. Non-equilibrium supersonic beam gas-surface scattering and differential condensation is shown to be a new and broadly applicable route to isotope enrichment. This enrichment is demonstrated with ^{36}Ar and ^{40}Ar isotopes reflecting from low temperature condensates of argon, with differences arising in the condensation coefficient, which depend on the degree of collisional energy exchange for each isotope at the interface. The enrichment factors were found to be tunable as a function of incident beam kinetic energy. For example, ^{36}Ar was found to be *enriched* relative to ^{40}Ar in the scattered fraction by greater than a factor of two, for a seeded beam of argon in helium having incident velocity 1650 m/s. In a separate and complementary experiment under the same conditions, the amorphous argon condensate was found to be *depleted* in its ^{36}Ar content, confirming this effect. This observed isotope selectivity during deposition introduces a new method for isotopic enrichment and purification as well as *in-situ* isotopic materials engineering.

11:40am **SS+HC+MI-MoM-11 Structural Reorganization of Sequentially Adsorbed Two-component Self-assembled Monolayers after Soft Ultraviolet Irradiation**, *C Gerber, Rebecca Quardokus*, University of Connecticut

Sequentially adsorbed anthracene dicarboxylic acid and octanethiol on Au(111) form ordered regions of octanethiol, gold vacancy islands, and areas of disorder near domain boundaries and vacancy islands. Vapor deposition of octanethiol after drop-cast deposition of anthracene dicarboxylic acid on Au(111) results in small ($\sqrt{3} \times \sqrt{3}$)R30° and c(4x2) octanethiol domains. Initial exposure to soft ultraviolet irradiation increases disorder with only a few small close-packed octanethiol domains remaining. Repeated exposure to soft ultraviolet irradiation shows some removal of octanethiol molecules and sequential imaging by scanning tunneling microscopy gives snapshots of the stepwise reordering of the domains that ultimately leads to a structurally reordered monolayer consisting of larger domains of low-coverage octanethiol in a $p \times \sqrt{3}$ structure.

Surface Science Division

Room 203C - Session SS+HC-MoA

Theory and Modeling of Surfaces and Reactions

Moderators: Liney Arnadottir, Oregon State University, Petra Reinke, University of Virginia

1:20pm SS+HC-MoA-1 Elucidating the Chemical Nature of Single-Site Catalysts from First Principles, A Hensley, Washington State University; *A Therrien*, Tufts University; *R Zhang*, Washington State University; *A Schilling*, Tufts University; *K Groden*, Washington State University; *C Sykes*, Tufts University; *Jean-Sabin McEwen*, Washington State University **INVITED** Automotive catalysis is more complicated than most applications of catalysts, because of the complex and dynamic changes in the exhaust gas environment. The ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable [1]. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions [2]. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we have studied low-temperature CO oxidation on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure. Through the use of scanning tunneling microscopy (STM), CO temperature programmed desorption (TPD), and density functional theory (DFT) techniques, we determined that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings [3, 4]. Furthermore, the state of the Pt single atoms before, during, and after reaction is determined through a combination of theoretical and experimental techniques. It is found that the Pt dosed to the "29" Cu oxide surface forms well dispersed single atom sites which are metallic in nature [5]. During catalysis, CO₂ forms from the combination of an oxygen from the "29" Cu oxide surface with the CO adsorbed on the Pt single atoms.

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2:00pm SS+HC-MoA-3 Unravelling the Complex Features in STM Images of O/Ag(110) System, Takat B. Rawal, University of Central Florida; *M Smerieri*, IMEM-CNR, UOS Genova, Italy; *J Pal*, University of Genova, Italy; *S Hong*, Brewton-Parker College; *M Alatalo*, University of Oulu, Finland; *L Savio*, *L Vattuone*, University of Genova, Italy; *T Rahman*, University of Central Florida; *M Rocca*, University of Genova, Italy

Elucidating the various structures involving oxygen adsorption on silver surfaces is a key issue in understanding the industrially relevant Ag oxidation process. Recently it was demonstrated that atomic oxygen can cause the extraction of substrate atoms off metal surfaces. In particular for Ag(110), the excavation process takes place already when O₂ is dosed at 175 K leading, at low coverage, to the formation of single Ag vacancies [1], which can serve as reactive sites. Vacancy creation proceeds thereby via the formation of O-Ag-O complexes, which involve a local reconstruction of the surface and ignite the disruption of the Ag substrate. Here, we present details of such processes and of the various structures formed by the O adatoms at very low coverage, for some of which the energetics had already been reported in ref. [2]. To this purpose we performed scanning tunnelling microscopy experiments and density functional theory calculations. A variety of features such as isolated grey dots, sombreros,

shallow grey and white structures oriented along [001] and [1-10], grey stripes, and lozenges were identified and assigned to the O adatoms in different configurations. Most of the oxygen ends up either in "zig-zag chain" or in pinned, "lozenge" shaped structures. The former interact strongly with the STM tip and are easily disrupted, giving rise to highly mobile, sombrero shaped, isolated O adatoms. Around 200 K, not only Ag vacancies are mobile with anisotropic migration rates and can merge at larger coverage into complex features, but also the mobile Ag atoms are trapped by O adatoms leading finally to the O-Ag chains oriented along [001] forming the well-known added row reconstruction.

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2:20pm SS+HC-MoA-4 First Principles Investigations on CO₂ Adsorption and Dissociation on Cu_{cluster} / Cu(111) Surfaces: Influence of Co-adsorbed CO Molecule, Allan Abraham Padama, University of the Philippines Los Baños, Philippines; *H Nakanishi*, *H Kasai*, National Institute of Technology, Akashi College, Japan; *J Ocon*, University of the Philippines Diliman, Philippines

Cheap Cu surfaces play important role in the synthesis of methanol and in reverse water gas shift reactions, in which, the interaction of the surfaces with carbon dioxide (CO₂) is an important process. Recent developments revealed the stable structures of Cu clusters on Cu(111) (Cu_{cluster} / Cu(111)) that is activated by CO adsorption [*Science* 351 (6272), 475-478]. Interestingly, it is found that the surface facilitates water dissociation. In connection to these, we see the importance of studying the adsorption and dissociation of CO₂ on this system which could provide additional insights to the use of Cu-based surfaces as catalyst in various reactions.

In this work, we performed first principles calculations based on density functional theory (DFT) to investigate the adsorption and dissociation of CO₂ on Cu_{cluster} / Cu(111), with and without the presence of co-adsorbed CO molecules. We modeled the system with three Cu atoms as cluster, which was experimentally identified as among the stable clusters on the Cu(111). The adsorption energy of CO₂ on Cu_{cluster} / Cu(111) is ~0.25 eV, comparable to the obtained adsorption energy of CO₂ on flat Cu(111). We found that the cluster and the presence of CO do not influence the dissociation of CO₂. An activation energy of ~1.6 eV accompanies the dissociation when it takes near the cluster which is similar to the barrier on pristine Cu(111). The dissociation barriers on the cluster region are ~1.0 – 1.2 eV, lower than on Cu(111), and it appears that co-adsorbed CO molecules do not significantly affect the dissociation process. CO₂ that dissociates directly on the cluster is only accompanied by ~0.6 eV activation barrier, but further diffusion of the adsorbed species away from the cluster increases the barrier. The geometric and electronic properties analyses that support the obtained results will be presented in the symposium.

2:40pm SS+HC-MoA-5 Step-Spacing Distributions Revisited: New Motivations from Curved Crystals and Other Systems, Theodore L. Einstein, University of Maryland, College Park

Recent experiments on curved crystals of noble and late transition metals (Ortega and Juurlink groups) have renewed interest in terrace width distributions (TWD) for vicinal surfaces. We first summarize refinements of TWD analysis that are absent from the standard reviews. Rather than by Gaussians, TWDs are better described by a single-parameter distribution with a power-law rise and a Gaussian decay, thereby including effects evident for weak step repulsion: skewness and peak shifts down from the mean spacing. Curved crystals allow analysis of several spacings with the same substrate, so that one can check the scaling with the mean width. This is important since such scaling confirms well-established theory. Failure to scale also can provide significant insights. Complicating factors can include step touching (local double-height steps), oscillatory step interactions mediated by metallic (but not topological) surface states, short-range corrections to the inverse-square step repulsion, and the offset between adjacent layers of almost all surfaces. We discuss how to deal with these issues. Many of the curved-crystal experiments involve in-plane misoriented (zig-zag) steps. There are formulas to describe the stiffness but not yet the strength of the elastic interstep repulsion. Some theory results are available for these orientations; more are needed. Other intriguing results have been reported for spacings of spiral steps around a dislocation.

Monday Afternoon, October 22, 2018

3:00pm **SS+HC-MoA-6 Small Molecule Activation Using Computational Catalysis and Machine Learning**, *Yousung Jung*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Electrochemical activation of small molecules (CO₂, N₂, etc) towards value-added products is an efficient and sustainable way to address energy problems and global climate changes. In this talk, I will discuss some of our recent efforts to understand and design new materials towards electrochemical catalysis using density functional calculations [1-4]. In addition, solid state materials are often complex, but can also be potentially highly tunable if there is a way to accurately extrapolate the large set of existing data for a new discovery, an area in which machine learning can help significantly accelerate the discovery process with improved accuracy. At the end of this talk, thus, I will briefly describe some of our initial efforts to use machine learning for chemical science [5-7] that can contribute greatly to creating solutions to catalysis and materials problems, in general.

[1] "Single-Atom Catalysts for CO₂ Electroreduction with Significant Activity and Selectivity Improvements", S. Back, J. Lim, N. Kim, Y. Kim, and Y. Jung, *Chem Sci* 8 1090-1096 (2017)

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[3] "On the active sites of Au and Ag nanoparticle catalysts for CO₂ electroreduction to CO", S. Back, M. Yeom, and Y. Jung, *ACS Catal* 5, 5089-5096 (2015)

[4] "Selective Heterogeneous CO₂ Electroreduction to Methanol", S. Back, H. Kim, and Y. Jung, *ACS Catal* 5, 965-971 (2015)

[5] "Actively learning with non-ab initio input features toward efficient CO₂ reduction catalyst", J. Noh, S. Back, J. Kim, and Y. Jung, *Chem Sci* (2018) (accepted)

[6] "A Local Electronic Descriptor for Machine-Learned Density Functional Theory at GGA Level", H. Ji and Y. Jung, *J Chem Phys* (under revision)

[7] "Artificial neural network for the configuration problem in solids", H. Ji and Y. Jung, *J Chem Phys* 146, 064103 (2017)

3:40pm **SS+HC-MoA-8 Elucidating Mechanisms of Alkanol Catalysis on SrTiO₃ Perovskite Surfaces using Density Functional Theory**, *Robert Chapleski*, S Roy, University of Tennessee Knoxville

Targeted at understanding observed differences in reaction dynamics for various alkyl alcohols on catalytic SrTiO₃ surfaces, we describe the results of our computational study of isopropanol adsorption and catalysis on SrTiO₃ (100). Using the PBE density functional with a Hubbard-U correction to initially probe the potential energy surface of adsorption, we have found a minimum-energy orientation for isopropanol adsorbed on the surface in good agreement with recent sum-frequency generation experiments. Continuing with this minimum, we followed multiple competing pathways and determined necessary transition states and intermediates in order to describe the kinetics and thermodynamics of these reactions. Armed with these results, we elucidate recent experimental findings favoring the formation of the dehydrogenation product acetone over the dehydration product propylene. Finally, we probed the adsorption potential energy surfaces of products in order to describe the contributions of product orientation and lateral surface diffusion to overall reaction dynamics. Our future work will consider different SrTiO₃ surfaces such as (111) and (110), as well as different alkanol adsorbates such as ethanol. Overall, these studies provide insight into the fundamental aspects of catalysis of this class of reagents on perovskite surfaces.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-TuM

Nanochemistry in Heterogeneous Catalysis

Moderator: Matthew Marcinkowski, Pacific Northwest National Laboratory

8:00am **HC+SS-TuM-1 Probing Oxide Supported Single Rh Atoms as Model Catalysts for CO Oxidation**, *Alex C. Schilling, C Sykes*, Tufts University

In recent years, single atom active sites have become a central topic in the creation of new catalysts with a focus on supported Rh atoms as a means of activating C-H bonds and catalyzing the water-gas shift reaction. These heterogeneous catalysts can operate at the single atom limit, decreasing the amount of precious metal on the support and thereby the price of the catalyst. However, debate still exists in the literature over the nature of the active sites and their mechanism of operation. We have taken a reductionist model study approach towards understanding these issues in well-defined single atom systems. Using surface-sensitive techniques, such as Temperature Programmed Desorption (TPD) and Reflection Absorption Infrared Spectroscopy (RAIRS), we assess the ability of single Rh atoms to oxidize CO. Experiments show that this system has the potential to convert the majority of Rh adsorbed CO to CO₂ at relatively low temperature. At low coverages of Rh (0.5-6%) preliminary experiments show two distinct desorption states for CO₂ at 325 K and 462 K. These TPD peaks account for 85% of all CO desorption from the Rh sites. The other 15% desorbs from Rh as CO at the same temperatures. Further work on this system will give insight into the nature of the active Rh sites, their interaction with both CO and support oxide, as well as the reaction mechanism.

8:20am **HC+SS-TuM-2 Methanol Partial Oxidation Mechanisms on a Single-site Catalyst Pt₁/ZnO(10-10): A First-principles Study**, *Tao Jiang*, University of Central Florida; *T Rawal*, Oak Ridge National Laboratory; *D Le, T Rahman*, University of Central Florida

The rational design of single metal atoms anchored on non-metallic surface has the great potential to offer catalysts with high activity and selectivity [1]. Towards this goal, we have carried out density functional theory based calculations of the catalytic behavior of singly dispersed Pt atoms on ZnO, Pt₁/ZnO(10-10), as a model system for methanol partial oxidation. We find that methanol adsorption is favored at the surface Zn site whereas oxygen prefers to adsorb at the Pt-Zn site. The adsorption of reaction intermediates CO, CO₂, and H₂ are favored at the Pt site, whereas H₂O prefers to sit at the Zn site. Secondly, along the reaction pathways for methanol dehydrogenation, we will illustrate that the O-H bond scission from methanol is slightly exothermic ($\Delta E = -13$ meV). The resultant methoxy then preferentially adsorbs at the Pt-Zn site, where C-H bond of methoxy can be easily activated. The dissociation of methoxy (CH₃O' → CH₂O+H) is exothermic ($\Delta E = -0.42$ eV) and that of formaldehyde (CH₂O → CHO+H) is endothermic ($\Delta E = +0.16$ eV). The results suggest that Pt₁/ZnO(10-10) is a potential single-atom catalyst for methanol oxidation. We will compare our findings with those for the related system Pd₁/ZnO(10-10) [1] and available experimental observations to evaluate their relative advantages for methanol partial oxidation.

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The work is partially supported by DOE grants DE-FG02-07ER15842

8:40am **HC+SS-TuM-3 Imaging the Ordering of Weakly Adsorbed CO₂ Molecules on Rutile Titania using Ambient Pressure Microscopy and Spectroscopy**, *Rebecca Hamlyn*¹, Brookhaven National Lab; *J Rodriguez, S Senanayake, M Mahapatra, F Xu, D Grinter, S Luo, P Liu, R Palomino, I Waluyo, S Kattel, D Stacchiola*, Brookhaven National Laboratory

Recently, great effort has been devoted to the capture, activation and conversion of carbon dioxide (CO₂), a ubiquitous greenhouse gas and by-product of many chemical processes. The high stability and non-polar nature of CO₂ leads to weak bonding with well-defined surfaces of metals and oxides. The interactions of CO₂ involve intermolecular forces with noncovalent bonding (van der Waals), and often a surface needs to be functionalized to create polar sites that can "capture" or bind CO₂. Images from ambient pressure scanning tunneling microscopy show that a substantial amount of CO₂ can reside on a TiO₂(110) surface at room temperature as a consequence of weak bonding interactions with the

substrate. Furthermore, the adsorbates exhibit a disorder-order transition on this surface, despite the lack of a strong interaction that may serve to impose its substrate periodicity on the adsorbed film. This phenomena is of interest to many areas of the surface science and chemistry community wherein condensation of van der Waals gases such as CH₄, N₂, or CO₂.

We have employed microscopic imaging under *in situ* conditions, soft X-ray spectroscopy and theory to decipher the unique ordering behavior seen for CO₂ on TiO₂(110).

9:00am **HC+SS-TuM-4 Using Sn Atomic Layer Deposition to Tune the Coking Resistance of Size-selected Pt Model Catalysts**, *Timothy Gorey*², *E Baxter, A Cass, S Anderson*, University of Utah; *B Zandkarimi, A Alexandrova*, University of California at Los Angeles

Size-selected cluster catalysts are powerful tools that enable us to probe and characterize specific catalytic reaction mechanisms controlled by the particle's size. By combining deposition of atomically-selected Pt clusters, with ALD to selectively add Sn atoms to the clusters, we obtain Pt-Sn alloy clusters with exactly known numbers of Pt atoms, and a narrow distribution of Sn atoms. In addition to being a powerful experimental tool, having size-selected model catalysts with well-defined compositions allow detailed theoretical simulations, providing insight into cluster structure, and the mechanistic origins of the size and alloying effects observed experimentally. It is found that tin alloying has a large and beneficial effect on both the branching between intact ethylene desorption vs. dehydrogenation/carbon deposition, and on the thermal stability of the clusters at temperatures to 700 K. Theoretical predictions for the structures and electronic properties of the thermally accessible ensemble of isomers are used to rationalize the observed effects in detail.

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9:20am **HC+SS-TuM-5 Synergistic Effects of Pd and PdO Domains on Thin Film TbO_x(111)/Pt(111)**, *Christopher Lee*³, *J Weaver*, University of Florida

Among the rare earth oxides (REOs), the terbium oxides exhibit favorable properties in selective oxidation catalysis due to the flexibility in the storage and release of oxygen within the lattice. Of particular note is the ease of structural rearrangement into well-ordered intermediates between the Tb₂O₃ and TbO₂ stoichiometries, providing a novel, dynamic surface interface for the promotion of oxidation reactions. We investigated the stabilization and reactivity of metallic Pd domains grown on top of ultrathin c-Tb₂O₃(111)/Pt(111) films in ultrahigh vacuum (UHV) and subsequently oxidized by plasma-generated gaseous atomic oxygen. XPS shows that while both the film and metallic domains are almost fully oxidized to both TbO₂ and PdO by atomic oxygen, subsequent annealing to ~600 K can significantly reduce the TbO_x supporting film while leaving the PdO largely unreduced. Our results provide evidence that the presence of Pd structures on the TbO_x surface greatly promotes the thermal reduction of TbO₂. Further annealing of the system at ~900 K results in PdO decomposition and agglomeration of metallic Pd domains as evidenced by the diminution of the XPS Pd 3d peaks.

The oxidation/reduction behavior of the Pd/TbO_x(111) system has enabled the study of oxidative reactions on three characteristic interfaces: PdO on TbO₂(111), PdO on Tb_nO_{2n-m}(111), and Pd on c-Tb₂O₃(111). TPD and TPRS experiments show that adsorbed CO and C₃H₈ only react with the stabilized PdO domains, with C₃H₈ desorption at ~200 K being characteristic of adsorbed propane σ -complexes observed previously on PdO(101) surfaces. Continual reduction of PdO with adsorbed CO and C₃H₈ also show that when thermal reduction is limited to ~600 K, the underlying TbO_x support will continually replenish the reduced PdO domains with oxygen. This is also noted by the substantially higher conversion of adsorbed CO to CO₂ compared with that seen on pure PdO(101) as conversion would be less limited if reactive oxygen is supplied from both PdO and the TbO_x support. This behavior suggests a strong synergy between the surface Pd/PdO domains and the underlying TbO_x film, such as a Mars-van Krevelen interaction in which TbO_x readily transfers O-atoms to Pd and thereby sustains oxidation chemistry.

