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-WeM1 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-WeM3 Computationally Assisted Correlative STEM and EXAFS Characterization for Multiscale Structure Determination of Tunable Rh/Au Bimetallic Nanoparticle Catalysts, *S. House, C.S. Bonifacio,* University of Pittsburgh*; J. Timoshenko,* Stony Brook University*; P. Kunal, H. Wan, Z. Duan, H. Li,* University of Texas at Austin*; **Judith Yang,** University of Pittsburgh*; A.I. 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 frame work 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.

[1] R. Ferrando, J. Jellinek, R.L. Johnston, Chem. Rev. **108** (2008), p. 845-910.

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

9:00am SS+HC-WeM4 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-WeM5 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.-L. Yan,* University of the Free State, China*; J.Y. Wand,* Shantou University, China*; H.C. Swart,* University of the Free State, Republic of 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 Guttmann'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-WeM6 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.V. 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 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:

[1]: Parkinson, G. S., Novotný, Z., Jacobson, P., Schmid, M. and Diebold, U. J. Am. Chem. Soc., **133** (32), 12650-12655 (2011).

[2]: Fester, J., García-Melchor, M., Walton, A. S., Bajdich, M., Li, Z., Lammich, L. and Lauritsen, J. V. Nat commun, **8**, 14169 (2017).

[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-WeM10 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-WeM12 Experimental and Theoretical Evaluation of Water Chemistry on Two-dimensional Silica and Aluminosilicate, *Jin-Hao Jhang, G.S. Hutchings,* Yale University*; J.A. Boscoboinik,* Center for Functional Nanomaterials Brookhaven National Laboratory*; E.I. 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 penetrates 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-WeM13 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.

[1] Z. Li *et al.*, Nat. Mater. **12**, 925 (2013)

[2] A. Kozbial *et al.*, Carbon **74**, 218 (2014)

[3] T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Chem. Phys. B **107**, 1345 (2003)

[4] Y. Maekawa, K. Sasaoka, and T. Yamamoto, Jpn. J. Appl. Phys. **57**, 035102 (2018)

[5] Y. Homma *et al.*, Phys. Rev. Lett. **110**, 157402 (2013)

[6] A. Akaishi, T. Yonemaru, and J. Nakamura, ACS Omega **2**, 2184 (2017)

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