Surface Science
Room 209 CDE W - Session SS-WeA

Heterogeneous Catalysis II

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, **Dan Killelea**, Loyola University Chicago

2:15pm **SS-WeA-1 "Single-Atom" Catalysis: Insights From Model Systems***, **Gareth Parkinson,*** TU Wien, Austria **INVITED**

Despite numerous successful syntheses and applications of single-atom catalysts (SACs), a fundamental gap persists between experimental approaches and theoretical modeling. Real-world catalysts are typically supported on complex powders and exposed to dynamic environments rich in potential ligands and contaminants. In contrast, density functional theory (DFT) calculations often rely on idealized models, such as low-index crystal facets and bulk-like atomic sites, which can oversimplify the real catalytic environment.

Model systems based on single-crystalline supports prepared under ultra-high vacuum (UHV) conditions offer a valuable bridge between theory and experiment. These well-defined systems provide a testing ground to validate theoretical assumptions and gain atomistic insights into catalyst-support interactions.

As a case study, I will present experimental results on iron oxide surfaces—materials widely studied in SAC literature due to reports of high catalytic activity for metal adatoms on FeOx. Notably, many DFT studies adopt the hematite (α-Fe_2O_3) (0001) surface as a model, though its atomic-scale structure remains complex and contentious. Instead, we investigate the (1$\bar{1}$02) facet of hematite, which presents a stable, bulk-truncated (1×1) termination ideal for fundamental studies.

Our results demonstrate the adsorption behavior of Ir, Pt, and Rh single atoms on this surface. Crucially, stabilization of these atoms never occurs through simple adsorption at bulk-continuation sites. Instead, it involves either coadsorption of ligands or significant restructuring of the support itself—mechanisms that need to be accounted for in theoretical models of SACs.

2:45pm **SS-WeA-3 Ligand-coordinated Supported Catalysts for Selective Hydrocarbon Chemistry***, **Steven Tait**[1],* Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group has applied principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Initial studies were conducted on model surfaces under ultrahigh vacuum conditions. Precise deposition control allowed for exploration of metal-ligand complexation requirements that would lead to highly stable 1D and 2D architectures. Reaction selectivity was tested by small exposures to reactive molecules. These systems provided models that have been adapted to high surface area supports under ambient conditions. Modified wet impregnation methods allow for loading of single-atom catalysts on high surface area powders at up to 1 wt%. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and X-ray absorption spectroscopy, electron microscopy, and CO adsorption measurements demonstrate single atom character of the catalysts. These ligand-coordinated supported catalysts have been shown to be effective for a variety of reactions, including hydrosilylation, hydrogenation, dehydrogenation, and water-gas shift. Here, we examine the significant roles of the coordinating ligands and of the oxide support on catalyst structure, activity, and stability. Defect sites on the support and the expressed facets of the oxide have a strong influence on the state of the metal centers and show a significant impact on reaction activity. We also see strong influences due to changing functional group substituents in the ligands. Synthetic routes have been developed to incorporate carboxylic acid groups into the ligand framework to increase metal-ligand and metal-surface interactions. We compare this with systems involving co-ligand deposition. By loading the metal and ligand directly on the oxide support, it is possible to maintain a close contact of the metal to the oxide. These results provide new insights into the design and chemistry of supported single-atom catalysts.

3:00pm **SS-WeA-4 Ethanol Oxidation over Single-atom Model Rh/Fe_3O_4(001) Catalysts***, **Daniel Baranowski,*** Physical and Computational Sciences Directorate and Institute for Integrated Catalysis, Pacific Northwest National Laboratory

The selective oxidation of alcohols like ethanol, a renewable feedstock, is of pivotal interest, both from a fundamental and industrial perspective.[1] Inspired by previous ultra-high vacuum studies performed on model single-atom Pd/Fe_3O_4(001) catalysts activating the low-temperature methanol to formaldehyde oxidation,[2] a series of model Rh/Fe_3O_4(001) catalysts were examined for the low-temperature ethanol to acetaldehyde oxidation. Distinct Rh active sites, including Rh adatoms, substitutional in-surface Rh, and Rh clusters, were prepared using different preparation conditions and amounts of Rh.[3] The catalyst structures and activities were characterized by combining thermal desorption and photoelectron spectroscopies, and it was found that all model catalysts significantly reduce the temperature of the acetaldehyde production when compared to the bare Fe_3O_4(001) surface. There are, however, significant differences in the selectivities, not just between Rh single-atoms and clusters but also among the different single-atom species. The activity of all model systems was further tested during the presence of carbon monoxide. Surprisingly, the so far rather inactive in-surface Rh atoms turned out to exhibit promising properties when it comes to the upgrading of oxygenates.