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² Heterogeneous Catalysis Graduate Student Presentation Award Finalist

³ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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9:40am **HC+SS-TuM-6 Copper Vapor Adsorption Calorimetry on $\text{Hf}_2\text{Nb}_3\text{O}_{10}$ (001) Nanosheets: Energetics and Adsorbate Structure**, *Wei Zhang¹, J Eichler*, University of Washington; *R Uppuluri, T Mallouk*, The Pennsylvania State University; *C Campbell*, University of Washington

The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the chemical bonding strength at such interfaces is of great interest. These strengths have been measured on single-crystal oxide films of a single metal element by metal vapor adsorption calorimetry in ultrahigh vacuum (UHV), but never before on mixed oxides of two or more metal elements, yet mixed oxides are often used as supports in catalysis with considerable improvement on various aspects of catalyst performance. The preparation of atomically-smooth single-crystal mixed-oxide films in well-defined composition that would be applicable in our adsorption calorimetry is very challenging. Mallouk et. al. have reported a class of lamellar $\text{Hf}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets which can be deposited in a layer-by-layer fashion on flat substrates using Langmuir-Blodgett (LB) techniques to make thin and well-ordered mixed-oxide films. These nanosheets can extend laterally for long distances (>1 μm) indicating that they have very high surface area with homogeneous surface sites and a huge ratio of terrace sites to sheet-edge sites. Furthermore, when used as supports for transition metal oxide (or hydroxide) nanoparticles, they display unusual stability against sintering. Here, we apply the surface chemistry techniques derived for single-crystal oxide films to the much more complex perovskite mixed-oxide films by investigating the adsorption of Cu atoms on the $\text{Hf}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets (~6.3 nm thick) at both 300 K and low temperature (<150 K). Cu atoms show an initial heat of 186 kJ/mol at 300 K, which is close to the DFT value for Cu monomers. The heat of adsorption then increases quickly to the heat of sublimation of bulk Cu(s) (337 kJ/mol). Low-energy He^+ ion scattering spectroscopy (LEIS) allows us to investigate the morphology and the number density of Cu particles. The possible chemical reactions between the Cu atoms and the $\text{Hf}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

11:00am **HC+SS-TuM-10 Adsorption and Adhesion of Ni on MgO(100) at 300 and 100 K by Calorimetry**, *Zhongtian Mao, W Zhao, Z Almuallem, C Campbell*, University of Washington

Metal nanoparticles anchored on the surface of oxide support form the basis of modern heterogeneous catalysts used for clean energy, pollution prevention and industrial-scale chemical production. Since the catalytic activity, selectivity and long-term stability of supported nanoparticles correlate with metal chemical potential which in turn decreases strongly with the metal/oxide interface adhesion energy, E_{adh} , it is crucial to understand how the properties of both metal and oxide control E_{adh} . Adhesion energies of metal nanoparticles to clean oxide surfaces were previously measured in ultra-high vacuum using either single-crystal adsorption calorimetry (SCAC) or particle-shape measurements by electron microscopy or grazing-incidence X-ray scattering. The results reveal a trend that E_{adh} on a given oxide surface increases linearly from metal to metal with increasing metal oxophilicity, defined as the magnitude of the heat of formation of the most stable oxide from gas-phase metal atoms.¹ The oxophilicity of Ni is so high that it is predicted by this trend to have 50% higher adhesion than any of the other metals that have been studied on MgO(100) (i.e., Pb, Ag, Au, Pd Cu and Pt). We report here calorimetric heats of adsorption of Ni gas onto MgO(100) which validate this prediction and thus prove the predictive ability of this trend. Oxide-supported Ni nanoparticles are widely used as industrial catalysts, so these results are of interest in catalysis research. The adsorption of Ni vapor onto MgO(100) films grown on Mo(100) is studied at 300 and 100 K using single crystal adsorption calorimetry. The Ni particle morphology is investigated using He^+ low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). Combining the heat of adsorption and this information on Ni particle morphology also allows the adhesion energy of Ni(solid) to MgO(100) to be found. The initial heat of adsorption at 300 K is 276.5 kJ/mol, 35.7 % lower than the saturation heat at high coverage (equal to the bulk heat of Ni sublimation). This initial heat corresponds to making Ni cluster that are ~0.53 nm in diameter. We also report the chemical potential of Ni versus particle size on MgO(100).

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11:20am **HC+SS-TuM-11 The atomic-scale Structure of the Active CoO(OH)/Au Interface in Electrochemical Water Splitting**, *J Fester, Z Sun, J Rodriguez-Fernandez*, Aarhus University, Denmark; *R Gutzler*, Max Planck Institute for Solid State Research, Germany; *D Grumelli*, Universidad Nacional de La Plata, Argentina; *K Kern*, Max Planck Institute for Solid State Research, Germany; *Jeppe Vang Lauritsen*, Aarhus University, Denmark

Cobalt oxides are promising earth-abundant catalysts for the oxygen evolution reaction (OER) in electrocatalytic water splitting in an alkaline electrolyte. For these materials, we lack basic knowledge on the morphology of the active interface, the nature of the active sites and the exact reaction pathways. Recent studies have also evidenced strong synergistic effects with noble metals such as gold but more information is needed on the promoting catalytic effect of this active interface. To study the atomic-scale structure and location of catalytically active sites under controlled conditions, we created a model system consisting of layered cobalt oxide nanoislands supported on Au(111) [1-3]. Here we take advantage of an experimental setup for transfer of an atomically well-characterized sample back and forth between an ultra-high vacuum scanning tunneling microscope (STM) and an electrochemical cell to measure the electrochemical activity while studying transformations of the active cobalt oxide interface as a function of electrical potential and the presence of the alkaline electrolyte. We compare the observed structures with those obtained by STM and X-ray Photoelectron Spectroscopy studies of the cobalt oxide structure obtained after water exposure under controlled vacuum and ambient water conditions, and identify the active interface as a single layer CoO(OH) on the Au(111) surface. A key conclusion is that the supporting gold substrate uniquely favors a wetted CoO(OH)/Au interface in the electrochemically active potential window and thus suppresses the formation of less active bulk cobalt oxide morphologies. The findings substantiate why optimum catalytic synergy is obtained for oxide coverages on gold close to or below one monolayer, and provide the first morphological description of the active phase during electrocatalysis.

[1] Walton et al. ACS Nano, 2015, 9 (3), 2445-2453

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11:40am **HC+SS-TuM-12 In situ Microscopy of Oxide Growth and Transformation under Reaction Conditions**, *Jan Ingo Flege*, University of Bremen, Germany

INVITED

Current research in heterogeneous catalysis aims to provide a deeper understanding of all the components in a real catalytic system, which depending on the conditions typically comprises both metals and oxides in nanoparticulate form. Significant progress has been achieved by studying carefully devised model systems that facilitate detailed investigation of the structure and chemistry of the individual constituents in controlled environments. While traditional approaches have focused on the role of oxide-supported metal nanoparticles, in the so-called inverse configuration a nanosized metal oxide is supported on a transition metal, thereby allowing us to assess the properties of the nanoscale metal oxide and its defect chemistry as well as to gain complementary access to the oxide-metal interface.

In this presentation, we will focus on the epitaxial growth of ultrathin metal oxide films and nanostructures on transition metals, with a special emphasis on rare-earth oxides. These materials have attracted considerable attention owing to their rich chemistry and enhanced reducibility in proximity to transition metals. We will demonstrate that real-time monitoring of their synthesis under vacuum conditions as well as their structural and chemical modifications on the nanometer scale in reactive gaseous environments is possible using low-energy electron microscopy and related methods [1]. Primary examples will address reversible structural transformations in ruthenium, platinum, and copper supported cerium oxide inverse model catalysts [2-5] upon thermal and chemical reduction, e.g., from CeO_2 via the cubic Ce_2O_3 phase to hexagonal Ce_2O_3 , concomitant with partial dissolution of the cerium oxide particles and considerable dispersion of metallic cerium on the substrate, resulting in irreversible morphological changes. Similar sesquioxide and dioxide phases are present directly after deposition of praseodymium oxide on the Ru(0001) surface [6, 7], illustrating an intrinsic nanoscale complexity and the importance of the oxide-metal interface.

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Surface Science Division

Room 203C - Session SS+HC+NS+PS-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:00am SS+HC+NS+PS-TuM-1 Bond Making and Bond Breaking at Wet and Dry Surfaces, *Angelos Michaelides*, University College London, UK **INVITED**

The making and breaking of chemical bonds at the surfaces of crystalline materials is key to an almost endless list of physical phenomena and technological processes. Increasingly computer simulation techniques are playing an important role in helping to understand such processes, acting as a complement and guide to experiments. In this talk I will discuss recent simulation work in which we are working at: (i) obtaining fundamental physical insight of chemical reactions at the surfaces of transition metal alloys; and (ii) understanding and improving the accuracy of electronic structure simulations of surface chemical processes.

8:40am SS+HC+NS+PS-TuM-3 Stability and Reactivity of Isolated Rh₁ Atoms on Fe₃O₄(001), *Gareth Parkinson*, TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe₃O₄(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe₃O₄(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh₁ species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh₁ diffusion is induced upon adsorption of O₂ and NO.

9:00am SS+HC+NS+PS-TuM-4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne, *T Wang, H Lv*, University of Science and Technology of China, China; *L Feng*, University of Science and Technology of China; *J Huang, X Wu*, University of Science and Technology of China, China; *Junfa Zhu*, National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China, China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by single-molecule dehydrogenation, similar as the mechanism of on-surface Ullman coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullman

reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am SS+HC+NS+PS-TuM-5 Sulfur-driven Switching of the Ullmann Coupling on Au(111), *Jonathan Rodríguez-Fernández, S Schmidt, J Lauritsen*, Aarhus University, Denmark

Ullmann coupling reaction has been attracted great interest in the last decades due to the advantage to build 1D-2D nanostructures from bottom-up fabrication like graphene nanoribbons, polymer, etc[1]. This reaction, it is used to generate covalent molecular linked coupling, C-C, by different halogen molecule precursors. The reaction is activated by the substrate, where the precursors will be dehalogenated. Thus, the substrate plays an important role in the success of the reactions. There are several challenges, one of them is the scaling-up production of high quality nanostructures, where defects or co-adsorbates can reduce the success of this process. It has been reported two cases, where the Ullmann coupling reaction are partially inhibited[2,3]. Here, we reported for the first time the reactivation of the reaction after inhibited on Au(111) by molecular gases[4].

In this work we describe a variable temperature Scanning tunneling microscopy (VT-STM) study that allows us to identify the switch on and off of the Ullmann coupling reaction of this molecule (2,8-Dibromodibenzothiophene) on Au(111). After low temperature deposition on pristine Au(111), the results show that surprisingly Ullmann coupling mechanism happen even at 100 K. We speculate that the modification of the herringbone reconstruction due to the strong interaction between S and Au atoms can facilitate the lifting of the Au adatoms inducing the reaction even at low temperature. On the other hand, when we firstly dose sulfur atoms on the pristine gold crystal by H₂S vapor and subsequently depositing DBDBT molecules, the Ullmann coupling reaction has been completely inhibited due to the formation of S-Au complexes, which is blocking the activation of the reaction due to the gold adatoms on the terrace and step-edges are not available. Dysprosium and Iodine atoms have reported similar partial inhibition on silver and copper, respectively. However, we are able to reactivate the reaction by removing the sulfur atoms from the substrate by exposing the sample to H₂ (gas). STM images show again the Ullmann coupling reaction has been switched on. This result shows the important of co-adsorbates on the substrate and also emphasizes the strong interaction between substrate adatoms (terraces and step edges) and the molecule precursors during the dehalogenation reaction.

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9:40am SS+HC+NS+PS-TuM-6 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde, *Xingyi Deng, D Sorescu, J Lee*, National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-¹⁸O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-¹⁸O at T = 100 K, whereas a partial oxidation product, formaldehyde-¹⁸O (~95% selectivity), and a small amount of carbon dioxide (C¹⁶O¹⁸O) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH₃O(ad)) intermediate, following the pathways CH₃OH(ad) → CH₃O(ad) + H(ad) → CH₂O(g) + 2H(ad) with an overall barrier of 19.0 kcal/mol. Formation of CO₂ was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde

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($\text{H}_2\text{CO}_{\text{lattice(ad)}}$), the proposed precursor leading to CO_2 . These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM-10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface**, *Junseok Lee, D Sorescu, X Deng*, National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM-11 Oxygen Reduction Reaction on Fullerene**, *Yosuke Kikuchi, J Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp^2 to sp^3 -like sp^2 , and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C_{60}) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al.* [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), oxygen molecule (O_2) is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the $4e^-$ pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are over-stabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

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11:40am **SS+HC+NS+PS-TuM-12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys**, *Dipna Patel, C Sykes*, Tufts University

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is

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promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM-13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules**, *Kotarou Takeyasu, Y Shimoyama, M Furukawa, S Singh, J Nakamura*, University of Tsukuba, Japan

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ($\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyrrophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M H_2SO_4) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyrrophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of 10 mA cm^{-2}) were 0.29 V, 0.28 V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyrrophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H...N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-TuA

A Tale of Two Scales: Catalytic Processes and Surface Science

Moderator: Ashleigh Baber, James Madison University

2:20pm **HC+SS-TuA-1** **CO₂ Reduction on the Surface of Cu/TiO₂ NPs Supported on Graphite Studied using Ambient Pressure-XPS and Differential Electrochemical Mass Spectrometer**, *Djawhar Ferrah, A Haines, R Galhenage*, University of California at Irvine; *A Javier*, California Institute of Technology; *J Bruce*, University of California at Irvine; *M Soriaga*, California Institute of Technology; *J Hemminger*, University of California at Irvine

Metal supported on metal oxide (M1/MO) catalyst systems are widely used in industry for the hydrogen production and CO₂/CO conversion to useful fuels. If incontrovertible evidence were founded for the role of the interface in the improvement of catalytic CO₂ hydrogenation efficiency, it would still be an incomplete understanding on the nature of the active sites and associated reaction pathways, namely reactive species adsorption, dissociation and/or activation and intermediate formation stability. The modulation of the reaction selectivity, through the synthesis of catalysts that exhibit specific active sites, is required to design «smart» catalytic systems. Therefore, the investigation of catalytic reactions under real conditions, to illustrate the relation between properties at the atomic level of the surface and reactivity, is needed. In this context, a model catalyst based on Cu/TiO₂ nanoparticles (NPs) supported on graphite (HOPG), have been synthesized and fully characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Using physical vapor deposition (PVD), a high density of 15 nm TiO₂ NPs are deposited on HOPG and are used to support Cu NPs. TEM studies reveal that most of the TiO₂ NPs have a rutile structure and display mainly (110) vicinal surface, which is favorable for CO₂ adsorption. A formation of thin layer of graphitic carbon at surface of TiO₂ NPs is also reported. Photodeposition of Cu on TiO₂ NPs by irradiating the band gap of TiO₂ in a CuCl₂ solution has been studied. In the present work, two different catalytic aspects for CO₂ reduction on CuO_x/TiO₂ NPs on HOPG systems will be reported: (1) thermocatalytic CO₂ hydrogenation and (2) electrochemical CO₂ hydrogenation. Efforts have been devoted to exploring different surface chemistry effects, as well as the oxidation states of Cu NPs (Cu₂O, Cu, and Cu₂O@Cu) with diameters ranging from 2 to 5 nm and TiO₂ surface encapsulation with thin layer of graphited carbon, on the CO₂ reduction mechanism in the temperature range of 300-550 K using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the National Synchrotron Light Source II (NSLS-II). Similarly, the CO₂ reduction on CuO_x/TiO₂ NPs on HOPG electrodes in aqueous KHCO₃ has been investigated using a Differential Electrochemical Mass Spectrometer (DEMS) to evaluate the reaction products. Ongoing Infrared reflection-absorption spectroscopy (IRRAS), and AP-XPS experiments on electrochemical CO₂ reduction will be introduced.

2:40pm **HC+SS-TuA-2** **Influence of Bi and Sb on the Structure of Pd-based Catalysts**, *Joo Kang, W Lee, P Vlasak*, The Dow Chemical Company; *A Kirilin*, The Dow Chemical Company, Netherlands; *H Clements, C Menzies, S Yusuf*, The Dow Chemical Company

Oxidative transformation of aldehydes to corresponding esters is a reaction of significant importance. Catalytic oxidative esterification of aldehydes and alcohols in the presence of heterogeneous catalysts is an attractive method for production of esters. Reaction can be carried out in the presence of palladium or platinum often with co-components to improve performance.

The influence of 4d and 5d metal promoters on Pd based catalysts was investigated using a suite of structure probing techniques including x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and X-ray Absorption Spectroscopy (XAS). Results on supported Pd, Pd-Bi and Pd-Sb catalysts allow new insight into active Pd structure and role of the promoters on Pd structure. We present formation of bimetallic phase in both Bi and Sb promoted Pd catalysts and discuss implication on catalytic performance.

3:00pm **HC+SS-TuA-3** **The Molecular Surface Chemistry Approach to Heterogeneous Catalysts**, *Peter Stair*, Northwestern University **INVITED**

The traditional route to solid catalyst materials involves solution phase deposition or liquid-surface reactions. Examples include impregnation, deposition-precipitation, and solution phase grafting of molecular precursors. Atomic Layer Deposition (ALD) is a gas-solid deposition methodology having enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions. This lecture will provide examples from the laboratories at Northwestern University and Argonne National Laboratory of ALD used to synthesize oxide supports, catalytic oxide overlayers, single-site catalysts, metal nanoparticles, and new porous structures.

4:20pm **HC+SS-TuA-7** **Formation and Stability of Subsurface Oxygen on Ag(111)**, *Marie Turano*, Loyola University Chicago; *S Isbill, S Roy*, University of Tennessee Knoxville; *R Farber*, Loyola University Chicago; *E Iski*, University of Tulsa; *D Killelea*, Loyola University Chicago

A long-standing challenge in the study of heterogeneously catalyzed oxidation reactions on silver surfaces is the determination of what surface species are of greatest chemical importance. This is due to the coexistence of several different types of oxygen on oxidized silver surfaces. A further wrinkle is subsurface oxygen (O_{sub}). O_{sub} are O atoms dissolved into the near surface of a metal, and are expected to alter the surface chemistry and structure, however, these effects have yet to be well characterized. To better understand the interactions of oxidized silver surfaces, synergy between experimental and theoretical studies is necessary. We have studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms using a combination of surface science techniques to determine the resultant surface structure. We observed that once 0.1 ML of O_{sub} has formed, the surface dramatically, and uniformly, reconstructs to a striped structure at the expense of all other surface structures. Furthermore, O_{sub} formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures (475-525K), and the predominance of the p(4x5√3) surface reconstruction at elevated temperatures. Recent DFT-calculated desorption energies of O atoms from Ag(111) agree well with experimentally-derived desorption energies, and provide qualitative insight into the formation and stability of O_{sub} at different oxygen coverages.

4:40pm **HC+SS-TuA-8** **Mechanistic Insights into Catalytic Transfer Hydrogenation and Decarbonylation of Aromatic Aldehydes on P_x-Ru(0001)**, *Abinaya Sampath, D Flaherty*, University of Illinois at Urbana-Champaign

Aromatic aldehydes constitute a significant weight fraction of bio-oil. Transition metal catalysts can hydrogenate these aldehydes using either gaseous H₂ or organic donors to produce valuable chemicals that may replace conventional petroleum derivatives. Here, we study selective decarbonylation of aromatic aldehydes (furfural and benzaldehyde) over Ru(0001) and P_x-Ru(0001) to determine how phosphorus introduces new reaction pathways, such as catalytic transfer hydrogenation (CTH) steps between organic reactants. The catalytic properties of Ru(0001) and P_x-Ru(0001) were probed with temperature programmed reaction (TPR) of furfural, benzaldehyde, and isotopically labeled forms of furfural under ultra-high vacuum conditions with Ru(0001) single crystal. P_x-Ru(0001) is formed by exposing Ru(0001) to 2.5 L of PH₃ at 300 K followed by flash annealing to 1400 K. The treatment produces a surface with an atomic ratio of P: Ru of ~0.4, determined by Auger electron spectroscopy.

On P_{0.4}-Ru(0001), ~68% of furfural adsorbed at 100 K decarbonylates to furan and CO, whereas on Ru(0001), furfural decomposes completely to CO, H₂, and C-atoms. Similarly, benzaldehyde decarbonylates to benzene with a selectivity that is 12-fold greater over P_{0.4}-Ru(0001) than on Ru(0001). Together, these results suggest that, P-modification of Ru(0001) results in selective decarbonylation of aromatic aldehydes. Charge transfer from Ru to P results in reduced electron back donation from Ru to the adsorbates, and causes adsorbates to interact more weakly with P_{0.4}-Ru(0001) than with Ru(0001). These electronic modifications reduce the extent of dissociative reactions leading to selective decarbonylation of aromatic aldehydes, although ensemble effects may also contribute.

TPR of furfural on P_{0.4}-Ru(0001), pre-covered with D* atoms, yields five times more per-hydrogenated furan (C₄H₄O) than mono-deuterated furan (C₄H₃DO), which demonstrates that the CTH does not involve chemisorbed

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H*-atoms. On $P_{0.4}\text{-Ru}(0001)$, TPR of isotopically labeled furfural (C_4H_3DO -CDO) forms two furan isotopologues (C_4H_4O , and C_4H_3DO). In addition, C_4H_3DO formed desorbs at a temperature 20 K higher than C_4H_4O , which indicates that intermolecular H-transfer determines the rate of furan formation. The comparisons of labeled furan products show that these critical H-atoms originate from the furfural ring and the carbonyl group of furfural. Hence, $P_{0.4}\text{-Ru}(0001)$ is more selective for decarbonylation of aromatic aldehydes over $Ru(0001)$, and the addition of phosphorus atoms facilitates CTH steps that do not occur on metallic $Ru(0001)$.

