

# Wednesday Morning, November 1, 2017

## Fundamental Discoveries in Heterogeneous Catalysis

### Focus Topic

Room: 24 - Session HC+NS+SS-WeM

## Nanoscale Surface Structures in Heterogeneously-Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

8:00am **HC+NS+SS-WeM1 The Role of Nanoparticle Edges in Water Dissociation and Oxidation/reduction Reactions in Layered Cobalt Oxides Supported on Au(111) and Pt(111)**, Jakob Fester, J.V. Lauritsen, Aarhus University, Denmark, M. Garcia-Melchor, Trinity College Dublin, A.S. Walton, University of Manchester, UK, M. Bajdich, Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, A. Vojvodic, University of Pennsylvania, Z. Sun, J. Rodríguez-Fernández, Aarhus University, Denmark

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

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

By recording in-situ STM movies during exposure of Co-O bilayer nanoislands to  $\text{H}_2\text{O}$  we showed that  $\text{H}_2\text{O}$  dissociates on edge sites of the nanoislands followed by migration of H to the basal plane which serves as a reservoir [3]. In combination with Density Functional Theory (DFT) calculations, a preferable dissociation pathway was revealed, also highlighting an assisting role of a second water molecule in the dissociation process.

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

1. Fester, J., et al., Gold-supported two-dimensional cobalt oxyhydroxide ( $\text{CoOOH}$ ) and multilayer cobalt oxide islands. *Physical Chemistry Chemical Physics*, 2017. **19**(3): p. 2425-2433
2. Fester, J., et al., Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au (111), Pt (111) and Ag (111). *Topics in Catalysis*, 2016: p. 1-10
3. Fester, J., et al., Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. *Nature Communications*, 2017. **8**

8:20am **HC+NS+SS-WeM2 Analysis of Bulk and Surface Properties of Catalytically-Active Nickel Carbide/Nitride Nanostructures using X-ray Techniques**, Samuel Gage, K. Fong, C. Ngo, S. Shulda, Colorado School of Mines, C. Tassone, D. Nordlund, SLAC National Accelerator Laboratory, R. Richards, S. Pylypenko, Colorado School of Mines

Transition metal carbides and nitrides are an ever-growing topic in the scientific community. These materials can be synthesized with varying composition and morphology to exhibit properties similar to platinum-group metal catalysts, which are relevant to industrial heterogeneous catalysis and energy development. Studies, which report promising catalytic performances of nickel carbide and nitride catalysts, have continued to increase in recent years. Wet-chemical approaches involving a top-down thermal decomposition of nickel salt precursors in the presence of product-directing solvents are particularly interesting. The degree of nitrogen present in the nickel salt precursor, as well as the choice of molecular ligand-based solvents, can influence the material properties of the nickel carbide/nitride ( $\text{Ni}_3\text{C}/\text{Ni}_3\text{N}$ ) products.

A series of nitrogen-rich and nitrogen-poor nickel salt precursors were thermally degraded in the presence of oleylamine. X-ray diffraction confirms the bulk hexagonal crystal structure belonging to  $\text{Ni}_3\text{C}/\text{Ni}_3\text{N}$ . However, a combination of bulk and surface X-ray characterization techniques, including the X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), small angle- and wide angle X-ray scattering (SAXS and WAXS) indicate that the material properties of the  $\text{Ni}_3\text{C}/\text{Ni}_3\text{N}$  nanostructures do vary depending on the precursor. Computationally guided experiments reveal that the unique bulk and surface properties of these nanostructures influence their catalytic activity, giving  $\text{Ni}_3\text{C}/\text{Ni}_3\text{N}$  nanostructures the potential to be earth-abundant substitutes for precious metal catalysts.

9:00am **HC+NS+SS-WeM4 Grain-Boundary-Supported Active Sites for Electrochemical Catalysis**, Xiaofeng Feng, University of Central Florida

Identification of active sites on a catalyst surface is the key to a rational design of heterogeneous catalysts. For nanoparticle catalysts, most efforts to tailor their surfaces have focused on controlling particle size, shape, and composition. The atomic surface sites underlying these structural features are mainly facets, steps, edges, and corner sites. These efforts have led to important progresses in heterogeneous catalysis, but it is unclear if the accessible structure space is sufficient for finding optimal catalysts. One alternative is to use bulk defects such as grain boundaries (GBs) to stabilize catalytically active surfaces. Here we show that the GBs in metal nanoparticles create new active sites for electrochemical catalysis. Through a careful design of metal nanoparticle catalysts with different GB densities, extensive TEM characterization, and electrochemical measurements, we discovered that the catalytic activity for  $\text{CO}_2$  reduction on Au and CO reduction on Cu is linearly correlated with the GB density in the catalysts [1, 2]. The quantitative GB-activity relationship implicates GB surface terminations as new active sites and lead to highly active and stable electrocatalysts for a two-step conversion of  $\text{CO}_2$  to liquid fuels such as ethanol and acetate. In addition, we found that the GBs in Au enhance its activity for oxygen reduction reaction, suggesting that GB engineering may be a general strategy to improve heterogeneous catalysis for renewable energy conversion.

### References:

- (1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.* **2015**, *137*, 4606–4609.
- (2) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *ACS Cent. Sci.* **2016**, *2*, 169–174.