(1) Gong, J.; Mullins, C. B. Selective Oxidation of Ethanol to Acetaldehyde on Gold. *Journal of the American Chemical Society* **2008**, *130* (49), 16458-16459. DOI: 10.1021/ja805303s.

(2) Marcinkowski, M. D.; Yuk, S. F.; Doudin, N.; Smith, R. S.; Nguyen, M.-T.; Kay, B. D.; Glezakou, V.-A.; Rousseau, R.; Dohnálek, Z. Low-Temperature Oxidation of Methanol to Formaldehyde on a Model Single-Atom Catalyst: Pd Atoms on Fe_3O_4(001). *ACS Catalysis* **2019**, *9* (12), 10977-10982. DOI: 10.1021/acscatal.9b03891.

(3) Sharp, M. A.; Lee, C. J.; Mahapatra, M.; Smith, R. S.; Kay, B. D.; Dohnálek, Z. Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe_3O_4(001). *The Journal of Physical Chemistry C* **2022**, *126* (34), 14448-14459. DOI: 10.1021/acs.jpcc.2c03426.

3:15pm **SS-WeA-5 Structure of Chemisorbed 1,3-Butadiene on the Cu(111) Surface and Its Influence on Selective Hydrogenation on a Pd/Cu(111) Single-Atom-Alloy***, **Mohammad Rahat Hossain**, Michael Trenary,* University of Illinois - Chicago

The selective hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) is essential for refining alkene streams in high-quality polymer production. Traditional catalysts such as Pd and Pt exhibit nearly barrierless H_2 activation but suffer from CO-induced coking and excessive activity, which lowers selectivity. Single-atom alloy (SAA) catalysts, such as Pd/Cu(111), offer a promising alternative by leveraging the selective properties of Cu while maintaining Pd's hydrogenation activity. We investigated BD adsorption and hydrogenation on Cu(111) and a Pd/Cu(111) SAA using reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and density functional theory (DFT). TPD and RAIRS studies reveal that BD adsorption on Cu(111) exhibits intermediate interaction strength—more substantial than physisorption on Ag(111) and Au(111) but weaker than chemisorption on Pd(110) and Pt(111). Unlike strongly reactive surfaces that induce BD dissociation upon heating, BD desorbs intact from Cu(111). DFT analysis suggests that BD adopts both di-π and tetra-σ chemisorbed configurations on Cu(111). Over a Pd/Cu(111) SAA, ambient-pressure hydrogenation experiments indicate a first-order reaction (1.12 ± 0.03) for H_2 and zero-order (-0.12 ± 0.01) for BD, with a turnover frequency of 36 s^{-1} at 380 K and an activation energy of 63.2 ± 2.8 kJ/mol. Complete BD conversion is achieved with 84% selectivity toward 1-B without butane formation. TPD in ultrahigh vacuum (UHV) shows that monolayer BD desorbs at 217 K. In contrast, multilayers desorb between 112 and 180 K. No surface-bound intermediates are detected during reaction conditions. Post-reaction Auger electron spectroscopy (AES) reveals no carbon deposition, indicating no BD dissociation. These findings provide insights into BD adsorption and selective hydrogenation mechanisms on Cu-based catalysts, with implications for improving alkene purification strategies.

3:30pm **SS-WeA-6 Well-Defined Cu-Delafossite Catalysts***, **Dario Stacchiola,*** Brookhaven National Laboratory

Cu-based catalysts are active for partial and full oxidation reactions. Deciphering the local atomic environment and oxidation state of active centers in supported copper catalysts, as well as the design of materials to

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control their stability under reaction conditions remains a great challenge. We show here that mixed-oxides of copper delafossites with gallium, aluminum or iron ($CuMO_2$, Cu^{1+} and M^{3+}; M: Ga, Al, Fe) in the form of porous nanoplates and films are promising materials as model catalysts to explore the activity and stability of Cu^{1+}-activated reactions. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

References

"$CuGaO_2$ Delafossite as a High-Surface Area Model Material for Cu^+ Activated Reactions"