5:00pm **HC+SS-TuA-9 Hot Electron Flux under Methanol Oxidation on Pt/TiO₂ Catalytic Nanodiode; Intrinsic Relation between Selectivity and Chemicurrent**, *Si Woo Lee, S Lee*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *H Lee*, Institute for Basic Science (IBS), Republic of Korea; *W Park, Y Jung, J Park*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Nonadiabatic electronic excitation in exothermic chemical reactions leads to the flow of energetic electrons with an energy of 1-3 eV which is called "hot electrons". Direct detection of hot electron flow and observation of its role in catalytic reactions are important for understanding metal-oxide heterogeneous catalysis [1, 2]. Using Pt/n-type TiO₂ Schottky nanodiode, we show the production of hot electron flow generated by methanol oxidation (P_{methanol} 4 Torr and P_{oxygen} at 760 Torr) on Pt thin film, and detect as steady-state hot electron current (chemicurrent) which is generated by exothermic chemical reactions on Pt catalyst surface. Under methanol oxidation, methanol can be converted to CO₂ by full oxidation or methyl formate by partial oxidation of methanol. We show that the activation energy of chemicurrent is quite close to that of turnover frequency, indicating that the chemicurrent was originated from the catalytic reaction on Pt thin film. In addition, the dependence of the partial pressure on the chemicurrent was investigated by varying partial pressure of methanol (1-4 Torr). The result shows that the selectivity toward methyl formate formation is well correlated with the chemicurrent. For fundamental understanding of correlation between selectivity and chemicurrent, we carried out the DFT calculation on the thermodynamic energy for each step, and found that the energy gain for partial oxidation reaction was higher than that of the full oxidation reaction, which is responsible for the higher flux of hot electron under methyl formate formation. We discuss the role of metal-oxide interfaces in determining the catalytic selectivity and chemicurrent yield.

Reference

1. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal-Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chem. Rev.* **2015**, *115* (8), 2781-2817.
2. Park, J. Y.; Kim, S. M.; Lee, H.; Nedrygailov, I. I., Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity. *Acc. Chem. Res.* **2015**, *48* (8), 2475-2483.

5:20pm **HC+SS-TuA-10 Online Kinetics Study of Oxidative Coupling of Methane over La₂O₃ for C₂ Activation: What is Behind the Distinguished Light-off Temperatures**, *Yong Yang, Z Liu, E Vovk, X Zhou, C Guan*, ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C₂ products (ethane and ethylene). The main difficulties from further investigation of this reaction are due to the nature of its high temperature and reaction exothermicity. In this work, a specially designed online characterization setup is applied for this reaction, which achieved both precise bed temperature control and real time product measurement. The setup combines a micro reactor and realtime mass spectroscopy. The reaction was performed under simulated industrial condition. For the first time, the Arrhenius plots of the major OCM products (CO₂, ethane and ethylene) were obtained, and their temperature dependence as well as the respective activation energy barriers were clearly differentiated, over a recently reported high performance nanorod La₂O₃ catalyst. Different from general expectation, CO₂, the fully oxidized carbon species, dominates all the products in the lower temperature region, and less oxidized C₂ species are only formed at much higher temperatures. Further analysis of the Arrhenius plots indicates that selectivity and apparent activation energy for both CO_x and C₂ products are strongly influenced by the oxygen concentration and temperature. Combined with density functional theory calculations and additional experimental measurements, significant insights are brought to this high temperature reaction of wide interest. Furtheranalysis specially focusing on this temperature region, applying XPS surface studies with *in-situ* high pressure cell and XRD bulk structure with *operando* reactor,

revealed that there are both intermediates and poisoning species formation. With these new experiment results with distinguished lights-off products temperature provide new insights for understanding OCM reaction.

5:40pm **HC+SS-TuA-11 Non-Innocent Solvents, Hydrogen Transfer, Oxygen Dissociation on Nanoparticles during the Direct Synthesis of H₂O₂**, *David W. Flaherty*, University of Illinois, Urbana-Champaign **INVITED**

Direct synthesis of H₂O₂ ($H_2 + O_2 \rightarrow H_2O_2$) could enable on-site, and even *in situ*, H₂O₂ production, which motivates searches for highly selective catalysts and process conditions. H₂O₂ formation rates and selectivities depend sensitively on the addition of other transition metals, adsorption of halides, and solvent identity. The reasons for these changes are not completely understood and are difficult to explain mechanistically.

Rate measurements, X-ray absorption spectroscopy, and computation were conducted for Pd and Pd-based bimetallic clusters to determine the mechanism of this reaction and to understand the reasons why alloying Pd often increases H₂O₂ selectivities. In aqueous alcohols, the change in H₂O₂ and H₂O formation rates with H₂ and O₂ pressures are not consistent with a Langmuirian mechanism, but instead suggest O₂* species react in steps mediated by the solvent. In addition, H₂O₂ formation rates in protic solvents are 10³ larger than those measured in aprotic liquids and large kinetic isotope effects ($k_H/k_D > 7$) strongly suggest that alcohols serve as reactants in the kinetically relevant steps for H₂O₂ formation. In parallel, O-O bonds within chemisorbed intermediates cleave to form H₂O with rates that are less sensitive to the solvent identity. Persistent organic surface residues introduce low barrier reaction pathways to reduce O₂* and increase those for O-O dissociation relative to reaction pathways in pure water. These results show that long-standing observations that H₂O₂ forms in greater yields within alcoholic solvent are not explained by simple differences in the solubility of H₂ in the liquid-phase.

Similar rate laws and solvent requirements indicate that these reactions proceed by the same pathways in the presence of strongly binding halide adsorbates and acids. These modifications change barriers for the formation of H₂O (significantly) with lesser effects on barriers for steps that lead to H₂O₂, and are consistent with electronic modifications of Pd active sites by intra-atomic orbital rehybridization or by charge transfer from Pd atoms, respectively. Overall, this work presents evidence for the mechanism for H₂O₂ formation and explains the roles of solvent identity and surface modification strategies on H₂O₂ selectivities.

Surface Science Division

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

Oxides/Chalcogenides: Structures and Reactions

Moderator: Andrew Teplyakov, University of Delaware

2:20pm **SS+HC+MI-TuA-1 New Eyes for Nanocatalysis: Atomic Scale Investigations of TiO₂ Chemistry**, *Melissa Hines*, Cornell University **INVITED**

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

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

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

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important implications for TiO₂ photocatalysis, as the self-assembled carboxylate monolayer resists desorption under environmental conditions while effectively blocking the transition metal sites typically implicated in photocatalysis.

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

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

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

3:20pm SS+HC+MI-TuA-4 Reversible Structural Evolution and Identification of the Catalytically Active Phase of NiCoO_xH_y During the Oxygen Evolution Reaction (OER), Bruce E. Koel, Princeton University

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

4:20pm SS+HC+MI-TuA-7 Understanding the Growth and Chemical Activity of Titania-Supported MoS_x Clusters, Donna Chen, University of South Carolina; *R Galhenage*, University of California at Irvine; *H Yan*, University of Louisiana Lafayette; *D Le, T Rawal, T Rahman*, University of Central Florida

MoS_x clusters have been grown on TiO₂(110) in order to provide a model surface for better understanding adsorbate interactions and chemical activity of supported MoS_x clusters; MoS₂ particles have exhibited excellent catalytic activity for a variety of reactions, particularly for hydrodesulfurization and photocatalysis, and interactions with the support are believed to induce new electronic properties. The MoS_x clusters were grown by deposition of Mo on titania in an atmosphere of H₂S, followed by annealing to 950 K in H₂S. Scanning tunneling microscopy experiments show that clusters with elongated, rectangular shapes and flat tops are

formed, and the long axes of the clusters have specific orientations with respect to the [001] direction on TiO₂(110). In contrast, deposition of Mo in the absence of H₂S results in a high density of smaller, round clusters that cover the majority of the surface. The morphologies of MoS_x clusters do not change after exposure to various gases (D₂, CO, O₂, methanol) in ultrahigh vacuum. However, exposure to higher pressures of O₂ (250 mTorr) or air causes the clusters to disintegrate as Mo in the clusters becomes oxidized. Temperature programmed desorption studies with CO on the MoS_x clusters show a distinct desorption peak at 275 K, which is not observed on metallic Mo or titania. Density functional theory calculations demonstrate that the presence of the titania support changes in the favored adsorption site for CO from the (-1010) edge in the pristine MoS₂ to the (10-10) edge for the supported MoS₂. Furthermore, the MoS_x/TiO₂(110) interfacial sites are not favored for CO adsorption.

*This work is partially supported by DOE grant DE-FG02-07ER15842.

4:40pm SS+HC+MI-TuA-8 Analyzing Single Atom Catalysts using Low Energy Ion Scattering (LEIS), Thomas Grehl, IONTOF GmbH, Germany; *R ter Veen*, Tascon GmbH, Germany; *D Kunwar, A Datye*, University of New Mexico; *H Brongersma*, IONTOF GmbH and Tascon GmbH, Germany

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

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

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

This contribution demonstrates the analysis of Pt/CeO₂ single atom catalysts using LEIS. During synthesis (atom trapping) the Pt precursor is heated in air at 800 C to form mobile Pt species that deposit on the support and are strongly bound. On high surface area ceria, metal loadings of 3 wt. % can be achieved while maintaining almost exclusively single atoms. We will describe how LEIS was essential to demonstrating the single atom nature of the catalyst. In conjunction with X-ray absorption spectroscopy (XAS), Aberration-Corrected Scanning TEM (AC-STEM) and Diffuse Reflectance Infrared Absorption Spectroscopy (DRIFTS) we were able to develop an accurate picture of the sites that bind Pt ions on the support. The atomistic model for the single atom Pt catalyst was corroborated by Density Functional Theory (DFT).

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

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

5:00pm SS+HC+MI-TuA-9 Synthesis and Characterization of Metals Supported on ZnO Nanoparticles, Amanda Haines, D Ferrah, J Hemminger, University of California at Irvine

Various metals on transition metal oxide supports, such as Cu/ZnO, have been widely studied to understand their role in CO₂ hydrogenation. However, there still remains a dispute as to the role of the oxide supports and the surface oxidation state of the active metal and its efficacy in the reduction of CO₂, namely on the nature of CO₂ adsorption and activation. Here, we have designed and characterized a model catalytic system that will enable us to explore the chemistry of various metals (M_i: i=Pt,Cu) on ZnO supports. ZnO nanoparticles (NPs) have been deposited on an inert highly oriented pyrolytic graphite (HOPG) substrate by physical vapor

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deposition (PVD). From scanning electron microscopy (SEM), we have seen that hexagonal shaped ZnO nanoparticles are formed on a defect-free HOPG substrate. Different surface plasma treatments have been explored to create defect sites on the HOPG substrate to better control the density of the ZnO NPs and various substrate temperatures have been studied to investigate its effect on the size, morphology, structure and chemistry of the NP growth process. Different metals, Pt and Cu, are photodeposited on the ZnO NPs and fully characterized using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and temperature programmed desorption (TPD) to gain fundamental information about the oxidation states and active sites of these M_i /ZnO NPs. Future work will involve reactivity studies on the fully characterized M_i /ZnO NPs using ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) to investigate the surface chemistry, intermediates and products of this catalyst to gain insight into the reaction mechanism of CO_2 hydrogenation.

5:20pm **SS+HC+MI-TuA-10 Molecular Water Adsorption and Reactions on $\alpha\text{-Al}_2\text{O}_3(0001)$ and α -Alumina Particles**, *Greg Kimmel*, *N Petrik*, Pacific Northwest National Laboratory; *P Huestis*, *J LaVerne*, University of Notre Dame; *A Aleksandrov*, *T Orlando*, Georgia Institute of Technology

Alumina and its interactions with water are important in areas ranging from electronics and catalysis to environmental science. However, a basic understanding of the adsorption and reactions of water on even the simplest alumina surface, the (0001) surface of α -alumina, remains elusive. We have investigated the adsorption and reaction of water on single crystal, $\alpha\text{-Al}_2\text{O}_3(0001)$ in ultrahigh vacuum, and α -alumina particles in ambient conditions, using temperature programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and other surface science techniques. For a water coverages of 1 and 2 $\text{H}_2\text{O}/(\text{surface Al}^{3+})$ on $\alpha\text{-Al}_2\text{O}_3(0001)$, no evidence for the surface hydroxyls expected from dissociative adsorption was observed, while the ν_2 vibration of molecular water was observed. Electron-stimulated desorption of molecular water at low coverages also indicated molecular or mixed (molecular plus dissociative) adsorption. In contrast with the single crystal results, IR spectra of water adsorption on alumina particles indicated the presence of surface hydroxyls that persist even after annealing to high temperatures in oxygen. The results, which are consistent with at most a small amount of water dissociation on the Al-terminated (0001) surface, are difficult to reconcile with calculations suggesting that the barrier to dissociation is small. However, the results are consistent with recent vibrational sum frequency experiments showing that the hydroxylation of the Al-terminated (0001) surface takes many days even at ambient pressures and temperatures.

5:40pm **SS+HC+MI-TuA-11 Applying Low Temperature Titration for Determination of Metallic Sites on Active Oxide Supported Catalysts**, *Jerry Pui Ho Li*, *Z Liu*, *Y Yang*, ShanghaiTech University, China

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

Chemisorption study is the common method for active site determination, but has limitations for active heterogeneous catalysts; particularly industrial catalysts because the method often cannot distinguish the redox on metallic sites and catalyst support. An online micro reactor combined with online mass spectroscopy was developed for kinetics studies within wide temperature (as low as liquid nitrogen) and pressure ranges. Pt and Cu based catalysts are used as demonstration of this technique for metallic sites quantitative calibration in this study. Pt catalysts were characterized using CO oxidation and Cu catalysts were characterized using N_2O decomposition. By comparing titration products curves (CO_2 for Pt catalysts, and N_2 for Cu catalysts) versus temperature for both supported samples, narrow subzero temperature windows are found for each catalyst, demonstrating that the titration products are only related with metallic sites. Pure metallic powder was analyzed for confirmation. Specialized chemisorption procedure was established for each sample. This procedure shows a reliable direct titration measurement recipe for the characterization of supported catalysts, quantifying only the metallic sites

for catalysts while being selective against surfaces that contribute secondary reactions often found with more complex supports.

We also present a specialized chemisorption technique applied for metallic sites determination of Au nanoparticles on TiO_2 support through CO at low temperature by comparing IR assignment.

6:00pm **SS+HC+MI-TuA-12 Giant Optical Anisotropy in Hexagonal Perovskite Chalcogenides with Quasi-1D Structures**, *Shanyuan Niu*, University of Southern California; *G Joe*, University of Wisconsin - Madison; *H Zhao*, *M Mecklenburg*, University of Southern California; *T Tiwald*, J.A. Woollam Co. Inc; *K Mahalingam*, Air Force Research Laboratory; *H Wang*, University of Southern California; *M Kats*, University of Wisconsin - Madison; *J Ravichandran*, University of Southern California

Optical anisotropy is a crucial building block to engineer the polarization of light in polarizing optics, light modulators, imaging and communication systems. While metamaterial architectures with form birefringence can overcome the limited optical anisotropy available in widely used natural anisotropic crystals, their deployment is limited by the demanding fabrication. We demonstrate the realization of giant optical anisotropy via chemically engineering the polarizability tensor in a natural material, BaTiS_3 , which has a highly anisotropic quasi-1D structure and features easily accessible in-plane anisotropy. Large single crystals were grown with the chemical vapor transport method. We report the observation of a large, broadband infrared birefringence and linear dichroism. As-grown crystals demonstrate strong dichroism with two distinct optical absorption edges for light with polarizations along two principal axes. To our knowledge, the unprecedented birefringence in the transparent region is more than twice as large as that in any other bulk crystal.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeM

Mechanisms and Reaction Pathways of Heterogeneously Catalyzed Reactions

Moderator: Johan Gustafson, Lund University

8:00am **HC+SS-WeM-1 Surface Reactions of Methanol on Fe₃O₄(001) and Pd/Fe₃O₄(001) Model Catalysts**, *Matthew Marcinkowski, N Doudin, R Smith, B Kay, Z Dohnalek*, Pacific Northwest National Laboratory

Single atom catalysts offer potential improvements in reactivity, selectivity, and decreased catalyst cost, but are often difficult to characterize and stabilize. Iron oxides are frequently used as catalyst supports, and recent studies have shown that Fe₃O₄(001) magnetite can stabilize isolated atoms of many transition metals.¹ This property makes the (001) surface of magnetite ideal for model studies of the catalytic activity of supported single atoms. In this study, we examine the adsorption and reaction of methanol on Fe₃O₄(001) and Pd/Fe₃O₄(001) surfaces using a combination of scanning tunneling microscopy, temperature programmed desorption, and x-ray photoelectron spectroscopy. We find that a monolayer of methanol saturates on Fe₃O₄(001) at a coverage of 5.8×10^{14} molecules/cm², which corresponds to one methanol per every surface Fe³⁺ ion. The majority of methanol desorbs molecularly by 280 K. Above 300 K, methanol dissociates to form methoxy and hydroxyl species.² The maximum coverage of methoxy that can be achieved is 1.2×10^{14} molecules/cm². The methoxy species form an ordered layer adsorbed on the Fe³⁺ sites above the subsurface cation vacancies. At elevated temperatures, the methoxy species react via one of two processes: recombining with hydroxyl to desorb as additional molecular methanol at 350 K, or further dehydrogenation to produce formaldehyde above 500 K. Production of formaldehyde is limited to 2.3×10^{13} molecules/cm². On single Pd atoms on Fe₃O₄(001), the production of formaldehyde above 500 K is suppressed while a new formaldehyde channel is observed at 300 K. Increasing the Pd atom concentration increases the magnitude of the low-temperature channel. Interestingly, the total amount of formaldehyde produced in these two channels remains constant throughout the range of Pd concentrations studied, indicating that the methoxy species are formed on the Fe₃O₄ substrate and Pd atoms only facilitate the conversion of methoxy species to formaldehyde. However, the appearance of the lower temperature reaction channel for formaldehyde shows that the Pd atoms lower the reaction barrier to dehydrogenate methoxy to formaldehyde by almost a factor of two.

1. R. Bliem et al. *Phys. Rev B* **92**, 075440 (2015)

2. O. Gamba et al. *Top. Catal.* **60**, 420 (2017)

8:20am **HC+SS-WeM-2 Hydrogen Activation and Spillover on Single Palladium Atoms Supported on Fe₃O₄(001) Surface**, *Nassar Doudin*, Pacific Northwest National Laboratory; *J Cheng Liu*, Tsinghua University, China; *M Marcinkowski, M Nguyen*, Pacific Northwest National Laboratory; *J Li*, Tsinghua University, China; *V Glezakou*, Pacific Northwest National Laboratory; *G Parkinson*, Vienna University of Technology, Austria; *R Rousseau, Z Dohnalek*, Pacific Northwest National Laboratory

Single-atom catalysts have recently attracted great attention due to their ultimate metal efficiency and the promise of novel properties. However, at the atomic level, little is known about their stability, interactions with the support, and mechanisms by which they operate. Recently it has been shown that on Fe₃O₄(001) surface, single metal atoms can be stabilized to temperatures as high as 700 K [1]. This high stability makes Fe₃O₄(001) a promising support for model studies of single atom catalysts. Here, we present a room-temperature study of H₂ dissociation on single Pd atoms on Fe₃O₄(001) followed by H atom spillover via scanning tunneling microscopy (STM) and density functional theory (DFT). The exposure to H₂ at 300 K results in the appearance of bright double protrusions located on surface iron (Fe_s) sites. Such protrusions were observed previously [2] following the adsorption of atomic H and hydroxyl formation (O_sH) on bare Fe₃O₄(001). By analogy, we attribute the features observed here to O_sH species. The DFT calculations further reveal that H₂ dissociates heterolytically and spills over both hydrogen atoms onto Fe₃O₄(001). When the exposure to H₂ is increased, the density of O_sH's is also observed to increase. With approximately every fourth surface oxygen atom hydroxylated, many areas show a local order with O_sH's spaced according to the (√2×√2)R45° surface reconstruction. STM data further indicate that H

atoms diffusion is accelerated in the presence of coadsorbed water. At highest coverages of O_sH's (approximately every second oxygen atom hydroxylated), the reconstruction is lifted, and the Pd atoms become destabilized. These studies clearly demonstrate that single Pd atoms can efficiently dissociate H₂ that spills over onto a reducible oxide support that can be extensively hydroxylated.

[1] R. Bliem et al. *Science* **346**, 6214 (2014).

[2] G. S. Parkinson et al. *Phys. Rev. B* **82**, 125413 (2010).

