Surface Science
Room 305 - Session SS-ThA

Rising Stars

Moderators: Prof. Liney Arnadottir, Oregon State University, **Dr. Dario Stacchiola**, Brookhaven National Laboratory

2:15pm **SS-ThA-1 Restructuring, Fluxionality and Dynamics of Heterogeneous Catalysts in Reaction Conditions from First Principles**, ***Philippe Sautet***, University of California at Los Angeles **INVITED**

The determination of the surface structure of heterogeneous catalytic systems in reaction conditions is a key aspect for a detailed understanding of the nature of active sites and for the rational design of efficient catalysts. However, catalysts are not static but dynamic, fluxional, metastable and they strongly evolve under reaction conditions, creating new active sites, not present for the as prepared catalysts.

We will show by atomistic modeling that rare, metastable catalytic sites play a paramount role to determine the activity of heterogeneous catalysts. These metastable active sites are created under reaction conditions and are not present for the as prepared catalysts. The first example will concern the nature of active sites for the zirconia on copper inverse catalyst under the conditions of CO_2 hydrogenation to methanol, on a model of highly dispersed Zr oxide clusters on Cu(111). The exploration of reaction-pathways on an ensemble of 83 formate configurations accessible under reaction conditions reveals that structural sensitivity is pronounced, and only 10 of the catalyst configurations are significantly active across the full pathway, with the energy of the methoxy intermediate as a key reactivity descriptor. As a second example we will consider large PtNi nanoparticles (more than 10,000 atoms) for which the 3D local atomic structure and chemical composition was determined by atomic electron tomography. The experimental 3D atomic coordinates have used by first-principles trained machine learning to identify the active sites of the nanocatalysts. A striking feature is the difference of the ORR activity by several orders of magnitude among the surface Pt sites on the nanocatalysts. As a third example we will present the dynamical behavior of large Pt nanoparticles for dehydrogenation and hydrogenation reactions. We found that hydrogen adsorption drives a size-dependent transformation from an amorphous to a crystalline structure, leading to sharp phase transitions for smaller nanoparticles and smooth transformations for larger ones. When modeling alkane dehydrogenation or ethylene hydrogenation, we show a marked discrepancy between the abundance of a surface site and its catalytic contribution, indicating that the active sites are rare, not the most common sites.

References

1. Z. Yang, S. Kumari, A. N. Alexandrova, P. Sautet, J. Am. Chem. Soc. 2025, 147, 15294–15306

2. Y. Yang, J. Zhou, Z. Zhao, G. Sun, S. Moniri, C. Ophus, Y. Yang, Z. Wei, Y. Yuan, C. Zhu, Y. Liu, Q. Sun, Q. Jia, H. Heinz, J. Ciston, P. Ercius, P. Sautet, Y. Huang, J. Miao, Nat. Catal. 2024, 7, 796–806.

3. D. Chen, P. Sautet, Angew. Chem. Int. Ed. 2025, e19209

2:45pm **SS-ThA-3 Probing Dynamic Catalytic Interfaces: Structure, Evolution, and Function**, ***Gengnan Li***, Center for Nanoscale Materials, Argonne National Laboratory

Catalytic reactions often occur at interfaces, which are inherently dynamic under operating conditions. Capturing the dynamic structural, electronic, and chemical evolution of these interfaces under relevant reaction environments is therefore critical for developing a fundamental understanding of structure-performance relationships in catalysis. Recent advances in multiscale in situ and operando characterization techniques have redefined the traditional structure – function paradigm by providing comprehensive insights into the local coordination environment, electronic structure, and dynamic behavior of material surfaces and interfaces. In this talk, I will present our recent work on the controlled engineering of IrO_x-CoO_x interfaces in $IrCoO_x$ electrocatalysts to improve IrO_x dispersion and reduce the overall cost of hydrogen production. Combined spectroscopic and microscopic analyses reveal distinct electronic structures and surface arrangements arising from different interfacial architectures. In situ spectroscopic measurements further identify the catalytic interface as an active, dynamically evolving region that governs reaction activity and selectivity. We show that interfacial defect populations, coordination environments, and metal-support interactions reorganize in response to the reaction environment, leading to emergent structure-function relationships that cannot be deduced from post-reaction analysis alone. These measurements provide unprecedented opportunities to elucidate the underlying reaction mechanisms under operating conditions.