EL Fornero, et al., *J. Catal.* **427**, 115107 (2023)

"PLD of Delafossite Oxide Thin Films on YSZ (001) Substrates as Solar Water Splitting Photocathodes"

C Zhou, et al., *Environ. Sci. Nano* **12**, 241-247 (2025)

4:15pm **SS-WeA-9 Formation of Monodispersed Palladium–Tellurium Nanoclusters on WTe_2(001): The Role of Excess Tellurium and Water**, ***Zdenek Dohnalek,*** Pacific Northwest National Laboratory **INVITED**

Understanding how metals and adsorbates interact with transition metal dichalcogenides is crucial for next-generation electronic, quantum, and catalytic applications. In this work, we explore palladium deposition on WTe_2(001) to reveal how mobile excess tellurium drives the formation of uniform, thermally stable $PdTe_x$ nanoclusters. Surprisingly, these clusters assemble independently of intrinsic surface defects. Upon annealing, they adopt identical size and structure, remaining stable up to ~500 K. Further investigation reveals that, contrary to common belief, the surface defects are hydroxylated rather than bare Te vacancies. The hydroxylation results from the adsorption and dissociation of background water, even under ultrahigh vacuum conditions. Density functional theory modeling supports these observations, explaining both the preferential nucleation of $PdTe_x$ clusters and the passivation of defects via water dissociation. These findings highlight how excess chalcogen atoms and water adsorption steer metal deposition, offering new pathways for creating robust, monodisperse nano-alloy structures for advanced quantum devices, microelectronics, and catalysts.

4:45pm **SS-WeA-11 Thermally Driven Chemical and Morphological Transition of Nb2O5 to NbO***, **Jasper Brown**, Van Do, Steven Sibener,* University of Chicago

The structure and morphology of niobium surfaces plays a crucial role in the performance of superconducting radiofrequency (SRF) cavities, particle accelerators, and other advanced technological applications that require high-purity and low-defect materials. The presence of a native Nb_2O_5 oxide layer on Nb and anodized Nb surfaces introduces irregularities that can negatively influence superconducting properties, necessitating precise control over oxidative states. In this study, the dissolution-driven modification of Nb and anodized Nb surface roughness associated with the thermal reduction of Nb_2O_5 under high-temperature vacuum annealing conditions is examined. Using *in-situ* atomic force microscopy (AFM) the topographical evolution of Nb surfaces before and after oxide dissolution is characterized and changes in roughness at the nanoscale are quantified. Additionally, *in-situ* X-ray photoelectron spectroscopy (XPS) is employed to confirm the alteration of the surface oxide from Nb_2O_5 to NbO, providing insights into the chemical state evolution that drives this transformation. By systematically varying heating rates, annealing temperatures, and annealing times, the specific thermal and temporal conditions necessary to achieve the transition from pentoxide to monoxide are determined.

5:00pm **SS-WeA-12 Size and Support Effects on Propanol Electro-Oxidation Catalyzed by Sub-Nano, Size-Selected Ptn Clusters***, **Zihan Wang**, Lokesh Saravanan, Ratul Khan, Thaylon Hernandez, Scott Anderson,* University of Utah

The electrocatalytic oxidation of 1-propanol and 2-propanol by size-selected Pt_n clusters supported on indium tin oxide (ITO) and highly oriented pyrolytic graphite (HOPG) has been investigated. Pt_n clusters are generated and mass selected in the gas phase, then soft landed (~2 eV/atom) onto electrode surfaces prepared in UHV with controlled surface chemistry and defect density. After deposition, samples are transferred into a load-lock chamber, where aqueous electrochemistry can be carried out without air exposure. Electrochemical activity is evaluated using cyclic voltammetry (CV), and the cluster size and support effects are analyzed in combination with X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM).

We find that both the activity and selectivity for propanol oxidation depend on Pt_n size and the support surface structure. Furthermore, catalytic activity correlates with Pt core-level binding energies measured by XPS, suggesting that electronic structure is tuned by the cluster size and the support.For each support, activity varies with cluster size; overall, clusters supported on HOPG exhibit higher activity than those on ITO. In addition, the activity depends strongly on the ITO surface composition, which was varied by sputtering with Ar and annealing in O_2. For HOPG, the problem is that the weak Pt-HOPG binding leads to facile sintering, and atomic anchors such as nitrogen or titanium atoms are implanted to stabilize the clusters.The effects of the anchors on both electrochemical activity and stability, and on the cluster electronic properties will be discussed. This work is supported by the NSF Center for Synthetic Organic Electrochemistry (CHE-2002158).