8:40am **HC+SS-WeM-3 Model Studies on Ligand-assisted Heterogeneous Catalysis**, *Swetlana Schauer mann*, Christian-Albrechts-University Kiel, Germany **INVITED**

Identifying the surface processes governing the selectivity in hydrogenation of α,β -unsaturated carbonyl compounds on late transition metals is crucial for the rational design of new catalytic materials with the desired selectivity towards C=O vs. C=C bond hydrogenation. In the present talk it will be shown that the selectivity of these reactions can crucially depend on the presence of specific ligand-like surface co-adsorbates. Specifically, I will present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) surface and Pd nanoparticles supported on a model oxide support.¹ We show for the first time that selective hydrogenation of the C=O bond in acrolein to form the desired reaction product – an unsaturated alcohol propenol – is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface highly selective towards propenol formation. By applying pulsed multi-molecular beam experiments and *in operando* IRAS we identified the chemical nature of the spectator and the reactive surface intermediate as oxopropyl and propenoxy species, respectively. The evolution of the surface concentration of the propenoxy intermediate monitored spectroscopically was found to closely follow the propenol formation rate detected in the gas phase.

In the second part, the catalytic surfaces modified with chiral adsorbates will be discussed. In heterogeneous catalysis, such chiral modification of the non-chiral metal surfaces allows to turn the catalytic processes asymmetric and produce enantiopure compounds. We will discuss the atomistic details of the chiral modification as well as the interaction between the chiral modifiers and the prochiral adsorbates on well-defined Pt(111) surface.

References:

1. Dostert, K.-H. et al, *J. Amer. Chem. Soc.* **2015**, *137*, 13496-13502.

9:20am **HC+SS-WeM-5 In situ Structural Studies and Gas Phase Visualization of Model Catalysts at Work**, *Sara Blomberg*¹, *J Zetterberg*, *J Zhou*, *J Gustafson*, *E Lundgren*, Lund University, Sweden

Catalysis is widely used in the production process of chemicals, pharmaceuticals, fuels or ammonia synthesis. The catalyst accelerates the chemical reaction but without being consumed. The materials system of a catalyst is complex and as a result, the catalytic process in most cases is not fully understood, and fundamental studies of the catalyst at operating conditions are close to impossible.

In the last decades, a number of *in situ* experimental techniques have been developed operating at semi-realistic condition to extend the fundamental knowledge on catalytic reactions and to bridge the pressure gap. We have therefore used Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) for surface and gas-phase studies and Planar Laser-induced Fluorescence (PLIF) for gas phase visualization.

Using APXPS to investigate the CO oxidation over a Pd(100) single crystal[2], we observe a pressure dependent CO desorption temperature, and therefore a pressure dependent ignition temperature of the reaction. The experiments were carried out by slowly increasing the temperature of the Pd(100) in a 1:1 ratio of CO and O₂ and systematically increasing the total pressure. The increasing ignition temperature of the catalyst is observed in conjunction with an increasing oxygen coverage on the surface measured immediately after the ignition. Remarkably, no CO could be detected neither in the gas phase nor adsorbed on the surface after the ignition of the reaction, despite a highly active surface.

To investigate the gas phase in more detail, we have developed PLIF, where an image of the gas distribution close to the surface is obtained [2]. PLIF was used to study *in situ* the change of the gas phase during CO oxidation,

¹ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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where the images visualize the build-up of a boundary layer of CO₂ close to the active surface, and the reaction is mass transfer limited by the diffusion of CO. Within this boundary layer the gas composition is significantly different as compared to the composition detected at the outlet of the reactor by a mass spectrometer (MS)[3]. The drastic drop in the CO pressure close to the surface explains the lack of detected CO in the APXPS experiments, which result in a partial pressure of CO below the detection limit of the APXPS.

[1] S. Blomberg et al. In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap, *Phys Rev Lett*, **110** (2013) 117601.

[2] Sara Blomberg et al. *Phys.: Condens. Matter* **28** (2016) 453002

[3] J. Zetterberg et al. Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence. , *Nat Commun*, **6** (2015) 7076.

9:40am **HC+SS-WeM-6 Adsorption, Thermal Stability, and Kinetics of Atomic Oxygen at Ag(111) and Ag(110) Surfaces**, *Sara Isbill*¹, *S Roy*, University of Tennessee Knoxville

Transition-metal surfaces are commonly used to catalyze transformations of small organic compounds, but the catalyst structures and catalytic mechanisms are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate adsorption, thermal stability, and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces and examine their effects on the structural and catalytic properties of silver. On Ag(111), it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption. In contrast, on Ag(110), surface adsorption remained more favorable than subsurface adsorption at all studied coverages. Our thermodynamic and kinetic models of O/Ag(111) based on DFT-computed equilibrium constants and activation energies show that the stability of subsurface oxygen is sensitive to coverage, thereby indicating that the participation of subsurface oxygen in catalysis would strongly depend on coverage. Overall, our results provide valuable qualitative insight into the formation and motion of subsurface oxygen on Ag(111) and Ag(110) surfaces, the importance of metal-adsorbate charge transfer in these systems, and the possible roles of subsurface oxygen in catalytic oxidation by silver.

11:00am **HC+SS-WeM-10 Understanding the Intrinsic Surface Reactivity of Multilayer vs. Single-layer PdO(101) on Pd(100)**, *Jason Weaver*, *V Mehar*, University of Florida; *M Kim*, Ohio State University; *M Shipilin*, Lund University, Sweden; *M van den Bossche*, Chalmers University of Technology, Gothenburg, Sweden; *J Gustafson*, Lund University, Sweden; *L Merte*, Chalmers University of Technology, Gothenburg, Sweden; *U Hejral*, Lund University, Sweden; *H Gronbeck*, Chalmers University of Technology, Gothenburg, Sweden; *E Lundgren*, Lund University, Sweden; *A Asthagiri*, Ohio State University

Understanding the intrinsic reactivity of different types of O-rich phases that form on Pd surfaces is central to developing accurate models of oxidation catalysis. In this talk, I will discuss results of a recent study in which we used temperature programmed reaction spectroscopy (TPRS) and surface IR spectroscopy (RAIRS) as well as DFT calculations to investigate the intrinsic CO oxidation activity of single and multiple-layer PdO(101) structures grown on Pd(100) in UHV. We find that CO binds more strongly on multiple vs. single-layer PdO(101) (~110 vs. 40 kJ/mol), and that CO oxidizes negligibly on single-layer PdO(101) whereas nearly 90% of a saturated layer of CO oxidizes on multiple layer PdO(101) during TPRS experiments. RAIRS further shows that CO molecules adsorb on both bridge and atop-Pd_{cus} sites (coordinatively-unsaturated Pd sites) of single-layer PdO(101)/Pd(100), while CO binds exclusively on atop-Pd_{cus} sites of multilayer PdO(101). Our DFT calculations reproduce the much stronger binding of CO on multiple layer PdO(101) as well as the observed binding site preferences, and reveal that the stronger binding is entirely responsible for the higher CO oxidation activity of multiple vs. single layer PdO(101)/Pd(100). We show that the underlying O-atom bonding partners,

present only in multiple layer PdO(101), modify the electronic states of the Pd_{cus} atoms in a way that enhances the CO-Pd_{cus} bonding. Lastly, we show that a simple kinetic model, with energetics determined from the present study, predicts that the intrinsic CO oxidation rates achieved on both single and multilayer PdO(101)/Pd(100) can be expected to exceed the gaseous CO diffusion rate to the surface during steady-state CO oxidation at elevated pressures, even though the intrinsic reaction rates are 4-5 orders of magnitude higher on multiple vs. single layer PdO(101)/Pd(100). Our findings help to resolve seemingly disparate conclusions about the CO oxidation activity of the single and multiple layer PdO(101) structures, as determined from previous *in situ* vs. UHV measurements, and highlight the importance of characterizing the intrinsic reactivity of catalyst surfaces for developing first-principles kinetic models that can accurately reproduce surface reactivity over a wide range of conditions.

11:20am **HC+SS-WeM-11 Simultaneous Study of Catalyst Structure, Gas Phase and Morphology**, *Sebastian Pfaff*, *J Zhou*, *S Albertin*, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *J Gustafson*, *S Blomberg*, *E Lundgren*, *J Zetterberg*, Lund University, Sweden

CO oxidation has long been studied as a model reaction for catalysis diagnosis. In recent time, increased focus has been given to study well-defined single crystal surfaces to further investigate the details of the involved reaction mechanisms[1]. During the past years, new techniques have been developed to study both the surface structure and gas phase in a semi-realistic environment such as High Energy Surface X-Ray Diffraction (HESXRD)[2] and Planar Laser Induced Fluorescence (PLIF)[3]. HESXRD is a technique well suited to gain knowledge about the surface structure, but without any macroscopic spatial resolution. Planar Laser Induced Fluorescence (PLIF) is a technique which excels at determining the structure and composition of the gas phase. One of the main advantages of this technique is its high spatial and immediate temporal resolution. Additionally, LED surface reflectance techniques have been developed, which provide a simple way of producing a macroscopic map of the entire single crystal, clearly visualizing changes on the surface[4].

In this work, the mentioned techniques were combined at the beamline P07 at PETRA III while performing CO oxidation over a Pd(100) single crystal sample. We have shown a clear spatial correlation between a reduced surface reflectance and an increased CO₂ concentration in the gas phase. Additionally, through the sub-second temporal resolution of PLIF, we have determined the delay between a measurable change of the surface structure using HESXRD and a change in gas composition as the catalyst switches between high and low activity.

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3. Zetterberg, J., et al., *Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence*. *Nature Communications*, 2015. **6**: p. 7076.
4. Zhou, J., et al., *Simultaneous Imaging of Gas Phase over and Surface Reflectance of a Pd(100) Single Crystal during CO Oxidation*. *The Journal of Physical Chemistry C*, 2017. **121**(42): p. 23511-23519.

11:40am **HC+SS-WeM-12 New Catalysis for Light Alkanes – From Methane Functionalization to Light Alkenes**, *Johannes Lercher*, Pacific Northwest National Laboratory and TU München, United States of America/Germany
INVITED

The abundant availability of light alkanes opened new opportunities to synthesize light alkenes and oxygenates, challenged only by the high dispersion of the carbon sources, requiring dedicated processes. Three different principal catalysis pathways will be discussed, the conversion of methane to methanol, the oxidative dehydrogenation of ethane and the dehydrogenation of propane to propene, eventually followed by aromatization. For the three approaches it will be shown, how the atomistic understanding of the catalyst properties including an atomistic description of the active site by combining electron microscopy and X-ray absorption spectroscopy and the molecular pathways by identifying elementary steps via NMR spectroscopy and isotope labeling allows to drastically develop catalysts and catalytic pathways. Combining rigorous kinetics with spectroscopy allowed for all three cases to describe rates linked to specific active sites and maximize their concentration. The

potential and limitations of this fundamental approaches to discover new catalysts and improve existing will be discussed.

Surface Science Division

Room 203C - Session SS+HC-WeM

Catalytic Alloys: Understanding Heterogeneity

Moderators: April Jewell, Jet Propulsion Laboratory, Jean-Sabin McEwen, Washington State University

8:00am **SS+HC-WeM-1 Toward Surface Science-informed Design of Bifunctional Deoxygenation Catalysts**, *J. Will Medlin*, University of Colorado Boulder

INVITED

A major challenge for catalysis is controlling the selectivity for desired reactions of biomass-derived compounds, including selective removal of oxygen atoms. Surface-level studies have the potential to provide deep insights into catalytic reaction mechanisms for deoxygenation. Using single-crystal metal surfaces as model catalysts, the elementary steps associated with both selective and non-selective reaction pathways can be mapped out in significant detail. Surface science studies have also elucidated roles of the different metals within bimetallic catalysts for complex deoxygenation reactions. This presentation will focus on how insights from such model studies have been used to inform efforts to design catalysts for deoxygenation and other key reactions of biomass-derived compounds. It will also discuss complications arising from the so-called pressure and materials "gaps" associated with the use of model surfaces, as well as opportunities for addressing these apparent limitations.

8:40am **SS+HC-WeM-3 Computationally Assisted Correlative STEM and EXAFS Characterization for Multiscale Structure Determination of Tunable Rh/Au Bimetallic Nanoparticle Catalysts**, *S House, C Bonifacio*, University of Pittsburgh; *J Timashenko*, Stony Brook University; *P Kunal, H Wan, Z Duan, H Li*, University of Texas at Austin; *Judith Yang*, University of Pittsburgh; *A Frenkel*, Stony Brook University; *S Humphrey, R Crooks, G Henkelman*, University of Texas at Austin

The acceleration of rational catalyst design by computational simulations is only practical if the theoretical structures identified can be synthesized and experimentally verified. Bimetallic catalysts have the potential to exceed the selectivity and efficiency of a single-component system but adding a second metal greatly increases the complexity of the system. Additionally, variation in the elements' mixing patterns and reconfiguration can affect the reaction mechanisms and thus catalytic performance [1]. Most experimental tools for the characterization of nanoparticles (NPs) provide structural data at the relevant length scales, but not enough to unambiguously determine the structure. Here we present our correlative theory-experiment design approach for addressing this issue, through application to the complex structures of Rh/Au bimetallic hydrogenation catalysts. Our calculations predict this system to exhibit superior allyl alcohol hydrogenation performance compared to single-element catalysts due to the ability to tune the hydrogen binding on the surface [2]. In this study, Rh/Au bimetallic NPs of different metal mixing ratios were synthesized via microwave heating and characterized using synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy and scanning transmission electron microscopy (STEM). EXAFS samples particle ensembles to extract information about atomic bonding (coordination, bond distances, etc.). TEM provides direct local characterization, down to the atomic scale, of particle size, morphology, and elemental distribution. The conventional approach to interpreting EXAFS – fitting to bulk reference spectra – is problematic for bimetallic NPs. We overcome this by using the STEM data to inform the generation of metal NP structures, calculated using interatomic potentials under the framework of the modified embedded-atom method (MEAM). EXAFS spectra for these structures were simulated and compared against the experimental EXAFS to iteratively refine the models, producing more atomic structures that were consistent with all experimental data, and will be more accurate for subsequent theoretical calculations. This work demonstrates that correlating the local characterization of TEM with the many-particle information from EXAFS grants a multiscale understanding not achievable with either approach alone.

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[2] S. Garcia, *et al.*, *ACS Nano* **8** (2014), p. 11512-11521.

9:00am **SS+HC-WeM-4 Designing Heterogeneous Alloy Catalysts from First Principles and Surface Science**, *Charles Sykes*, Tufts University

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. 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).

9:20am **SS+HC-WeM-5 Extracting Diffusing Parameters for Cu and S from Surface Segregation Data Recorded with AES on a Ni-Cu(S) Ternary Alloy**, *Jacobus Terblans*, University of the Free State, South Africa; *X Yan*, University of the Free State, China; *J Wand*, Shantou University, China; *H Swart*, University of the Free State, Republic of South Africa, South Africa

The catalytic selectivity and activity of Cu-Ni bimetallic catalysts, used for oil hydrogenation, have been investigated extensively over the years. A catalytic surface that is Cu rich have higher selectivity than a Ni rich surface. The Cu-Ni alloy system has a simple phase diagram and forms a solid solution in the entire compositional range. In this study the segregation of Cu and S to the surface of a Cu-Ni alloy with 21.3 at.% Cu and 7 ppm S was measured by using Auger electron spectroscopy (AES) coupled with a linear programmed heater. It was found that first the Cu segregated to the surface and reached a maximum surface coverage of 40 %. Once the Cu reached a maximum surface coverage, it started to desegregate as it was replaced by the S that was also segregating to the surface. The measured segregation data were fitted by Fick's and Guttman's ternary segregation models and the diffusing parameters (namely segregation energy (ΔG), interaction parameter (Ω), pre-exponential factor (D_0) and the diffusion activation energy (Q)) for both Cu and S were extracted from the data.

9:40am **SS+HC-WeM-6 Atomic and Electronic Structure of CoO Nanoislands on Au(111)**, *Ana Sanchez-Grande*, IMDEA Nanoscience, Spain; *J Rodriguez-Fernandez*, Aarhus University, Denmark; *E Carrasco, B Cirera, K Lauwaet*, IMDEA Nanoscience, Spain; *J Fester*, Aarhus University, Denmark; *R Miranda*, Universidad Autonoma Madrid, Spain; *J Lauritsen*, Aarhus University, Denmark; *D Ecija*, IMDEA Nanoscience, Spain

Oxides have found applications in various problems in the fields of chemistry, physics and materials science, notably for use in catalysis, encouraging investigation of fundamental properties of oxides. Hereby, transition metal oxides have been proposed as promising catalysts in the oxygen evolution reaction for water splitting, of crucial relevance in clean energy. Equipped with state-of-the-art scanning probe and sample-average techniques, atomistic insights for FeO [1] and CoO [2], [3] and their activity towards water splitting have been recently reported.

Despite this activity, there is a lack of knowledge about the precise atomic and electronic structure of most of these oxides. To understand better the activity of such catalysts, we have selected CoO nanoislands as an archetype model catalyst for water splitting. Our results show the complex atomic and electronic structure of CoO islands on Au(111), revealing the emergence of a Moiré pattern within the nanoislands. Such nanostructures show a higher density of states in the conduction band at the top moirons inside the nanoislands, while present an increase of the valence band

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states at the borders of the islands and at the bottom moirons inside the nanoislands. Importantly, oxygen dislocation lines induce profound electronic changes in adjacent regions (beta regions) within the nanoislands.

The exposure of such catalyst to water highlights that activity towards water splitting depends on substrate temperature. At room temperature [3], the water is adsorbed and dissociated, affording the formation of hydroxyls, which are located predominantly at the bottom moirons. However, at low temperatures the water is adsorbed intact exclusively on the beta regions and can be manipulated with the STM tip, affording a multi-level electronic molecular nano-switch.

Our results shed light into the atomistic adsorption and dissociation of water on a very promising catalysts and reveal that such a process is temperature dependent.

References:

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- [3]: Walton, A. S., Fester, J., Bajdich, M., Arman, M. A., Osiecki, J., Knudsen, J. and Lauritsen, J. V. *Acs Nano*, **9** (3), 2445-2453 (2015).

11:00am **SS+HC-WeM-10 Using Water as a Co-catalyst in Heterogeneous Catalysis to Improve Activity and Selectivity, Lars Grabow**, University of Houston **INVITED**

“What happens when you add water?” is possibly the most frequently asked question after presentations in heterogeneous catalysis. In this talk, I will demonstrate that this question is indeed paramount and that the presence of even minute amounts of water can drastically change reaction rates and product selectivities. Examples include water-mediated proton hopping across a metal-oxide surface, oxidation of carbon monoxide at the gold/titania interface, and hydrodeoxygenation of phenolic compounds over titania supported ruthenium catalysts. Together, these examples demonstrate that water can act as co-catalyst in a variety of catalytic reactions and by varying the amount of water it may be possible to tune reaction rates and product selectivity.

11:40am **SS+HC-WeM-12 Experimental and Theoretical Evaluation of Water Chemistry on Two-dimensional Silica and Aluminosilicate, Jin-Hao Jhang**, G Hutchings, Yale University; J Boscoboinik, Center for Functional Nanomaterials Brookhaven National Laboratory; E Altman, Yale University

The participation of water in zeolites is widely seen in catalysis, ion-exchange, and wastewater treatment. Water adsorption, dissociation and desorption all play critical roles in forming catalytically active Brønsted and Lewis acid sites. Recently, two-dimensional (2D) silica and aluminosilicate bilayers were fabricated on different substrates successfully. Prior studies have suggested that protonated 2D aluminosilicate can be formed and these protonated sites may be analogous to those in acid zeolites. Thereby, the 2D aluminosilicate shows its potential as a zeolite model. In this work, we studied water chemistry on 2D silica and aluminosilicate grown on a Pd(111) substrate by combining density function theory (DFT), thermal desorption spectroscopy (TDS), and ambient pressure photoelectron spectroscopy (AP-PES). We found that protonated 2D aluminosilicate on Pd(111) is thermally stable with both dehydrogenation and dehydration of the protonated surface energetically infeasible under 1000 K. Based on the theoretical and experimental results, once the aluminosilicate surface is protonated, no further water dissociation will take place. The AP-PES study suggests that molecular water can penetrate through the 2D bilayers and stays at the bilayer-substrate interface, leading to core-level shifts in the 2D bilayers due to changes of dipole moments. These findings show that the Brønsted acid sites on the Pd-supported 2D aluminosilicate are robust, and thereby provide fundamental information on the more complex zeolite surfaces.

12:00pm **SS+HC-WeM-13 Double Layer Formation of Water Molecules on Graphene, A Akaishi, T Yonemaru, Jun Nakamura**, The University of Electro-Communications (UEC-Tokyo), Japan

While graphite is known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as hydrocarbons on the surface are removed [1,2]. The contact

angle estimated by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. On the other hand, water molecules have been confirmed to form layered structures on a graphene surface [4] and on the surface of carbon nanotubes [5]. But, the wettability of pristine graphene surfaces remains unsettled.