9:20am **HC+NS+SS-WeM5 Molecule-Surface Interaction on  $\text{TiO}_2$  and  $\text{MoS}_2$** , Zhenrong Zhang, Baylor University **INVITED**

Interaction of molecules with surfaces of catalysts is critical for understanding catalytic reaction mechanisms. We have studied the interaction of various probe molecules with  $\text{TiO}_2$  and  $\text{MoS}_2$  using scanning tunneling microscopy (STM) and tip-enhanced Raman scattering (TERS). Two-dimensional material,  $\text{MoS}_2$ , has attracted tremendous attention due to promising applications in electronics, photonics, and catalysis. Here we compared the difference in the interaction of sub-monolayer copper phthalocyanine ( $\text{CuPc}$ ) molecules with  $\text{MoS}_2$  and Au. The relative Raman peak ratio and Raman peak position shift from a partial TERS mapping show the difference in the adsorbates-adsorbates interaction and the adsorbates-substrates interaction on Au and  $\text{MoS}_2$  substrates. We have investigated the limits of Raman signal enhancement on  $\text{MoS}_2$ . Employing carboxylic acid, acetone, and formaldehyde as probe molecules, we studied how reactive sites affect the chemical activity of  $\text{TiO}_2(110)$ . This unique methodology enables us to achieve the atomic-level understanding of the key elementary reaction steps — adsorption, dissociation, diffusion, and coupling reaction — taking place in heterogeneous catalytic reactions.

11:00am **HC+NS+SS-WeM10 Enantioselectivity: The Quintessential Structure Sensitive Surface Chemistry**, Andrew Gellman, P. Kondratyuk, D. Rienicker, M.A. Payne, Carnegie Mellon University **INVITED**

Enantioselective heterogeneous catalysis and surface chemistry are quintessential forms of structure sensitive surface processes. Selectivity is driven purely by the diastereomeric relationship between the structural handedness of a chiral reagent or transition state and the structural handedness of a chiral surface. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are described as having flat low Miller index terraces separated by kinked step edges, therefore lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on ~500 different single crystal planes exposed by the surfaces of Cu(111) and Cu(100) Surface Structure Spread Single Crystal ( $\text{S}^4\text{C}$ ).  $\text{S}^4\text{C}$ s are single

crystals polished into a spherical shape that exposes continuous distributions of surface orientations vicinal to primary orientation. During isothermal decomposition of TA and Asp, XPS has been used to map the temporal evolution of coverage at points across the Cu(111) and Cu(100) S<sup>4</sup>Cs. The D- and L-TA (D- and L-Asp) coverage maps across the S<sup>4</sup>Cs following heating at 450 K to decompose ~70% of the initially adsorbed molecule reveal the symmetry of the substrate surface and the enantiospecific decomposition kinetics on the chiral surfaces with R- and S- orientations. The fourfold symmetry of the Cu(100) substrate is apparent, and the enantiospecificity of the decomposition kinetics is revealed by the spiral nature of the two maps and their opposite sense of handedness for D- and L-TA. These data can be analyzed to yield the enantiospecific rate constants for TA decomposition as functions of surface orientation.

11:40am **HC+NS+SS-WeM12 Understanding the Growth and Chemical Activity of Pt-Re Clusters on HOPG and Titania Surfaces**, *Donna Chen, T.D. Maddumapatabandi, A.J. Brandt, G. Seuser*, University of South Carolina

The growth and chemical activity of bimetallic Pt-Re clusters supported on highly-oriented pyrolytic graphite (HOPG) and TiO<sub>2</sub>(110) surfaces are studied as model systems for understanding Pt-Re catalysts in the water gas shift (WGS) and methanol oxidation reactions. STM experiments demonstrate that both Pt and Re atoms are mobile on unmodified HOPG surfaces and form large clusters that preferentially located at step edges. However, Ar<sup>+</sup> sputtering creates defect sites that serve as nucleation sites and result in smaller clusters with uniform size distributions. At high metal coverages, exclusively bimetallic clusters are formed from both the deposition of Pt on Re or Re on Pt. The cluster surfaces are Pt-rich even for the Re on Pt clusters due to the lower surface free energy of Pt compared to Re and the high mobility of atoms within clusters. Similarly, Pt-rich Pt-Re clusters have also been grown on titania supports. The activities of the Pt-Re bimetallic clusters are investigated in a microreactor coupled to an ultrahigh vacuum chamber so that the surfaces can be characterized by X-ray photoelectron spectroscopy (XPS) before and after reaction. In the WGS reaction, Re remains metallic, and Pt on Re surfaces exhibit higher activity than pure Pt. In methanol oxidation, oxygen-diffusion of Re to the surface occurs under reaction conditions, and the formation of volatile Re<sub>2</sub>O<sub>7</sub> results in Re sublimation from the surface. Furthermore, the titania support appears to stabilize Re<sub>2</sub>O<sub>7</sub> against sublimation, whereas Re oxidation is enhanced by the presence of Pt in the bimetallic clusters.

12:00pm **HC+NS+SS-WeM13 Single Atom Alloys for Efficient and Cost-effective Catalysis**, *E. Charles Sykes*, Tufts University

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

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

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