5:15pm **SS-WeA-13 Adsorption of Carboxylic Acids and Reaction-driven Morphological Changes on the Fe3O4(001) Surface***, Jose Ortiz-Garcia*[1]*, Marcus Sharp, Benjamin Jackson, Mal Soon Lee, Peter Rice, Bruce Kay, **Zbynek Novotny**, Zdenek Dohnalek,* PNNL

Understanding the adsorption and conversion of carboxylic acids, such as formic acid and acetic acid, on oxide surfaces, including the cleavage of their C-O and C-H bonds, is essential for understanding CO_2 reduction and C-C coupling reactions. Formate acts as a key intermediate in CO_2 hydrogenation, while acetate serves as a crucial reactant in C-C coupling ketonization reaction. To unravel the catalytic activity and mechanistic details of these reactions, it is crucial to understand the interactions of carboxylic acids with model catalytic systems. We investigate the adsorption and reactions of formic acid (FA) and acetic acid (AA) on Fe_3O_4(001) using STM, XPS, LEED, and TPD. On the pristine surface, a $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction is observed, attributed to subsurface cation vacancies. FA and AA adsorb dissociatively, forming bidentate species and surface hydroxyls. At room temperature, both fully saturate the surface, exhibiting (1×1) periodicity from ordered bidentate species and hydroxyls, and (2×1) from distinct monolayer packing. Differences emerge upon annealing. For FA, annealing to 500 K leads to a rearrangement to the lowest energy (1×1) configuration, while at 600 K, partial recovery of the surface reconstruction and potential formation of single oxygen vacancy defects occur. Increasing the temperature to 700 K results in complete conversion of formate species and the formation of extended pits along the Fe rows. In contrast, AA shows stability up to 450 K without considerable morphological changes. Conversion begins at 550 K, with significant surface etching occurring at 650 K, leading to an irregularly pitted surface primarily elongated along the Fe rows. In comparing total etching for both molecules, AA leads to significantly more at approximately 21% of the surface area while FA etches only 3.3% of the surface. Higher etching for AA stems from additional hydrogen atoms leading to more H_2O formation via the Mars-van Krevelen mechanism and nonstoichiometric formation of CO_2 and CO, resulting in extensive pitting. Complete surface recovery is achieved via oxygen annealing at 930 K. To further understand the nature of the etch pit structures formed by these carboxylic acids, we employed density functional theory calculations, which provided insights into the atomic-scale structure of the etch pits. Simulated STM images closely align with experimental observations, reinforcing our understanding of the structural characteristics of the etched regions. Our findings highlight the importance of understanding carboxylate interactions with oxide surfaces, which is crucial for overcoming kinetic barriers in reaction pathways.

5:30pm **SS-WeA-14 Oxidation of a Rh(111)/(322) Bisected Crystal***, **Maxwell Gillum**, Alexis Gonzalez, Elizabeth Serna-Sanchez, Allison Kerr, Stephanie Danahey,* Loyola University Chicago*; Arved Dorst, Johhanes Dietrich,* Georg-August Universität, Göttingen, Germany*; Tim Schäfer,* georg-August Universität, Göttingen, Germany*; Dan Killelea,* Loyola University Chicago

Metal-catalyzed oxidation reactions are a major application of heterogeneous catalysis and are a widely applied synthetic route for the production of chemicals and reagents essential to modern society. The studies herein further investigate the influences that step density has on the formation of oxygen-induced surface reconstructions, linking lab-based single crystal studies to the high defect density surfaces present in industrial catalysis. The experiments focus on gaining structural information about the oxygen species present on the surface of a Rh(111)/(322) bisected crystal under various oxidative conditions utilizing low energy electron diffraction (LEED). These techniques are used in unison with temperature programmed desorption (TPD) and Meitner-auger electron spectroscopy (MAES) to identify optimal conditions for further study. We

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found that the (322) facet of the surface shows presence of oxide formation under oxidative conditions that are not aggressive enough to form oxide on the flatter (111) Rh surface. This indicates that the step edges play a much larger role in the formation of oxide on the Rh surface than previously thought.

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