To investigate the water wettability of graphitic surfaces, we use molecular dynamics simulations of water molecules on the surface of a single graphene layer at room temperature [6]. The results indicate that a water droplet spreads over the entire surface and that a double-layer structure of water molecules forms on the surface, which means that wetting of graphitic surfaces is possible, but only by two layers of water molecules. No further water layers can cohere to the double-layer structure, but the formation of three-dimensional clusters of liquid water is confirmed. The surface of the double-layer structure acts as a hydrophobic surface. Such peculiar behavior of water molecules can be reasonably explained by the formation of hydrogen bonds: The hydrogen bonds of the interfacial water molecules form between the first two layers and also within each layer. This hydrogen-bond network is confined within the double layer, which means that no “dangling hydrogen bonds” appear on the surface of the double-layer structure. This formation of hydrogen bonds stabilizes the double-layer structure and makes its surface hydrophobic. Thus, the numerical simulations indicate that a graphene surface is perfectly wettable on the atomic scale and becomes hydrophobic once it is covered by this double layer of water molecules.

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Biomaterial Interfaces Division

Room 104B - Session BI+AC+AS+HC+NS+SS+TF-WeA

Current and Future Stars of the AVS Symposium II

Moderator: David Boris, U.S. Naval Research Laboratory

2:20pm **BI+AC+AS+HC+NS+SS+TF-WeA-1 Medard W. Welch Award Lecture: A Surface Scientist's Journey from Small Molecules to Biomolecules and Biomaterials, David G. Castner¹**, University of Washington **INVITED**

Surface science plays an important role in a wide range of research and development areas such as catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface scientist allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface scientist is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. We have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface science instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface science techniques, there still remain many significant challenges for surface scientist. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science as well as discuss opportunities for addressing future challenges.

3:00pm **BI+AC+AS+HC+NS+SS+TF-WeA-3 Invited Talk-Future Stars of AVS Session: Making, Studying, and Designing Hierarchically Structured Soft Materials, Keith A. Brown²**, Boston University

Nature realizes extraordinary materials by structuring them precisely from the molecular scale to the macroscopic scale. While nature may have perfected this process over evolutionary time scales, synthetically recapitulating this level of control is tremendously difficult due to the large number of length scales involved and our limited knowledge of interactions between these scales. Faced with the daunting challenge of synthetically realizing soft hierarchical materials, we have adopted a three pronged strategy to: (1) make structures with control from the molecular scale to the macroscopic scale by directing bottom-up growth processes with top-down control, (2) learn how the properties of such materials emerge from their hierarchical structure, and (3) design the best performing structures using novel approaches borrowed from machine learning and autonomous research. In this talk, we will report recent progress in this complementary areas of making, studying, and designing hierarchical materials. In particular, we will focus on two major classes of materials, nanoparticle-based structures where the assembly and organization of particles leads to emergent mechanical properties at the bulk scale and polymer-based materials where we are connecting the synthesis, patterning, and properties of polymer structures across scales. In addition to lessons about the fundamental properties of hierarchically organized

soft matter, we will highlight the synergies possible when combining, synthesis, detailed characterization, and advances in materials design.

3:20pm **BI+AC+AS+HC+NS+SS+TF-WeA-4 Invited Talk-Future Stars of AVS Session: Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Processing Kinetics and Applications, Mark Losego³**, Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel chemical, electrical, optical, and/or physical properties. These new hybrid materials have demonstrated applications including chemical separations, photovoltaics, and microelectronics patterning. This talk will focus on our development of a fundamental VPI processing kinetics phenomenology to create a pathway for rational design of material composition and structure. By measuring VPI compositional profiles as a function of space or time and temperature, we can extract fundamental energy barriers for the sorption, diffusion, and reaction processes and delineate amongst different rate limiting steps. In our materials development, we often find that partial infiltration of a polymer film, fiber, or foam is sufficient to impart desired properties; so rational design of the infiltration kinetics can enable desired performance without waste in processing time or materials. Here, we will demonstrate several examples including our work to create chemically insoluble polymers and membranes. We find, for example, that infiltration depths of about 0.75 microns are sufficient to yield PMMA chemically insoluble in organic solvents regardless of whether it is in a thin film geometry or a macroscopic plexiglass object of centimeters in dimension. In PIM-1 membranes used for chemical separations, we find that we can achieve > 30 wt% inorganic loading with a single infiltration exposure. After infiltration, these membranes become stable in new separations solvents that previously swelled and/or dissolved the polymer.

(Submitted for the Future Stars of the AVS Symposium.)

4:20pm **BI+AC+AS+HC+NS+SS+TF-WeA-7 Invited Talk-Future Stars of AVS Session: Surface Preparation Methods for the Selective Oxidation of Ethanol to Acetaldehyde over TiO₂/Au(111), Ashleigh Baber⁴, D Boyle, J Wilke, V Lam, D Schlosser**, James Madison University

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of hydrogen from alcohols. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. The redox chemistry of small alcohols, including methanol and propanol, has been studied on Au(111) supported TiO₂ nanoparticles, yet the active site for the chemistry has not yet been elucidated. Depending on the surface preparation conditions, Au(111) supported TiO₂ nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectivity form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO₂/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO₂/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO₂/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO₂ nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO₂/Au(111). The presence of TiO₂ nanoparticles on Au(111), ~25 nm in diameter, led to the catalytic conversion of ethanol to acetaldehyde at temperatures greater than 400 K. Low coverages of fully oxidized TiO₂ nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

4:40pm **BI+AC+AS+HC+NS+SS+TF-WeA-8 Invited Talk-Future Stars of AVS Session: Single Atom Catalysis: An Atomic-Scale View, Gareth Parkinson⁵**, TU Wien, Austria

Single-atom catalysis is a rapidly emerging area of research that aims to maximize the efficient usage of precious metals through "single atom" active sites. Although catalytic activity has been demonstrated for several single-atom catalyst systems, an inability to accurately characterize the catalyst based on single atom active sites ensures that that the field remains controversial, and little is really known about how a single atom

¹ Medard W. Welch Award Winner

² Future Stars of the AVS

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³ Future Stars of the AVS

⁴ Future Stars of the AVS

⁵ Future Stars of the AVS

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adsorbed on a metal oxide support catalyzes a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies.

The surface stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to unprecedented temperatures as high as 700 K. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms at work. Several examples of our recent work will be used to illustrate the trends discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to rapid sintering, and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction.

5:00pm **BI+AC+AS+HC+NS+SS+TF-WeA-9 Invited Talk-Future Stars of AVS Session: Multimodal Chemical and Functional Imaging of Nanoscale Transformations Away from Equilibrium, Olga Ovchinnikova¹**, Oak Ridge National Laboratory

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe microscopy and mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous quantitative nanomechanical properties and quantitative chemical analysis. In this talk I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. We have applied this approach to the study of systems and processes that underlie energy capture, conversion and storage, including photovoltaics and oxide ferroelectrics, which have historically eluded comprehensive understanding of the mechanisms behind the spatially heterogeneous interfacial chemistry and its link to material performance. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

5:20pm **BI+AC+AS+HC+NS+SS+TF-WeA-10 Invited Talk-Future Stars of AVS Session: Expanding the Structural Toolkit to Characterize Heavy Actinide Complexes, Rebecca Abergel²**, Lawrence Berkeley Lab, University of California, Berkeley; *G Deblonde, A Mueller, P Ercius*, Lawrence Berkeley National Laboratory; *A Minor*, Lawrence Berkeley Lab, University of California, Berkeley; *C Booth, W de Jong*, Lawrence Berkeley National Laboratory; *R Strong*, Fred Hutchinson Cancer Research Center

Structural characterization of actinide elements from actinium to einsteinium can be a challenging task due to the high radioactivity and limited availability of some of the isotopes of interest. However, significant work is needed to address a certain lack of understanding of the fundamental bonding interactions between those metal centers and selective ligands. Such understanding presents a rich set of scientific challenges and is critical to a number of applied problems including the development of new separation strategies for the nuclear fuel cycle, the need for decontamination after a nuclear accident or the use of radioisotopes for new cancer treatments. Our studies utilize luminescence sensitization, UV-Visible, X-ray absorption, and X-ray diffraction spectroscopic techniques as well as transmission electron microscopy and electron energy loss spectroscopy to investigate specific heavy actinide

coordination features. Using simple inorganic complexes but also strong hard oxygen-donor ligands as well as more elaborate higher molecular weight protein assemblies allows the differentiation of heavy actinide species even when limited to minute amounts of materials. Innovative structural characterization approaches based on X-ray absorption, X-ray diffraction and electron microscopy that were applied to series of isostructural systems and used to derive coordination trends in the later 5f-element sequence will be discussed.

5:40pm **BI+AC+AS+HC+NS+SS+TF-WeA-11 Invited Talk-Future Stars of AVS Session: Trends in Adsorbate Interactions with Bimetal Surfaces, Liney Arnadottir³, L Sprowl**, Oregon State University

Surface chemistry plays an important role in a large range of applications and technologies, such as catalysis and electrocatalysis, device fabrication through film growth, and degradations through oxide formation, carbonization, and corrosion. Bimetal surfaces are of increasing interest for single atom catalysis and corrosion resistance of alloys. Previous studies have shown correlations between adsorbate interactions and d-band shifts for different metals as well as for alloying effects of metal sandwich structures, but for mixed metal surfaces the nature of the adsorption site can change (ensemble effect) as well as the number of electrons in the surface layer which effects the d-band center. Here we explore correlations of adsorbate interactions with mixed metal surfaces through density functional theory calculations of adsorbate interactions with different facets, (100) and (111), of pure Ni and eleven Ni-based surface alloys as well as Ni in different host metal. We find that the addition of surface alloying atom has little effect on the binding of CO and C but C binding varies for different facets. On the other hand, O binding is highly dependent on the alloying element due to ensemble effect. This has an interesting effect on the predicted reaction energies of CO dissociation which is endothermic on the (111) facet and exothermic on the (100) facet governed by C interactions but the changes in the reaction energy within each facet are mostly governed by the ensemble effect on O adsorption. The relationship between the formation energy of the mixed metal surface and adsorbate interactions will also be discussed.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeA

Theory and Dynamics of Heterogeneously Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

2:20pm **HC+SS-WeA-1 First-Principles Kinetic Monte Carlo Simulation of CO Oxidation on PdO(101): Role of Oxygen Vacancies, Minkyu Kim⁴, A Asthagiri**, 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, O₂ dissociation, and CO₂ formation can be decreased by 20-40% in the presence of O vacancies, while O₂ 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 O₂ 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 CO₂ 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

¹ Future Stars of the AVS

² Future Stars of the AVS

³ Future Stars of the AVS

⁴ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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simulations at steady state conditions of low CO and O₂ pressures (P_{CO}: 510⁻⁹Torr / P_{O₂}: 1.510⁻⁸Torr), show that the rate-limiting step is O₂ 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 be healed by gaseous O₂. In addition, we will discuss kMC simulations under reaction conditions at varying CO/O₂ partial pressures.

2:40pm HC+SS-WeA-2 Surface Reactivity of Activated CO₂, Richard van Lent¹, Leiden University, Netherlands; *A Walsh, M Gleeson*, DIFFER, Netherlands; *L Juurlink*, Leiden University, Netherlands

Catalytically converting CO₂ into renewable fuels is a promising avenue that addresses the current fuel and energy storage challenges. Depending on the process, conversion of CO₂ may involve initial breaking of the OC=O bond. If so, this highly endothermic step is likely rate limiting to the overall process. Ultra-high vacuum (UHV) research on well-defined surfaces can provide fundamental insight into such processes, e.g. how dissociation may be aided by internal energy in CO₂, the metal's identity and the surface structure.

Internal energy has been shown to promote the highly activated dissociative adsorption of CO₂ on Ni(100) [1]. Rovibrationally state-resolved measurements for CH₄ on Ni(100) have shown that excitation of the ν_3 antisymmetric stretch vibration has a promoting effect that approximately equals kinetic energy for Ni(100) surfaces [2,3]. For other metal surfaces and CH₄ vibrations, the relative efficacy of vibrational and kinetic energies varies between 0.4 and 1.4 [2].

To start unravelling how CO₂ dissociates on a surface, we combine standard supersonic molecular beam techniques with high resolution continuous wave (cw) IR laser excitation. We study the effect of ν_3 antisymmetric stretch excitation of CO₂ on dissociative adsorption on a Ni(711) surface.

For excitation, we use a 3.9–4.6 μm single mode optical parametric oscillator (OPO). The OPO is frequency-stabilized by locking onto the derivative of the Lamb dip of the specific rovibrational transition of interest. Frequency-stabilized IR radiation is crossed with a supersonic molecular beam that impinges onto the cleaned Ni(711) surface under UHV conditions. We use methods to determine absolute reactivities for CO₂ molecules with and without laser excitation. We extract rovibrational state-dependent absolute sticking probabilities as a function of kinetic energy. From this data, we determine the relative efficacy of vibrational and kinetic energy in overcoming the large activation barrier to dissociation.

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3:00pm HC+SS-WeA-3 Shining Light on Complexity: State- and Energy-Resolved Studies of Gas-Surface Reaction Dynamics and Mechanism, Arthur Utz, Tufts University **INVITED**

Gas-surface reactions on a metal surface can be far more complex than their net chemical equation would suggest. The heterogeneity of the surface, and its ability to restructure, impact the availability and energetics of reaction sites, energy redistribution processes triggered by the gas-surface collision dictate transition state access, and many coupled chemical processes can influence the reaction's outcome.

The talk will survey the ability to vibrational state selected measurements of gas-surface reactivity to systematically unravel important aspects of this complexity and provide molecular-level mechanistic insights that can guide our understanding and predictions about these processes. The experiments use infrared light to excite a single quantum rotational and vibrational level of the gas-surface reagent molecule and a molecular beam to define its incident kinetic energy. In this way, we are able to make energy-resolved measurements of reactivity while systematically varying the distribution of energy among the system's energetic degrees of freedom. Computational studies by our collaborators inform and guide our interpretation of the data.

Recent results will be featured and examine the impact of a vibrationally excited reagent molecule's symmetry on surface-induced energy redistribution, the quenching lifetime of a vibrationally excited molecule on a metal surface, the role of surface atom motion on reaction energetics, the ability to use these measurements to benchmark DFT electronic

structure calculations, and how isolated surface structural features, including steps and adatoms, modify reaction energetics.

4:20pm HC+SS-WeA-7 Vibration-driven Reaction of CO₂ on Cu Surfaces via Eley-Rideal Type Mechanism, Junji Nakamura, J. Quan, T. Kozarashi, T. Mogi, T. Imabayashi, K. Takeyasu, T. Kondo, University of Tsukuba, Japan

We have long studied the formation of formate (HCOO_a) intermediates as an intermediates of methanol synthesis by hydrogenation of CO₂ on Cu surfaces [1-4]. It has been suggested based on the kinetic analysis for the high pressure bulb experiments that the formate formation proceeds via Eley-Rideal type mechanism, in which CO₂ directly reacts with adsorbed hydrogen atom on Cu. In order to clarify the mechanism and dynamics, we carried out CO₂ molecular beam studies with the translational energy of 1.12-1.97 eV and the nozzle temperature of 800-1100 K. It was found that hot CO₂ in the molecular beam reacts directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces at 120–220 K to form formate adspecies (CO₂ + H_a → HCOO_a). That is, even at the low surface temperatures, formate species is formed rapidly when supplying energy only to CO₂. This indicates that the energy to overcome the reaction barrier comes from the hot CO₂ molecule itself instead of the Cu surface. The vibrational energy of CO₂ was much more effective for the reaction compared to the translational energy; and the reaction rate was independent of the surface temperature. The independence of surface temperature indicates the E-R type mechanism that the CO₂ molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a. If the impinging CO₂ molecule chemisorbs on the Cu surfaces before reacting with H_a, the reaction rate should be dependent on the surface temperature, rather than the kinetic and the internal energies of CO₂. We evaluated the barrier distribution factors (*W*) of so-called Luntz equation by analysis of the reaction probability curves, which shows significant efficacy of the vibrational energy on the reaction of CO₂, which has not been observed before. DFT calculations are consistent with the experimental observations [5]. The direct reaction of CO₂ with adsorbed hydrogen atom can be regarded as the first example of vibration-driven bond formation reactions on surfaces.

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4:40pm HC+SS-WeA-8 First Principles Reaction Kinetics over Metals, Oxides and Nanoparticles, Henrik Grönbeck, Chalmers University of Technology, Gothenburg, Sweden **INVITED**

A major challenge in heterogeneous catalysis research is the determination of dominating reaction paths and kinetic bottlenecks. One reason for the challenge is the dynamic character of the kinetics, where the active sites may change with reaction conditions. Nevertheless, it is atomic scale information that allow for catalyst development beyond trial-and-error approaches. Kinetic modeling based on first principles calculations have over the past decade grown into an important tool for investigating the importance of different catalyst phases and reaction paths. In this contribution, I will discuss work where we have used density functional theory in combination with kinetic modeling to investigate catalytic reactions over metals, oxides and nanoparticles. The examples cover different aspects of kinetic modeling including determination of adsorbate entropies, importance of attractive adsorbate-adsorbate interactions and the complexity of many types of active sites.

Complete methane oxidation to carbon dioxide and water is used as one example and we have investigated the reaction over metallic Pd(100) and Pd(111) [1] as well as PdO(101) [2]. The reaction paths are shown to be

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markedly different on the metallic and the oxidized surfaces. We find that the catalytic activity is highly sensitive to adsorbate-adsorbate interactions which for PdO(101) are attractive owing to electronic pairing effects. This effect is crucial and common for oxide surfaces [3].

Reactions over platinum nanoparticles are investigated using a recently developed scaling relation Monte Carlo technique [4]. Taking CO oxidation as a model reaction, we find that the overall activity is determined by complex kinetic couplings. Effects of particle shape as well as internal and external strain will be discussed [5].

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5:20pm **HC+SS-WeA-10 Formation of Pd/Ag Sandwiches, a Stable PdAg Subsurface Alloy, and the Pd Segregation induced by CO and O₂, Studied with STM, Ambient-pressure XPS, and DFT, *Matthijs van Spronsen*, Lawrence Berkeley National Laboratory; *K Duanmu*, UCLA; *R Madix*, Harvard University; *M Salmeron*, Lawrence Berkeley National Laboratory; *P Sautet*, UCLA; *C Friend*, Harvard University**

Efficient chemical production requires the use of materials able to selectively catalyze complex chemical reactions. High selectivity can be obtained by using noble metals. To improve activity, while retaining selectivity, small amounts of an active metal can be added. These species can function as active sites for, e.g., O₂ activation.

A promising alloy for selective hydrogenation is AgPd. The challenge using this material as a catalyst is the larger surface free energy of Pd, compared to Ag. This difference leads to Ag enrichment of the surface, hence, more Pd, both costly and scarce, is needed to ensure that Pd is present in the surface.

Here, the stability of Pd was probed in (sub)surface alloys formed by depositing sub-monolayer amounts of Pd on pure Ag single crystals, in order to evaluate the feasibility of using surface alloys as catalysts. These surface alloys would use much less Pd, but depend critically on understanding and control of the alloy composition and stability.

Mild annealing (~400 K) under ultra-high vacuum, leads to extensive migration of Ag and the formation of a Ag capping layer on the Pd. These measurements were based on scanning tunneling microscopy and X-ray photoelectron spectroscopy, supported by modeling (density functional theory). The etching, due to the loss of Ag, and the increase in island height, due to the capping, results in three-layer-high islands, covering both the terraces and the steps of the Ag(111) surface. The absence of significant amounts of Pd in the surface was confirmed by the lack of CO adsorption at 120 K.

The exposure of the Ag/Pd/Ag(111) surface alloy to gas atmospheres, either pure CO or O₂ (0.5 & 1 Torr, respectively), reverses the energetics, thus making Pd resurface. This was concluded from large core-level shifts observed in AP XPS measurements. Due to the proximity of Pd to the surface, the required temperature for Pd to segregate was rather low, in fact, for CO it was detected for 300 K. Resurfacing, and subsequent oxidation, of Pd was much slower, requiring cycling the temperature between 300 and 400 K in the O₂ atmosphere, several times. The difference stems from the fact that O₂ needs to be dissociated before it can form strong bonds to Pd, while CO can adsorb directly to Pd. The initial O₂-dissociation activity of the Ag-capped Pd is expected to be rather small.