3:00pm **SS-ThA-4 Site-Specific Deuterium Adsorption in Nitrogen-Doped Graphene and Porous Carbon Materials**, *Buddhika S. Alupothe Gedara, Peter S. Rice, Prescott Evans, Tom Autrey, Bojana Ginovska, Mi Yeon Byun, Zdenek Dohnálek,* ***Zbynek Novotny***, PNNL

Nitrogen-functionalized carbon materials are investigated as promising candidates for hydrogen activation and storage. However, the role of specific nitrogen functionalities in facilitating hydrogen adsorption and activation remains poorly understood. To address this scientific gap, we investigated deuterium adsorption on three model systems: N-doped highly-oriented pyrolytic graphite (N-HOPG), N-doped graphene/Ru(0001), and porous nitrogen-carbon (NC) synthesized by pyrolysis of glucose and graphitic carbon nitride. For the first two systems, a variable N concentration was introduced using ion irradiation. Nitrogen incorporation occurs preferentially in two configurations: graphitic N (GN; N substituted in the hexagonal C lattice), and pyridinic N (PN; substitutional N adjacent to a C vacancy). The relative concentrations of GN and PN can be controlled by varying the ion dose, annealing temperature, and the choice of substrate [1,2]. Atomic deuterium was generated by D_2 cracking over a hot tungsten filament. For all probed materials, X-ray photoelectron spectroscopy showed that D exposure at 220 K induces a shift of the PN peak (398.0 eV) to higher binding energy by +1.1 eV, while the GN peak (400.6 eV) remains unchanged, demonstrating that deuterium binds selectively to PN sites. A near complete saturation of PN sites with D atoms was observed for N-HOPG (85%). Only a partial saturation of PN sites was observed for N-doped graphene/Ru(0001) (30%, due to the necessity to cleave the N-Ru bond before D adsorption) and in porous NC (6%, consequence of limited accessibility due to pore confinement effects). Deuterium fully desorbed from N-HOPG above 900 K, whereas on N-doped graphene/Ru(0001), a complete D desorption from PN is observed at ~700 K, indicating that the Ru metal weakens the N-D bond strength [2]. Moreover, the NC exhibited nearly the same desorption behavior as N-HOPG, demonstrating that well-defined model systems can effectively capture the behavior of more complex N-doped carbon materials, providing insight into the role of nitrogen dopants in hydrogen activation at carbon surfaces and interfaces.

[1] B.S.A. Gedara, P.S. Rice, P.E. Evans, D. Baranowski, M.A. Sharp, T. Autrey, B. Ginovska, Z. Dohnálek, Z. Novotny, *Adv. Mater. Interfaces*, 12 (2025) 2500142.

[2] B.S.A. Gedara, M.Y. Byun, M.L. Sushko, B. Ginovska, Z. Dohnálek, T. Autrey, P.S. Rice, Z. Novotny, *J. Alloys Compd.*, 1053 (2026) 186206.

3:15pm **SS-ThA-5 Developing a Nanoscopic Understanding of Electronic Metal-Support Interactions: From Model Systems to Powder Catalysts**, *Lindsey Penland, Hirushan Hetti Arachchige, Nadith Dissanayake,* ***Rachael Farber***, University of Kansas

Electronic metal-support interactions (EMSI), characterized by charge transfer across the metal/support interface, are often cited as an origin of enhanced selectivity and efficiency for oxide-supported metal nanoparticle catalysts. The coexisting factors influencing EMSI makes it difficult to predict EMSI in oxide-supported metal nanoparticle systems. This presentation will highlight recent work investigating EMSI in **1)** model TiO_2(110) catalysts and **2)** Mo/KIT-6 powder catalyst samples.

Rutile TiO_2(110) was used as a model oxide support to determine the spatially resolved electronic consequences of Cu nanoparticle size and defect density on EMSI. Using a combination of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and dI/dV mapping, a pristine and intentionally defected TiO_2(110) surface was characterized to reveal the relationship between local coordination environment and the observed local density of states (LDOS). On the pristine TiO_2(110) surface, STS measurements highlighted the attenuation of the LDOS at the Cu/TiO_2(110) interface and within a fixed distance of the Cu particle, suggesting that the region beyond the immediate metal/oxide interface may be significant for chemical activity. Ongoing work focuses on understanding how the increased defect density of the sputtered TiO_2(110) surface influences the thermal stability of Cu nanoparticles and the LDOS of the Cu/TiO_2(110) system. Preliminary results suggest increased thermal stability of adsorbed Cu on the sputtered TiO_2(110) surface while dI/dV mapping indicates unique electronic features due to the incorporation of Cu nanoparticles on the sputtered TiO_2(110) surface.

In an effort to bridge the materials gap between ideal systems and actual catalysts, powder Mo/KIT-6 catalysts, shown to be effective for propylene epoxidation, were investigated with STM and STS. STM data demonstrated that Mo nanoparticles decorate the KIT-6 surface for high loading (1.5wt%) catalysts while the low loading catalyst (0.5wt%) has dispersed Mo adsorbates. Interestingly, the low loading catalyst was shown to be more active towards propylene epoxidation, suggesting that isolated Mo sites are more active than Mo nanoparticles. STS data of KIT-6 and the Mo/KIT-6 powders demonstrate the emergence of electronic states within the bandgap of KIT-6 for both low and high loading catalyst samples, suggesting a surface-wide attenuation in the LDOS following the incorporation of Mo onto the KIT-6 support. These results contribute to the structural and electronic characterization of the Mo/KIT-6 surface, providing deeper insight into the origins of observed chemical activity.