To conclude, precise understanding of the stability of active metals with a high surface free energy is required to control the composition of surface alloys and its potential as active/selective catalyst.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-ThM

In-situ Analysis of Heterogeneously Catalyzed Reactions

Moderator: Sharani Roy, University of Tennessee Knoxville

8:00am HC+SS-ThM-1 Structural Characterization of ZnO on Cu(111) by using STM and XPS: Role of Cu-ZnO Interface in Methanol Synthesis, *Mausumi Mahapatra, J Rodriguez*, Brookhaven National Laboratory

The ZnO-copper interface plays an important role in the synthesis of methanol from the hydrogenation of ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{OH} + 2\text{H}_2\text{O}$). The deposition of nanoparticles of ZnO on Cu(111), $\theta_{\text{oxi}} < 0.3$ monolayer, create a stable and highly active interface between ZnO and Cu. The ZnO-copper catalysts may be prepared by two different methods: 1) Zn vapor deposited on Cu(111) at ~600 K in an oxygen ambient (reactive vapor deposition), 2) Zn vapor deposited on Cu(111) at 300 K following by heating the surface with oxygen to 600 K (oxidation of surface alloy). The reactivity and stability of the catalysts prepared by the above two methods were tested under CO_2 hydrogenation reaction conditions in a reactor and by using AP-XPS: 1) The ZnO-copper catalyst prepared by method 1 was stable whereas that prepared by method 2 was not stable at the elevated temperatures (500–600 K) used for the CO_2 hydrogenation. The temperature dependent growth and the structural characterization of the ZnO/Cu(111) catalyst, $\theta_{\text{oxi}} < 0.3$ monolayer was explored by using STM. Our results show that the size and shape of the ZnO nanoparticles are dependent on the growth temperature. The ZnO/Cu(111) surface prepared by reactive vapor deposition at 450–600 K results in large ZnO triangular islands. However the surface oxidation of a Zn/Cu(111) alloy resulted in very small ZnO clusters.

8:20am HC+SS-ThM-2 Dissociative Adsorption of CO_2 on Cu-surfaces, *Benjamin Hagman*, Lund University, Sweden; *A Posada-Borbón, A Schaefer*, Chalmers University of Technology, Gothenburg, Sweden; *C Zhang*, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *N Martin*, Chalmers University of Technology, Gothenburg, Sweden; *E Lundgren*, Lund University, Sweden; *H Grönbeck*, Chalmers University of Technology, Gothenburg, Sweden; *J Gustafson*, Lund University, Sweden

Due to the urgent problem of global warming, there is a need to reduce the release of the greenhouse gas CO_2 into the atmosphere. A potential approach to limit the CO_2 release is to convert it into useful chemical products, such as methanol [1]. However, the recycling of CO_2 is a challenging task as the molecule is rather inert, which makes it difficult to activate for reduction and subsequent hydrogenation. The most used metal for this activation is Cu, and a fundamental understanding of how CO_2 interacts with Cu surfaces would promote the development of new catalysts for the reduction of CO_2 [2].

We have studied the CO_2 interaction with both Cu(100) and stepped Cu(911) surfaces at elevated CO_2 pressures using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS gives us the ability to probe the changes of the surface during the chemical reaction. In our case, we see that CO_2 chemisorbs on the surface and dissociates to O and CO, of which CO desorb, while the atomic oxygen remains on the surface.

For the Cu(100) surface, we observe that the rate of oxygen uptake from CO_2 dissociation is constant until the atomic oxygen coverage approaches 0.25 ML, where the rate decreases. After 0.25 ML the rate remains constant until a saturation appears as the oxygen coverage approaches 0.5 ML. Density Functional Theory (DFT) calculations indicate that CO_2 can adsorb and dissociate on both the terraces and steps on Cu(100), however, the dissociation is expected to take place mainly on the step as the barrier for the dissociation is lower at such sites. The atomic oxygen, from the dissociation at the step, is expected to diffuse away from the step to the terrace, leaving the number of active sites constant, and explaining the constant oxygen uptake rate. Both the experiment and DFT calculations indicate that the atomic oxygen from the dissociation of CO_2 poisons the adsorption and dissociation of CO_2 at an oxygen coverage above 0.25 ML, however, we believe that the step can remain active after 0.25 ML.

To confirm the role of the steps on Cu(100), we have also studied the interaction of CO_2 and Cu(911). We observe the CO_2 adsorption is significantly facilitated by the presence of the steps on the Cu(911) surface as compared to the flat Cu(100). The effect of the facilitated CO_2 adsorption on the subsequent dissociation will be discussed.

References:

8:40am HC+SS-ThM-3 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) Surface Under Ambient Pressure Conditions, *C Kruppe, Michael 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 150 Torr of carbon dioxide, a peak is observed at 1294 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 150 Torr of $\text{H}_2(\text{g})$ at 300 K, the 1294 cm^{-1} peak of CO_2 is greatly diminished, while new peaks appear due to gas phase water. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. When the Cu(111) surface is annealed to higher temperatures, numerous changes occur in the spectra revealing the formation of a series of surface intermediates containing C–H bonds, including methoxy, OCH_3 . The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be easily detected with RAIRS.

9:00am HC+SS-ThM-4 Oxide Formation on Ir(100) Studied by in-Situ Surface X-ray-Diffraction, *Stefano Albertin, U Hejral*, Lund University, Sweden; *R Felici*, SPIN-CNR, Italy; *R Martin*, University of Florida; *M Jankowski*, ESRF, France; *J Weaver*, University of Florida; *E Lundgren*, Lund University, Sweden

Methane (CH_4) conversion into higher added value hydrocarbons is done through a number of complex catalytic steps, and has been studied for many years [1]. The initial and often rate limiting step in the reaction is the dissociation of the molecule on the metal catalyst surface. Because alkane C–H bonds are among the least reactive known, no process for direct conversion of CH_4 into methanol (CH_3OH) has so far been developed.

$\text{IrO}_2(1\ 10)$ surface grown on Ir(100) has shown facile dissociation of CH_4 at liquid nitrogen temperatures [2], as well as oxidizing H_2 to $-\text{OH}$ [3]: two steps that could have importance for the development of a new direct methane-to-methanol catalysts.

In this contribution we will present recent results from in-situ Surface X-ray Diffraction (SXRD) recorded at beamline ID03 at the ESRF from the oxidation of a Ir(100) surface. We find that the Ir(100) surface oxidizes into a bulk oxide at a temperature of 775 K and a pressure of 5 mbar of O_2 similar to what observed in [2], forming a predominantly rutile $\text{IrO}_2(110)$ oriented surface. Our study also demonstrates that lowering the partial O_2 pressure or the temperature results in the formation of a number of different Ir sub-oxides similar to the ones found for Ir(111) [4], and the structures formed will be discussed in this contribution.

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9:20am HC+SS-ThM-5 Dynamic Nanocatalysts: Environmental Effects, *Beatriz Roldan Cuenya*, Fritz-Haber Institute of the Max Planck Society, Germany

INVITED

In order to comprehend the catalytic performance of metal nanostructures, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanocatalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. Furthermore, deactivation phenomena taking place under reaction conditions can only be understood, and ultimately prevented, if sufficient information is available on the catalyst morphology, structure, chemical state, and surface composition while at work.

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I will first describe novel approaches for the synthesis of size- and shape-controlled nanoparticles and nanostructured metallic films (e.g. Au, Cu, Ag, Zn, CuZn, CuCo, CuNi, AgSn, NiGa) and their functionalization/activation based on plasma treatments. Subsequently, I will illustrate how to follow the evolution of their morphology and surface composition under different gaseous and liquid chemical environments in the course of a catalytic reaction. This will be implemented using a synergistic combination of *in situ* and *operando* microscopy (EC-AFM, STM, TEM) and spectroscopy (XAFS, AP-XPS) methods. It will be highlighted that for structure-sensitive reactions, catalytic activity, selectivity, and stability can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas- and liquid-phase oxidation of 2-propanol and the gas-phase hydrogenation and electrochemical reduction of CO₂. Emphasis will be given to elucidating the role of the size, shape, composition, chemical state, surface defects and roughness of the catalysts in the activity and selectivity of the former reactions.

11:00am **HC+SS-ThM-10 Atomic Layer Deposition (ALD) Synthesis of Au/TiO₂/SBA-15 Catalysts**, *W Ke, X Qin, Francisco Zaera*, University of California, Riverside

Au/Titania catalysts have received much attention in recent years because of their ability to promote photocatalytic water splitting as well as selective low-temperature oxidation reactions. The uniqueness of these catalysts is ascribed to both the nanometer-size of the gold nanoparticles and the reducibility of the titania support. Here we report results from studies on the use of ALD to control the titania film thickness, to tune its degree of reducibility and explore the role of that reducibility in catalysis. SBA-15, a mesoporous solid with well-defined pore structure, was used as the base material in order to be better able to characterize the deposited titania films. Surface reducibility was tested as a function of film thickness by CO infrared-absorption spectroscopy titrations and by EPR, and the catalytic performance via kinetic measurements for CO oxidation. Unique trends were observed at intermediate (2-4 ALD cycles) film thicknesses.

11:20am **HC+SS-ThM-11 Enhanced Stability of Pt/Cu Single-Atom Alloy Catalysts: In Situ Characterization of the Pt/Cu(111) Surface in an Ambient Pressure of CO**, *Juan Pablo Simonovis Santamaria*, Brookhaven National Laboratory

Research in catalysis has steered towards the design and synthesis of more efficient catalysts that can yield better quality products at lower costs. In this regard, bimetallic alloys where the active metal is mono-atomically dispersed have shown unique activity, selectivity and stability compared to their monometallic counterparts. These so called single atom alloys (SAA) are of interest since small amounts of active metals can be used reducing catalysts cost. However, the chemical interactions between active site and reacting molecules are still poorly understood, thus careful characterization of these moieties under reaction conditions is needed to elucidate fundamental reaction steps that can clarify the role of the active site during the catalytic process.

In this study, we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) performed at the 23-ID-2 (IOS) beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory to compare the stability of Pt/Cu(111) SAA in ultrahigh vacuum (UHV) and ambient pressure conditions, particularly how its surface structure and composition can be influenced by the presence of a reactant gas such as CO. Because of the surface and chemical sensitivities of AP-XPS, we can directly probe the Pt atoms to clearly identify surface/subsurface layers of the metal and monitor its evolution under different experimental conditions.

Our study showed that the Pt (0.05 ML)/ Cu(111) SAA is thermally unstable above 400 K under UHV conditions, since higher temperatures cause Pt on the surface to migrate to the subsurface and, eventually, to the bulk. This metal diffusion into the subsurface could lead to the deactivation of a potential catalyst. However, under ambient pressures of CO, the surface and subsurface Pt are thermally stable up to 500 K, resisting diffusion into the bulk. In fact, thermal treatment in CO of a sample that was previously heated under UHV conditions lead to the recovery of Pt that had diffused to the subsurface, suggesting that, within 300-500 K the diffusion process is reversible to some extent. However, this thermal stability as well as surface recovery in CO comes at the expense of slightly enhanced CO-Pt interactions likely caused by the presence of neighboring subsurface Pt resulting from the thermal-induced restructuring of the subsurface layer. Whether the post-heated surface still resists the poisoning effects of CO remains to be seen, but these results demonstrate the importance of studying not only the changes in the surface of a catalyst under reaction

conditions but also the near-surface region, which may also influence the reactivity of the catalyst.

11:40am **HC+SS-ThM-12 Multiscale Modelling of Metal Oxide Interfaces and Nanoparticles**, *Kersti Hermansson, P Mitev, J Kullgren, P Broqvist*, Dept of Chemistry-Ångström, Uppsala University, Sweden

INVITED

Redox-active metal oxide surfaces and interfaces – such as electrodes, catalysts, and sensors – play crucial roles in our society and in the development of new materials and greener technologies. In the scientific literature, a full arsenal of experimental methods are being used to help characterize such interfaces. At the same time, the number of theoretical studies in the literature steadily increases, providing mechanistic information at a detail that is hard to beat by experiment. *Are such theoretical results accurate enough?*

I will describe some of our efforts to develop multiscale modelling protocols for metal oxide surfaces and nanoparticles (e.g. of CeO₂, ZnO and MgO). We combine a range of theoretical methods including *DFT, tight-binding-DFT* [1], *and reactive force-field models* A key question is whether it is really possible to model redox-active metal oxides *without including the electrons?*

The O₂ chemistry of reducible oxides is rich and famous and I will therefore also discuss various aspects of how adsorbed oxygen on nanoparticles and clusters can stabilize in the form *superoxide ions* (O₂⁻) and the implications that this may have on their reactivities. Microkinetic modelling results to mimic experimental TPD spectra will be presented as well as mechanistic detail that is currently only possible to obtain from modelling.

The H₂O molecule deserves special attention as *hydroxylation/hydration* changes the properties and reactivities of metal oxides, often with far-reaching consequences. We recently studied a thick water film on a ZnO(10-10) surface using MD simulations from a neural-network-generated potential landscape of DFT quality combined with anharmonic vibrational frequency calculations.[2] and were able to relate H-bond structure and frequencies in a meaningful way. In an attempt to reach a step further in terms of understanding found that a *parabola-like 'OH frequency vs. in-situ electric field' relation* holds for both intact and dissociated water molecules on ionic surfaces [3], and for both thin and thick films (unpublished).

I will also inform about the European Materials Modelling Council (<https://emmc.info/>), which aims to promote the use of materials modelling in –not least– industry.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-ThA

Bridging Gaps in Heterogeneously Catalyzed Reactions

Moderator: Ryan Brown, Clarkson University

2:20pm HC+SS-ThA-1 Hydrogen Adsorption and Reaction on RuO₂(110) Surface, *A Dahal, I Lyubinetsky, Zdenek Dohnalek*, Pacific Northwest National Laboratory

Ruthenium dioxide is used extensively as a co-catalyst in a wide range of photocatalytic water splitting systems. As such, understanding how it promotes the evolution of hydrogen and oxygen is of high importance. In our studies, we employed scanning tunneling microscopy in combination with molecular beam scattering and temperature programmed desorption studies to follow adsorption, reaction, and thermal evolution of hydrogen on a model RuO₂(110). In our temperature-dependent studies, we find that at low coverages ($H_2/Ru < 0.2$) H₂ dissociates heterolytically and forms hydride-hydroxyl pairs below 100 K. At higher coverages ($H_2/Ru > 0.2$), H₂ adsorbed on Ru sites neighboring the hydride-hydroxyl pairs chemisorbs molecularly. Upon annealing the hydride species convert to hydroxyls and most of the chemisorbed H₂ desorbs. Upon heating, the low and high H₂ covered surfaces transform to partially and fully hydroxylated surface, respectively, above 250 K. Molecular beam scattering studies reveal that the adsorption probability of hydrogen on this surface is strongly temperature-dependent, decreasing from ~0.4 at 25 K to <0.01 at 300 K. These combined studies unravel a complete adsorption and dissociation mechanism of H₂ on this model ruthenium dioxide surface.

2:40pm HC+SS-ThA-2 The Role of Oxides for CO Oxidation over Pd and Rh, and How to Deal with Oxygen Poisoning, *Johan Gustafson*, Lund University, Sweden; *O Balmes*, MAX IV Laboratory, Sweden; *C Zhang*, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *A Schaefer*, Chalmers University of Technology, Gothenburg, Sweden; *B Hagman*, Lund University, Sweden; *L Merte*, *N Martin*, *P Carlsson*, Chalmers University of Technology, Gothenburg, Sweden; *M Jankowski*, ESRF, France; *E Crumlin*, Advanced Light Source, Lawrence Berkeley National Laboratory; *E Lundgren*, Lund University, Sweden

Catalytic CO oxidation is a seemingly simple reaction between CO and O₂ molecules, one of the reactions in automotive catalytic converters, and the fruit-fly reaction in model catalysis. Surprisingly, the phase responsible for the catalytic activity is still under debate, despite decades of investigations. We have performed a simple but yet conclusive study of single crystal Rh and Pd model catalysts, resolving this controversy. For Rh, the oxygen covered metallic surface is more active than the oxide, while for Pd, thin oxide films are at least as active as the metallic surface, but a thicker oxide is less active [1]. The difference between these oxide structures is that the thin PdO films expose coordinatively unsaturated (CUS) metal atoms that act as active sites, while Rh oxides and thicker PdO films do not expose such sites and are hence less active. Similar results have also been found for methane oxidation over Pd [2].

Under highly oxidizing conditions, which are, for instance, desirable for optimal efficiency of combustion engines, there is a general problem of deactivation of catalysts due to too high oxygen exposure, so-called oxygen poisoning. With the above results in mind, this problem is likely related to the formation of oxides that do not expose CUS sites. We therefore believe that the problem of oxygen poisoning over Pd catalysts can be solved by growing a PdO film on top of a more inert metal such as Ag or Au, as this will limit the thickness of the oxide film and hence stabilize the active oxide surface.

In this presentation, we will discuss the active phase of Pd and Rh for CO oxidation, and hopefully show the first results of lower degree of oxygen poisoning for CO and methane oxidation over Pd/Au and Pd/Ag systems.

References

1. J. Gustafson et al., The Role of Oxides in Catalytic CO Oxidation over Rhodium and Palladium, *ACS Catal.*, 2018, 8, 4438–4445.
2. A. Hellman et al., The active phase of palladium during methane oxidation, *J. Phys. Chem. Lett.* 2012, 3, 678–682.

3:00pm HC+SS-ThA-3 Simplifying the Relationships between Catalyst Structure and Reaction Rates for Complex Mechanisms, *Charles T. Campbell*, University of Washington

INVITED

Better catalysts and electro-catalysts are essential for many energy and environmental technologies of the future. Designing better catalysts requires knowing the relationships between catalyst structure and catalytic reaction rates, which are in general poorly understood. I will review here some concepts that clarify and simplify these relationships. While a typical catalytic reaction has a dozen or more adsorbed intermediates and elementary-step transition states, Degree of Rate Control (DRC) analysis can be applied to a microkinetic model of the best known catalyst material to show that the net rate really only depends upon the energies of a few (2 to 4) of these. For related materials, one only needs to know how the change in material affects the energies of these few 'rate-controlling species' to understand how rates relate to structure. This offers opportunities for designing better catalysts. DRC analysis also provides a simple way to predict kinetic isotope effects (KIEs), which can be compared to simple KIE experiments to verify the energy accuracy of a microkinetic model (that is often based on DFT energies). Such DFT energies can be used with DRC values to predict faster catalysts.

The chemical potential of metal atoms (μ_m) in supported catalyst nanoparticles provides another simplifying concept for developing structure – rate correlations in catalysis. It has been known for years that this chemical potential enters directly into the rate equations for catalyst deactivation by sintering. I will show here that it also correlates strongly with the strength with which surface metal atoms bind adsorbed reaction intermediates (and transition states), which correlate with rates as outlined above. I will then review what aspects of catalyst structure control metal chemical potential. It can be tuned to lower values (relative to large particles of the pure metal) by mixing the metal with another metal with which it forms an exothermic alloy, and tuned higher by making the nanoparticles smaller and putting them on a support to which they have a smaller adhesion energy (E_{adh}). Quantitative equations that predict how μ_m varies with size and E_{adh} , and how E_{adh} depends on the metal element and the oxide surface used as the catalyst support will be presented. These also offer opportunities for predicting faster catalysts.

· Work supported by NSF and DOE-OBES Chemical Sciences Division.

4:00pm HC+SS-ThA-6 Spectroscopic Techniques for Identifying Reactive Intermediate Structures during Decomposition of Formic Acid over Metals and Metal Oxides, *Megan Witzke, D Flaherty*, University of Illinois at Urbana-Champaign

Identifying reactive intermediates within an "organometallic zoo" of species that form on surfaces of metal nanoparticles and metal oxides during reactions is a long standing challenge in heterogeneous catalysis.¹

We use a combination of spectroscopic techniques and data analysis methods to isolate and extract spectral features of the reactive intermediates present under relevant operating conditions. Modulation excitation spectroscopy coupled with phase sensitive detection selectively filters spectra to show only reactive intermediates and suppress features of spectating species.² The combined spectra of all reactive species are deconvoluted using singular value decomposition techniques that provide distinct spectra and estimate surface coverages for independent species.³ Comparisons of spectra obtained at different modulation frequencies exploit differences in intrinsic free energy barriers between reactive intermediates by removing species that are unable to form at higher stimulated frequencies. We combine these techniques to molecularly interpret infrared spectra to identify compositionally similar surface intermediates formed in situ during decomposition of formic acid (HCOOH) over anatase TiO₂ and Au-TiO₂. Operando and transient measurements determine the sequence of elementary steps that decompose HCOOH and identify surface species that do not form CO and CO₂. Transient measurements show that HCOOH adsorbs and deprotonates to form bidentate formates over TiO₂ while monodentate intermediates do not lead to CO or CO₂ formation. Selective inhibition of Au sites with co-fed CO over Au-TiO₂ indicate monodentate reactive intermediates evolve into bidentate formates on Au at higher coverages. Distinguishing the structure, composition, and orientation of reactive intermediates provides complimentary evidence to measured rates and DFT to depict reaction mechanisms and provide insight into how surface properties dictate rate and selectivity.

References:

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4:20pm **HC+SS-ThA-7 Self-sustained Reaction Oscillations in a New Light, Uta Hejral, S Albertin, J Zhou, S Pfaff**, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *S Blomberg*, Lund University, Sweden; *O Gutowski, A Dippel*, Deutsches Elektronen-Synchrotron DESY, Germany; *J Gustafson, J Zetterberg, E Lundgren*, Lund University, Sweden

Catalysts are complex material systems accelerating desired chemical reactions in chemical industry, fuel cells and car exhaust treatment. To improve their performance, an atomic-scale understanding of the interplay between catalyst structure, the surrounding gas composition and the catalyst activity under realistic reaction conditions is inevitable. Self-sustained reaction oscillations, in which the catalyst shuts its activity periodically off, have been studied for many years [1, 2] with the aim (1) to avoid reactor instabilities or even reactor explosions, and (2) to understand and make use of the underlying catalyst structures leading to higher conversion rates and selectivities often present during the oscillations. However, no general mechanism, especially for the structure leading to the activity increase and decrease, has been put forward.

Here we combined High Energy Surface X-Ray Diffraction (HESXRD) [3, 4], Planar Laser Induced Fluorescence (PLIF) [5], in-situ Mass Spectrometry (MS) and optical LED reflectance [6] at beamline P07 (DESY) at a photon energy of 77 keV to study self-sustained reaction oscillations during CO oxidation over Pd(001). This allowed, with sub-second time resolution, for correlating the catalyst structure (HESXRD) to the sample's CO₂ production (PLIF, MS) and hence its catalytic activity. The LED light, reflected from the sample surface, provided in addition immediate information on the surface roughness. Our data indicate that the oxidation and reduction of (111)-oriented Pd islands on top of an epitaxial PdO(101) oxide layer, previously reported under reducing conditions close to UHV [7], play a crucial role in the underlying mechanism for the self-sustained reaction oscillations.

References:

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4:40pm **HC+SS-ThA-8 Operando Catalysis--A First-Principles Perspective, William Schneider**, University of Notre Dame **INVITED**

First-principles computational methods have had a profound impact on the science of heterogeneous catalysis. One of the challenges in making these models more rigorous, for instance to establish quantitative relationships between experimental observations of rates, rate orders, and models, is to faithfully account for the influence of the catalytic reaction conditions on the state of a catalytic material and on mechanism. "Operando"

experiments interrogate catalysts at the conditions at which they are functioning. In the same way, by incorporating finite temperatures and pressures through statistical mechanical and ab initio dynamics models, and by recognizing that a catalytic material may present a heterogeneous array of sites, it is in principle to model a catalyst "operando" from first principles. In this presentation I first discuss our efforts to model finite-temperature adsorption behavior at metal surfaces, including the translational motions that control adsorption free energies and the interactions between adsorbates that can modify surface reaction kinetics.

I then discuss our recent work to describe how the rates of surface reactions might be altered by the imposition of an external plasma, showing how changing the "environment" is an alternative and promising way to control catalytic reactivity.

5:20pm **HC+SS-ThA-10 Chiral Selectivity in Heterogeneous Catalysis, R Chapleski, Sharani Roy**, University of Tennessee Knoxville

Developing powerful next-generation technologies for catalysis, energy conversion, and energy storage relies on understanding and controlling molecular transformations at complex interfaces. However, relatively little is known about the fundamental molecular-scale phenomena driving

chemical selectivity at functional and complex interfaces. Our work aims to investigate mechanisms of enantioselectivity in heterogeneous catalysis. Specifically, by investigating hydrogenation reactions of both the (R)- and (S)- enantiomers of limonene on the chiral Pt(532) surface, we will provide insight into the adsorbate-surface interactions that lead to enantiomeric excess in the formation of the chiral product, menthene. Here, we report our initial results of this work, which uses computational methods to probe molecular adsorption of limonene followed by catalytic hydrogenation. Our approach utilizing density functional theory combined with the results of recent experimental sum-frequency generation experiments, reveals likely adsorption orientations and reaction pathways of both enantiomers on the Pt(532) surface. A comparison of adsorption and reaction mechanisms across both enantiomers leads to a fundamental description of the atomic-scale interactions that produce enantioselectivity in adsorption and reactions of limonene on a chiral platinum surface. We hope that these results provide qualitative insight into how enantioselectivity is achieved in heterogeneous catalysis at intrinsically chiral metal surfaces.

5:40pm **HC+SS-ThA-11 Combining in situ Environmental TEM and Multiscale Simulations to Study the Dynamic Processes of Copper Oxidation, Meng Li, M Curnan, W Saidi, J Yang**, University of Pittsburgh

Cu-based materials are widely used in industrial catalysts applications, including methanol synthesis and H₂ production from the water-gas shift reaction. Across these applications, maximizing the Cu surface area improves the catalytic performance. However, side effects such as poor stability and deactivation also occur due to oxide formation at active sites over long-term use. Therefore, developing a fundamental understanding of the nanoscale mechanisms initiating Cu surface oxidation is essential to addressing these issues. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Of these three stages, the initial stage – which spans from the oxygen chemisorption to the onset of oxide nucleation – is least understood, as it is inaccessible to traditional surface science and bulk material experimental methods. Despite recent improvements in computational methods, current computational capabilities have yet to simulate O chemisorption directly leading to oxide nucleation, given the resources required to complete such simulations over sufficiently large time and size scales.

In this work, by combining Environmental TEM (ETEM) with multiscale atomistic simulation, the dynamical processes enabling initial stage copper oxidation were explored. Our ETEM (Hitachi H-9500, 300 kV, LaB₆) results show that over surface step defects of various facet orientations, oxide nucleation preferences vary over adjacent facet edges, potentially leading to known differences in observed reconstructions on differently oriented surfaces. Surface reconstructions on Cu(100) and Cu(110) facets were observed, followed by Cu₂O island nucleation and growth in a layer-by-layer manner. Investigation of the dynamical processes leading to oxide nucleation on these reconstructed surfaces is done via a multiscale computational approach. Single initial oxidation stage events from oxygen chemisorption to surface reconstruction are first modeled using the Nudged Elastic Band (NEB) method on systems modeled with Reactive Force Field (RFF) potentials. Oxide nucleation and growth is then affordably modeled at size and time scales consistent with ETEM results, applying structures and energies resolved in RFF NEB calculations to rate tables used by adaptive kinetic Monte Carlo simulations. This simulation methodology forms a feedback loop with ETEM results, allowing computational and experimental results to validate one other. Ultimately, this cross-validation will be used to explain how oxide nucleation can be prevented by controlling factors like surface and defect orientation, temperature and pressure.

Thursday Afternoon, October 25, 2018

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 202A - Session SA+AS+HC+SS-ThA

IoT Session: Multi-modal Characterization of Energy Materials & Device Processing

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory

2:20pm **SA+AS+HC+SS-ThA-1 Revealing Structure-Function Correlations in Fuel-Cells and Batteries.**, *Klaus Attenkofer, E Stavitski, M Liu, D Lu, M Topsakal, D Stacchiola, M Hybertsen*, Brookhaven National Laboratory

INVITED

To reveal the structure and even more important, the structure-function correlation of materials are essential prerequisites to the optimization and rational design of materials in energy storage and conversion applications. The complex processes resulting in the function typically involve not only the initial chemical reaction but a wide range of reorganizations, phase transitions, and transport phenomena which finally determine the efficiency of the material and its reliability in applications. The characterization challenge of visualizing changes on multiple length scales of ordered and disordered materials is one aspect of the characterization problem; to correlate the identified changes with the function of the material and distinguish the essential changes from other non-correlated alternation is the second equally important task.

In the talk we will show on various examples from the field of fuel cells and batteries, how high throughput hard X-ray spectroscopy can be combined with data analytics and theory to reveal the atomic structure of the ordered and disordered materials. In a next step a true imaging tool like transmission electron microscopy is used to verify this structure. The high throughput aspect of this approach provides not only a new opportunity to use database approaches to guarantee an unbiased method for the structure identification and optimization with a "field of view" in the nanometer range but also provides a new strategy to use data analytics, especially data mining approaches, to establish the structure-function correlation. The combination of ex-situ and operando experiments provides a statistical relevant data quantity and a diversity of the data necessary to this approach and is minimizing at the same time challenges caused by sample damage.

3:00pm **SA+AS+HC+SS-ThA-3 Soft X-ray Spectroscopy for High Pressure Liquid**, *Ruimin Qiao, J Guo, W Chao*, Lawrence Berkeley National Laboratory

INVITED

Soft X-ray spectroscopy (~50-1500eV), including both X-ray absorption and emission, is a powerful tool to study the electronic structure of various energy materials. Its energy range covers the K-edge of low-Z elements (e.g. C, N, O and F) and the L-edge of transition metal. Important information such as chemical valence, charge transfer and different ligand field could be directly extracted from the spectra. However, its application has been largely limited in materials that could be placed in vacuum (such as solid, below-ambient-pressure gas and liquid) because of the short penetration depth of soft x-ray. In this presentation, I will talk about the recent development of soft x-ray spectroscopy for high pressure liquid (up to 400 bars) at Advanced Light Source in Lawrence Berkeley National Lab.

4:00pm **SA+AS+HC+SS-ThA-6 Surface Action Spectroscopy Using FHI FEL Infrared Radiation**, *Zongfang Wu, H Kuhlbeck, W Schöllkopf, H Freund*, Fritz-Haber Institute of the Max Planck Society, Germany

In model catalysis and general surface science studies, the vibrational characterization of a surface is usually performed with HREELS (high-resolution electron energy loss spectroscopy) or IRAS (infrared reflection absorption spectroscopy). Both methods have disadvantages: HREELS suffers from its low resolution and (in the case of ionic samples) the presence of intense multiple phonon losses, while IRAS requires normalization of the spectrum with the spectrum of a reference sample, which leads to a contamination of the spectrum with features of the reference sample. Action spectroscopy with rare-gas messenger atoms [A. Fielicke et al., Phys. Rev. Lett. 93, 023401 (2004)] is an established method for vibrational spectroscopy of gas-phase clusters that avoids these disadvantages. Rare-gas atoms attached to gas-phase clusters may desorb when the incident infrared (IR) radiation is in resonance with a cluster vibration. The fragmentation rate, as monitored with a mass spectrometer, represents a vibrational spectrum, which can be used to draw conclusions regarding the cluster structure. Clusters, in this case deposited on a surface, are also highly relevant in model catalysis since they greatly

influence catalytic reaction paths of supported catalysts. Both cluster shape and size matter. With this topic in mind a new apparatus for the application of IR FEL radiation to action spectroscopy of solid surfaces was set up at the Fritz Haber Institute (FHI), the $V_2O_3(0001)/Au(111)$ (~10 nm thick) and a $TiO_2(110)$ single crystal surface were studied as first test systems. The machine is connected to the FHI FEL, which is able to provide intense and widely tunable (3 – 60 μm) IR radiation. For $V_2O_3(0001)/Au(111)$ the well-characterized vanadyl surface vibration and other surface vibrations could be detected, while bulk states turned out to be invisible to the method. Presumably, anharmonic vibrational coupling between the primary excited vibration and the rare-gas vs. surface vibration leads to desorption. This explains the surface sensitivity of the method as well as its insensitivity to bulk vibrations. In the case of the $TiO_2(110)$ single crystal also rare-gas desorption resulting from an IR induced increase of the crystal temperature could be observed. This led to a better understanding of polaritons in rutile.

4:20pm **SA+AS+HC+SS-ThA-7 Spectroscopic Insight into Resistive Switching Processes in Oxides**, *C Baeumer, C Schmitz*, Forschungszentrum Juelich GmbH, Germany; *A Kindsmüller*, RWTH Aachen University, Germany; *N Raab, V Feyer, D Mueller, J Hackl, S Nemsak*, Forschungszentrum Juelich GmbH, Germany; *O Menten, A Locatelli*, Elettra-Sincrotrone Trieste, Italy; *R Waser, R Dittmann*, **Claus Michael Schneider**, Forschungszentrum Juelich GmbH, Germany

Nonvolatile memories play an increasing role in modern nanoelectronics. Among the various storage concepts, resistive switching promises a high scalability. In oxides, the physical mechanism behind resistive switching involves electrically controlled local redox processes, which result in the formation and migration of oxygen vacancies. We studied these redox processes and their influence on the resistive switching in the model systems $SrTiO_3(STO)$ and ZrO_2 with a full suite of synchrotron-radiation based spectroscopy techniques. The resistive switching in STO proceeds via the growth of nanoscale conductive filaments, which poses considerable challenges to the spectroscopic characterization. Employing nanospectroscopy in an *operando* configuration we could unanimously relate the conductivity changes between the ON (low resistance) and OFF states (high resistance) to the redox-induced changes of the valencies and the formation of oxygen vacancies [1,2]. The retention time of the ON state in STO is determined by a reoxidation of the previously oxygen-deficient region and can be controlled by inserting an oxygen diffusion barrier. With respect to the reproducibility of the switching process, we find that the individual switching event is governed by a competition within a network of subfilaments, which has been created in the initial forming step. Upon resistive switching, one of these subfilaments becomes the current-carrying filament. However, during repeated switching the different subfilaments may become active, resulting in a cycle-to-cycle variation of the location and shape of the current-carrying filament, which determines the low-resistance state [3].

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4:40pm **SA+AS+HC+SS-ThA-8 Visualizing Electronic Structures of Topological Quantum Materials by Synchrotron Based Photoemission Spectroscopy**, *Yulin Chen*, Oxford University, UK

INVITED

The electronic structure of matter is critical information that determine its electric, magnetic and optical properties. The precise understanding of such information will not only help understand the rich properties and physical phenomena of quantum materials, but also guide the design of their potential applications.

Angle-resolved photoemission spectroscopy (ARPES) is an effective method in determining the electronic structures of materials: with its energy and momentum resolution, ARPES can directly map out dispersions of electronic bands in the reciprocal space with critical parameters (such as the energy gap and width of bands, carrier type, density and the Fermi-velocity, etc.).

In this talk, I will first give a brief introduction to this powerful experimental technique, its basic principle and the rich information it can yield by using synchrotron radiation light source, then focus on its recent application to

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topological quantum materials (including some of our works on topological insulators, Dirac and Weyl semimetals [1]). Finally, I will review the recent development in ARPES and give a perspective on its future directions and applications.

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5:20pm **SA+AS+HC+SS-ThA-10 Electronic Structure of FeO, γ -Fe₂O₃ and Fe₃O₄ Epitaxial Films using High-energy Spectroscopies**, *German Rafael Castro*, Spanish CRG BM25-SpLine Beamline at the ESRF, France; *J Rubio Zuazo*, Spanish CRG BM25-SpLine at the ESRF, France; *A Chainani*, Condensed Matter Physics Group, NSRRC, Taiwan, Republic of China; *M Taguchi*, RIKEN SPring-8 centre, Japan; *D Malterre*, Institut Jean Lamour, Université de Lorraine, France; *A Serrano Rubio*, Spanish CRG BM25-SpLine Beamline at the ESRF, France

Today, one of the materials science goals is the production of novel materials with specific and controlled properties. Material composites, which combine different materials, with specific and defined properties, mostly of multilayer thin films, are a promising way to create products with specific properties, and, in general different of those of the constituents. The chemical, mechanical, electric and magnetic properties of such materials are often intimately related to their structure, composition profile and morphology. Thus, it is crucial to yield with an experimental set-up capable to investigate different aspects related with the electronic and geometric structure under identical experimental conditions, and, in particular, to differentiate between surface and bulk properties. There are few techniques able to provide an accurate insight of what is happening at these interfaces, which in general are buried by several tens of nanometres inside the material. The Spline beamline Branch B at the ESRF, the European Synchrotron, offers unique capabilities in this respect.

In this contribution we will present the study of the electronic structure of well-characterized epitaxial films of FeO (wustite), γ -Fe₂O₃ (maghemite) and Fe₃O₄ (magnetite) using Hard X-ray Photoelectron Spectroscopy (HAXPES), X-ray Absorption Near Edge spectroscopy (XANES) and electron energy loss spectroscopy (EELS). We carry out HAXPES with incident photon energies of 12 and 15 keV in order to probe the bulk-sensitive Fe 1s and Fe 2p core level spectra. Fe K-edge XANES is used to characterize and confirm the Fe valence states of FeO, γ -Fe₂O₃ and Fe₃O₄ films. EELS is used to identify the bulk plasmon loss features. A comparison of the HAXPES results with model calculations for an MO₆ cluster provides us with microscopic electronic structure parameters such as the on-site Coulomb energy U_{dd} , the charge-transfer energy Δ , and the metal-ligand hybridization strength V . The results also provide estimates for the ground state and final state contributions in terms of the d^n , $d^{n+1}L1$ and $d^{n+2}L2$ configurations. Both FeO and γ -Fe₂O₃ can be described as charge-transfer insulators in the Zaanen-Sawatzky-Allen picture with $U_{dd} > \Delta$, consistent with earlier works. However, the MO₆ cluster calculations do not reproduce an extra satellite observed in Fe 1s spectra of γ -Fe₂O₃ and Fe₃O₄. Based on simplified calculations using an M2O7 cluster with renormalized parameters, it is suggested that non-local screening plays an important role in explaining the two satellites observed in the Fe 1s core level HAXPES spectra of γ -Fe₂O₃ and Fe₃O₄.

5:40pm **SA+AS+HC+SS-ThA-11 Single-Bunch Imaging of Detonation Fronts Using Scattered Synchrotron Radiation**, *M Nielsen, J Hammons, M Bagge-Hansen, L Lauderbach, R Hodgkin, K Champley, W Shaw*, Lawrence Livermore National Laboratory; *N Sinclair*, Washington State University; *Trevor Willey*, Lawrence Livermore National Laboratory

Radiographic imaging using a series of single pulses from synchrotron storage rings or x-ray free-electron lasers gives new insight into dynamic phenomena. One limitation of these sources is that the native and natural beam size at most end-station hutches is, at best, of mm-scale dimensions. Here, we describe a method for collecting full-field, radiographic images of cm-scale phenomena using focused pink-beam and scattering the x-rays, effectively creating point-source images. Although currently photon starved and highly dependent on parameters chosen (such as source-to-object and source-to-detector distances, scattering material, etc.) we are continuously improving the technique. At the Dynamic Compression Sector at the Advanced Photon Source, we use this capability to image detonation phenomena, particularly direct imaging of detonator performance, imaging initiation and run-up to detonation, imaging differences in ideal vs. non-

ideal explosives, and have a goal to determining density during detonation at 10's of microns in resolution. In this presentation, we summarize our progress developing and using this technique in creating movies of dynamic phenomena as fast as 153.4 ns between frames, and as a method for imaging samples prior to, for example, collecting dynamic small-angle x-ray scattering or diffraction to observe nanodiamond growth kinetics and composition evolution during detonation.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room Hall B - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic Poster Session

HC-ThP-1 Analyses of Nano-Crystalline Structure in Precipitated Iron-Based Catalysts for Fischer-Tropsch Synthesis, Dong Hyun Chun, G Rhim, J Park, Korea Institute of Energy Research, Republic of Korea; C Kim, Kookmin University, Republic of Korea; J Bae, M Youn, H Jeong, S Kang, H Lee, J Yang, H Jung, Korea Institute of Energy Research, Republic of Korea
FTS (Fischer-Tropsch synthesis) is a process invented by two German researchers, Franz Fischer and Hans Tropsch, in the 1920s, which catalytically convert syngas ($H_2 + CO$) into hydrocarbon products: $nCO + \{2n(+1)\}H_2 \rightarrow C_nH_{2n(+2)} + nH_2O$. Iron-based catalysts are highly promising for the FTS due to their high activity and low cost. A precipitation technique is one of the commercially proven methods for preparation of iron-based FTS catalysts as this technique can easily generate nano-crystalline particles. In general, the as-prepared precipitated iron-based catalysts are known to be composed of hematite ($\alpha-Fe_2O_3$) that are inactive for the FTS. Thus, the as-prepared catalysts must be subjected to a proper activation treatment to change the as-prepared catalysts into active phases such as Fe_5C_2 and Fe_2C . This means that the crystal structure of as-prepared catalysts and their reduction and carburization behavior can critically influence the catalytic performance of precipitated iron-based FTS catalysts. But, it is very difficult to reveal the exact relationship among the crystal structure of as-prepared catalysts, their reduction and carburization behavior, and the catalytic performance for FTS because high-performance iron-based FTS catalysts are usually composed of a mixture of several iron species with nano-crystalline structure. In this presentation, we analyzed the crystal structure of precipitated iron-based FTS catalysts in detail by X-ray diffraction and Mössbauer spectroscopy. We found that a significant amount of ferrihydrite ($FeOOH \cdot nH_2O$, $0 < n < 1$) can coexist with hematite in the as-prepared catalysts, which depends on the precipitation conditions. Furthermore, we revealed that the ferrihydrite plays a crucial role in determining the catalytic performance as well as the reduction and carburization behavior of the catalysts.

HC-ThP-2 In situ Infrared and Catalytic Reaction Studies of Active Sites on Pt Nanoparticles Supported on Nanosponge Oxides under CO oxidation, Sunyoung Oh, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; C Jung, Institute for Basic Science (IBS), Republic of Korea; H Ha, Chungnam National University, Republic of Korea; C Jo, Institute for Basic Science (IBS), Republic of Korea; S Moon, Y Kim, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; W Doh, Institute for Basic Science (IBS), Republic of Korea; H Kim, Chungnam National University, Republic of Korea; R Ryoo, J Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea
Platinum-based heterogeneous catalysts are mostly used in various commercial chemical processes because of their highly catalytic activity influenced by the metal-oxide interaction. To design the rational catalysts with high performance, it is crucial to understand the reaction pathway. Here, Pt nanoparticles supported on nanosponge oxides such as TiO_2 and SnO_2 with advantage of high surface area, thermal stability, and quite high interfacial sites were synthesized and utilized in CO oxidation reaction to prove the interaction of the metal and support. CO oxidation results show high activity for Pt supported on TiO_2 nanosponge catalyst, which is associated to the O_2 dissociation at the Pt/ TiO_2 perimeter sites. *In situ* infrared (IR) spectroscopic observation indicates that oxygen molecule bond is activated at the Pt/ TiO_2 interface by neighbor CO molecules on the Pt surface. The computational calculations for proposed reaction mechanism for O_2 activation at Pt/ TiO_2 interface are consistent with experiment results. In contrast, we directly observe that absence of adsorbed CO on Pt surface for Pt/ SnO_2 catalyst by using IR because the Pt surface as active site was covered with a shell of tin oxide after hydrogen pre-treatment. These results allow us to obtain the insight into the nature of metal-support interface between Pt and nanosponge oxide supports and reaction pathways of CO oxidation for Pt-based supported catalysts.

HC-ThP-3 Activity of Bimetallic Pt-Re Surfaces and Influence of the Support for the Water-Gas Shift Reaction, Amy Brandt¹, T Maddumapatabandi, D Shakya, S Farzandh, D Chen, University of South Carolina

Bimetallic Pt-Re clusters are systematically investigated on model supports in order to understand the effects of metal-metal interactions and metal-support interactions on cluster formation and catalytic activity for clean hydrogen production via the water-gas shift (WGS) reaction. Bimetallic catalysts have exhibited unique characteristics different from their single metal constituents, and interactions with the support are believed to have an influence on the chemistry taking place at the interface. Pure and bimetallic Pt-Re surfaces were prepared in ultrahigh vacuum (UHV) by vapor-deposition on model supports of $TiO_2(110)$, Pt(111), and highly oriented pyrolytic graphite (HOPG). WGS activity was studied in a UHV-coupled microreactor operating at a temperature of 160 °C and pressures of ~1 atm. On the TiO_2 support, bimetallic clusters consisting of Pt at the surface and Re residing subsurface were found to have the highest activity for the WGS reaction, with turnover frequencies (TOF) nearly twice as high as monometallic Pt on TiO_2 . The TOF on the Pt single crystal was lower than Pt clusters supported by TiO_2 . A Pt-Re alloy with pure Pt at the surface and Re residing subsurface showed enhanced activity over pure Pt(111). Pt clusters deposited on TiO_2 were investigated by scanning tunneling microscopy and found to have an increasing number of perimeter atoms compared to total atoms at decreasing Pt coverages. WGS experiments revealed a trend of increasing TOF for Pt coverages with increasing perimeter atom percentages, suggesting the Pt/ TiO_2 interfacial sites contribute to WGS activity. An alternative support of HOPG confirmed that Pt clusters on TiO_2 have a greater TOF than Pt clusters on HOPG for the WGS reaction. In contrast to bimetallic Pt-Re clusters on TiO_2 , Pt-Re clusters on HOPG consisted of higher concentrations of Re at the surface, leading to lower TOFs for Pt-Re clusters on HOPG than the monometallic Pt on HOPG surface.

HC-ThP-4 In-Operando Photoluminescence Imaging of a Single-Layer Molybdenum Disulfide Catalyst, Koichi Yamaguchi, University of California - Riverside; S Naghibi, W Coley, L Bartels, University of California, Riverside
 MoS_2 is the key industrial catalyst for hydrodesulfurization (HDS) of crude oil. Atomistic investigation of the HDS reaction is hampered by the elevated pressures and temperatures required for HDS. There is close correlation between the current industrial catalyst material and model single-layer MoS_2 flakes. We developed a new experimental approach that relies on strong photoluminescence (PL) of monolayer MoS_2 that we grow efficiently on an inert SiO_2 substrate. We find that wide-field PL imaging is possible even under near in-operando condition and can serve as a reporter of the chemical state and spatial variation of the catalyst material. Our experiments proceed under up to 1atm of hydrogen, any volatile thiol, and at temperatures of up to 400 °C. Spatially resolved images allow us to distinguish between reactions at island edges and the basal plane; desulfurization and binding of organic species to the catalyst are reported as bleaching of the photoluminescence. Concomitant mass spectrometric analysis allows us to correlate the variation in the island PL with different reaction regimes.

HC-ThP-5 Efficient Photoelectrochemical Water Splitting in Band Edge Engineered Metal Oxide Heterostructure Photoanode for Solar Fuel Production, Nisha Kodan, Thin Film Laboratory, Department of Physics, IIT Delhi, India; A Singh, Division of Chemical Physics, Department of Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden; B Mehta, Thin Film Laboratory, Department of Physics, IIT Delhi, India

Solar induced splitting of water in a photoelectrochemical (PEC) cell into hydrogen and oxygen appears to be the most promising, economically viable and sustainable way for the production of hydrogen. PEC cells integrate solar energy harvesting and water electrolysis into a single event on photoactive material surfaces. The efficient separation of photogenerated electron-hole pairs and stability against corrosion are critical preconditions for a photoelectrode to achieve a high photoelectrochemical performance. However, the (photo)oxidation of water is a challenging electrochemical reaction demanding robust but inexpensive electrode materials. For large-scale photoelectrochemical (PEC) hydrogen production, systematic efforts towards design of inexpensive and stable semiconductor photoelectrode materials, permitting sustained splitting of water in PEC cells are desirable. Yet, finding an optimal material for PEC cell is a very difficult task due to three

¹ Morton S. Traum Award Finalist

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main requirements in a single material system: 1) chemical stability 2) visible light absorption and 3) band edges matching to redox levels of water. The band edge engineering strategy, i.e., band re-alignment in $\text{TiO}_2/\text{BiVO}_4$ and $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ heterostructure was achieved by gas-phase modification technique i.e. hydrogenation of the top TiO_2 layer which strongly promotes interfacial interaction at the junction and leads to an effective interfacial charge separation and charge transport. The hydrogen treated $\text{TiO}_2/\text{BiVO}_4$ heterostructure photoanode exhibit significant enhancement of visible light absorption and improve the photoelectrochemical response with a photocurrent density of 4.44 mA/cm^2 as compared to pristine BiVO_4 (0.84 mA/cm^2) and $\text{TiO}_2/\text{BiVO}_4$ (0.28 mA/cm^2) photoanodes. Using electronic structure calculations, an alteration of the band alignment is predicted at the heterojunction from type I to type II by hydrogen treatment of the top TiO_2 layer which results in improved PEC performance of hydrogenated $\text{TiO}_2/\text{BiVO}_4$ heterostructure photoanode.

HC-ThP-6 Comparative Reactivity of Oxide and Metallic Phases on Rh(111), *R Farber, M Turano, W Walkosz, Christopher Smith, D Killelea*, Loyola University Chicago

Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, similar to bulk oxides, they are now believed to be effective promoters of selective catalysis. We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Using atomic oxygen (AO) as an oxidizing agent, high coverage oxygen adlayers and oxides can be formed under ultra-high vacuum (UHV) conditions. Careful control of the AO exposure parameters allowed for the selective growth of the RhO_2 surface oxide, surface adsorbed oxygen, and subsurface oxygen. Furthermore, formation of the RhO_2 surface oxide was shown to rely not only on the presence of defects, as evident by the selective growth along step edges (Figure 1), but also on high concentrations of oxygen absorbed below the surface of the metal.

Utilizing our surface preparation techniques to carefully prepare specific oxidized Rh(111) surfaces, we use carbon monoxide (CO) as a probe molecule to track surface structure specific reactivity via CO oxidation. Exposing RhO_2 to CO, TPD and STM are employed to gather information on CO_2 production, residual O_2 population, and surface structure evolution during CO oxidation reactions. In order to determine the actual reaction mechanism of CO oxidation on oxidized Rh(111), STM is needed to provide atomic scale resolution of the active surface adsorbates during the reaction progression, as shown in Figure 1. By combining spatially resolved structural information with CO_2 production and oxygen consumption, we will be able to identify which oxidic species and surface sites contribute to CO oxidation. This information will help in determining the exact reaction mechanism occurring during CO oxidation over an oxidized Rh surface.

HC-ThP-7 Hybrid Adsorbent Catalyst for Siloxane Removal: Fe-BEA Zeolites, *Alba Cabrera-Cadony*, University of Girona, Spain; *E Santos-Clotas, M Martin*, University of Girona

Different types of both natural and synthetic zeolites, covering a wide range of physical and chemical properties, were evaluated as adsorbents/catalyst for siloxane removal in lab-scale gas phase adsorption tests of octamethylcyclotetrasiloxane (D4). After bed exhaustion, wet oxidation processes were used for the regeneration of the spent zeolite samples, including ozonation and Fenton-like treatment of the Fe-amended zeolites using hydrogen peroxide. New adsorption tests were performed after these AOP-driven regeneration processes.

The results on the uptake of gaseous D4 by various zeolites led to the conclusion that BEA type materials presented the highest catalytic activity for the siloxane ring-opening and formation of α - ω -silanediols due to the high content of Bronsted and Lewis acidic sites. Those silanediols formed on the BEA surface were detached from the catalytic acidic sites when water was available, and were narrow enough to diffuse into the channels, hence enhancing the removal efficiency for D4.

The water soluble α - ω -silanediols formed by the catalytic activity of the iron exchanged Fe-BEA type zeolites during D4 adsorption were easily removed by wet regeneration treatment with water, however, the regeneration was incomplete, i.e. the adsorption capacity was partially recovered. Adding H_2O_2 in a heterogeneous Fenton-like regeneration treatment led to a complete recovery of the adsorption capacity of the Fe-zeolites samples.

However, on successive adsorption/regeneration cycles, the recyclability of the Fe-zeolites catalysts was hampered by the accumulation of

carbonaceous materials on the material surface, which caused a loss of the catalytic activity, affecting both the adsorption and the regeneration stages.

Bronsted acidic sites (BAS) and Lewis acidic sites (LAS) promoted the D4 transformation into silanediols, as shown in Figure 1, which was the fundamental step that ruled the D4 uptake on the gas adsorption process. At the same time, the iron exchanged in Fe-BEA type zeolites promoted the catalytic activity towards Fenton-like reactions for the regeneration of the exhausted materials.

Surface Science Division

Room 203C - Session SS+AS+HC-FrM

Near/Ambient Pressure and Bridging Gaps between Surface Science and Catalysis

Moderators: Donna Chen, University of South Carolina, Janice Reutt-Robey, University of Maryland

8:20am **SS+AS+HC-FrM-1 Ambient Pressure Electron Spectroscopy (XPS, XAS) and Electron Microscopy Studies of the Structure and Chemistry of Nanostructured Model Catalysts, John Hemminger, University of California Irvine** **INVITED**

We use physical vapor deposition to create a high density of metal oxide nanoparticles on highly oriented pyrolytic graphite (HOPG). Photoelectrochemical methods are then utilized to selectively decorate the metal oxide nanoparticles with transition metal nanoparticles. This talk will describe our studies of the Pt/TiO₂/HOPG ; Cu/ZnO/HOPG systems. The nanostructured surfaces are characterized by SEM, TEM, XPS, and synchrotron based XAS. Lab-based and synchrotron based ambient pressure XPS experiments have been used to study the CO oxidation reaction on Pt/TiO₂/HOPG and the CO₂ reduction reaction on CuO_x/TiO₂/HOPG. In addition, the catalytic activity of CuO_x/TiO₂/HOPG for electrochemical CO₂ reduction has been studied using differential electrochemical mass spectrometry (DEMS).

9:00am **SS+AS+HC-FrM-3 In-operando Investigation of the Initial Oxidation Stages for NiCr-(W) Alloys with X-ray Photoelectron Spectroscopy, Cameron Volders, V Angelici Avincola, P Reinke, University of Virginia**

Ni-Cr alloys are of technical interest as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation, and limits catastrophic events such as pitting and crevice corrosion. A wide range of Ni-Cr alloys have been developed to satisfy industrial needs and the properties for each alloy differ slightly based on its application. The properties are controlled by manipulating Cr content as well as adding minor alloying elements such as Mo or W, which have been shown to enhance corrosion resistance. The ideal composition for these alloys has been optimized over many decades but the mechanistic understanding of the role of Mo or W additions is not fully developed.

The current work presents an *in-operando* ambient pressure – X-ray photoelectron spectroscopy (AP-XPS) study which investigated the early stages of oxidation for four alloy concentrations; (1) Ni-5% Cr, (2) Ni-15% Cr, (3) Ni-30% Cr, and (4) Ni-15% Cr-6% W by weight percent between 573 and 773 K and p(O₂) < 0.1mbar. The primary objectives were to elucidate how varying Cr content in the alloys and the addition of W impacts the nucleation and growth of different oxide phases. The modulation of alloy and oxide composition and bonding was observed over an extended time period delivering a detailed view of the reaction pathways.

A key result from this work is the Cr surface segregation in the alloys prior to oxidation, which contributes to the rapid nucleation of Cr-oxides in the first reaction step with O₂. The surface enrichment of Cr influences the initial nucleation of the different oxide species and prejudices the progression of oxide growth. The main portion of this work will focus on the time evolution of the different oxide phases and the kinetics of Ni-oxide and Cr-oxide formation for all alloys, which allows to build a detailed model of the reaction. An additional component accounts for a substantial portion of the oxide signal, and is interpreted as the combination of spinel and non-stoichiometric oxide. The addition of W in the alloy resulted in a near complete suppression in the formation of Ni oxide species, and different models to interpret the impact of W on the progression of the oxidation reaction will be discussed.

9:20am **SS+AS+HC-FrM-4 Surface Hydroxylation of Polar (000-1) and Non-polar (11-20) ZnO Probed with AP-XPS, Sana Rani, A Broderick, J Newberg, University of Delaware**

The interaction of ZnO with water vapor has been an important topic of research due to the relevance for numerous catalytic processes including water-gas shift reaction, methanol synthesis, olefin hydrogenation, and gas sensor applications. ZnO based humidity nanosensors were found to have high sensitivity towards humidity and fast response time in heterogeneous catalysis. The presence of water strongly modifies the surface properties depending on the substrate and coverage. The adsorbed water can catalyze

heterogeneous reactions and corrosion by proton transfer and solvating products. Dissociation of adsorbed water is of particular interest for catalysis, as this may be the first step in the activation of water molecules for chemical reactions. In this work, surface thermodynamic calculations were applied to synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data to investigate the interface between water vapor and the low index polar (000-1) and non-polar (11-20) ZnO surfaces. Three isobaric experiments were performed over a range of temperatures from 10 to 500°C. It is hypothesized that observed hydroxyl groups, adsorbed water and carbonates on the ZnO surface can significantly influence heterogeneous catalytic reactions under ambient conditions.

9:40am **SS+AS+HC-FrM-5 Reason of High Stability and Reactivity of Ni/silicalite-1 Catalyst for Dry Reforming of Methane, Evgeny Vovk, X Zhou, Z Liu, C Guan, Y Yang, ShanghaiTech University, China; W Kong, Shanghai Advanced Research Institute, China; R Si, Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, China**

Dry reforming of methane (DRM) is an environmentally favored process transferring two greenhouse gases (CH₄ and CO₂) into syn-gas (H₂+CO). Ni-based catalysts demonstrate good potential in this application because of comparable reactivity and low cost. DRM is highly endothermic reaction which requires high operating temperatures. At high temperatures sintering is a common issue of catalyst deactivation. Deactivation of Ni catalyst in DRM process is also accompanied by carbon deposition (coking) induced by methane decomposition and CO disproportionation (Boudouard reaction).

In the current work we investigated catalyst obtained by encapsulating Ni clusters (2.5±0.2 nm) into microporous silicalite-1 (aluminum free zeolite with MFI structure). No deactivation and coking under a wide range of conditions where carbon formation is thermodynamically favorable were observed for this sample. This atom-economical Ni/silicalite-1 catalyst was compared with Ni/SiO₂ catalyst prepared by impregnation method. XPS study has been performed in ThermoFischer ESCALAB 250X photoelectron spectrometer. The gas treatments of catalysts (up to 1 bar) was performed in high pressure gas cell (Model HPGC 300, Fermi Instruments) connected to the spectrometer.

XPS analysis of Ni/silicalite-1 demonstrates the presence of a peak with binding energy (BE) 856.2 eV in Ni 2p_{3/2} region. Nickel silicate has a similar spectrum shape with close BE. The presence of this peak in Ni/silicalite-1 sample suggests of the Ni-O-Si species and strong metal-support interaction. After oxidation of this sample at 400°C there are no changes of the Ni-O-Si species. At the same time nickel in Ni/SiO₂ catalyst which has shown mostly metallic Ni⁰ state with minor content of Ni-O-Si upon oxidation transforms into NiO. Reduction of Ni/silicalite-1 catalyst in hydrogen at 650°C leads to partial reduction of nickel into Ni⁰ while a significant portion of Ni-O-Si still remains. The behavior of Ni-O-Si feature in both oxidizing and reducing conditions clearly indicates its very high stability. We attribute this feature to the Ni-O-Si formed at the interface between Ni nanoparticles and the silicalite support. The Ni/silicalite-1 novel oxygen-philic interfacial catalyst system consists of very small metallic Ni clusters intercalated into silicalite framework and surrounded by Ni-O-Si species. Ni-O-Si provides high stability of Ni nanoparticles and prevents sintering and carbon deposition making this catalyst also very interesting for commercial application.

10:00am **SS+AS+HC-FrM-6 Recent Development in XPS and Ambient Pressure XPS Techniques, Lukasz Walczak, PREVAC sp. z o.o., Poland**

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressure photoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

Friday Morning, October 26, 2018

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10:20am **SS+AS+HC-FrM-7 Quantum Mechanics and Reaction Kinetics Study on SiO₂ and SiN Dry Isotropic Chemical Etching Process**, *Taiki Kato, M Matsukuma, K Matsuzaki, L Chen*, Tokyo Electron Technology Solutions Limited, Japan

Dry isotropic chemical etching processes are important for semiconductor manufacturing, but such processes often require subtle process tuning to achieve high etching rates and the desired etching selectivity between SiO₂ and SiN. For example, the dry chemical etching solely with HF gas (Process 1) requires fine tuning of conditions for SiN etching rate because it has a peaky dependence on the process temperature; whereas dry chemical etching with NH₃/HF binary gas mixtures (Process 2) requires subtle tuning to simultaneously maximize etching rate and SiO₂:SiN selectivity. Notably, in Process 2, SiN etching rate increases with the etching time while SiO₂ etching rate slows down with the etching time. This slowdown is attributed to the formation of an etchant diffusion barrier from the solid byproduct, AFS (Ammonium fluorosilicate). Because of these contradictions, it has been difficult to achieve highly selective and rapid SiO₂ etching, thus a better understanding of the etching mechanisms is important to further develop the high selectivity required for the formation of scaled multicomponent semiconductor device structures. This study therefore focuses on revealing these mechanisms by using the quantum mechanics and by the analysis of reaction kinetics.

Firstly, Process 1 was studied with a quantum mechanical analysis by using the GRRM (Global Reaction Route Mapping) program. For this study, GRRM searched possible etching reaction paths automatically. From this reaction path search, it was revealed that SiN etching by HF gas, when used by itself, is much more rapid than SiO₂ etching. Further analysis was conducted by the reaction kinetics analysis. The kinetics parameters comprised HF adsorption, desorption and etching reactions. This model shows good agreement with the experimental SiN etching behavior.

Moreover, Process 2 was studied with similar quantum mechanics and kinetics analyses. Quantum mechanics analysis revealed that NH₃ combined with HF enhances both SiO₂ and SiN etching reactions. An NH₄F etching model was then added to the kinetics model. Because the etching byproduct, AFS, may be both an SiN etching accelerator and an SiO₂ etching decelerator, we could model the SiN etching kinetics initiated by NH₄F and propagated by NH₄F + AFS. This model quantitatively agrees with the experimental SiN etching data. Likewise, the SiO₂ kinetics model is composed of NH₄F etching, the diffusion resistance through solid AFS and the sublimation of AFS. This model also shows good agreement with experiment.

These analyses reveal the chemical etching mechanisms and enable process optimization. Further discussion will be presented on AVS 65th.

10:40am **SS+AS+HC-FrM-8 Viscosity and Surface Tension Effects on Metal Sputtered onto Low Vapor Pressure Liquids**, *Mark De Luna, M Gupta*, University of Southern California

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications.

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