3:30pm **SS-ThA-6 Reconciling Metal Coordination in g-C_3N_4-based Single Atom Catalysis: A Surface Science Study of Melem-Metal Interactions on Au(111)**, ***Faith Lewis,*** TU Wien, Austria*; Nicolò Allasia,* Polytechnic University of Milan, Italy*; Ola Alayan,* IMEM-CNR and Università degli Studi di Genova, Italy*; Moritz Eder, Viktoria Waidbacher, Margareta Wagner,* TU Wien, Austria*; Letizia Savio,* IMEM-CNR and Università degli Studi di Genova, Italy*; Gianvito Vilé,* Polytechnic University of Milan, Italy*; Gareth S. Parkinson,* TU Wien, Austria

Single-atom catalysis (SAC) is a rapidly growing field of research that combines the advantages of solid supports from heterogeneous catalysis with the tunability of active sites in homogeneous catalysis. SACs also lead to well-defined single-atom centers which can achieve high selectivity. Recently, graphitic carbon nitride (g-C_3N_4) has been identified as a framework to stabilize SACs that facilitate reactions such as the ORR and HER. The precursor, melem (2,5,8-triamino-heptazine) is typically polymerized, and the resulting structure features a network of 6-fold nitrogen pockets which stabilize the single atoms. The g-C_3N_4 framework is a common conceptual baseline for these catalysts, yet its structural specifics are increasingly debated, with recent studies directly challenging the prevailing model.[1] X-ray absorption spectroscopy (XAS) suggests a 4-fold metal coordination with equal bond lengths, a geometry that cannot exist within the often-proclaimed 6-fold pocket of g-C_3N_4.

In this work, we use the surface science approach to reconcile this contradiction through scanning probe microscopy (SPM) and X-ray photoelectron spectroscopy (XPS). On an Au(111) single crystal, melem forms a honeycomb overlayer that is stabilized through hydrogen bonding of the amino groups on the corners with the pyridinic nitrogens on the sides of the triangular molecule. When melem and metals, specifically Ni and Fe, were co-deposited at various temperatures onto Au(111), different overlayers formed. At lower temperatures, more densely packed regions of the same triangular features form next to the honeycomb structure. At higher temperatures, two different motifs form depending on the metal. With Fe, the densely packed regions observed at lower temperatures dominate, while for Ni a new structure appears in which the triangular melem molecules are no longer recognizable on the surface. We conclude this is the result of polymerization and formation of a 2D layer.

Our results indicate that, under these conditions, the Fe-melem species forms dimeric complexes centered by a metal atom. The resulting square-planar coordination environment aligns closely with recent XAS observations, offering a structural explanation for the 4-fold coordination.

1. Allasia, Nicolò, Shuai Xu, Sadaf Fatima Jafri, et al. 2025. “Resolving the Nanostructure of Carbon Nitride-Supported Single-Atom Catalysts.” *Small* 21 (23): 2408286. https://doi.org/10.1002/smll.202408286.

3:45pm **SS-ThA-7 Exploring Reactive Oxygen Species for Epoxidation on AgCu Bimetallic Surfaces**, ***Ashleigh Baber,*** James Madison University

Surface science provides a powerful framework for exploring the fundamental nature of model heterogeneous catalysis, with the goal of enhancing reactivity, improving selectivity, and identifying active sites. Our research group utilizes ultrahigh vacuum temperature-programmed reaction spectroscopy to probe catalytic reactivity, complemented by low-temperature scanning tunneling microscopy for atomic-scale visualization of model catalysts. We explore the role of hydroxyl groups as reactive oxygen species in the epoxidation of ethylene and propylene over Ag/Cu(111) model catalysts. The presence of Ag and hydroxyls promotes selective partial oxidation to epoxides while suppressing overoxidation to combustion products. By elucidating the relationship between surface structure and catalytic activity, this work contributes to the rational design of more efficient catalysts for industrial applications enhancing performance, reducing waste, and mitigating CO_2 emission.

4:00pm **SS-ThA-8 Peter Mark Award Talk: Tip-Enhanced Raman Spectroscopy with Scanning Ion-Conductance Microscopy**, ***Naihao Chiang***[1]*,* University of Houston **INVITED**

Tip-enhanced Raman spectroscopy (TERS) combines the single-molecule chemical sensitivity of surface-enhanced Raman spectroscopy with the nanoscale spatial resolution of scanning probe microscopy. Over the last decade, TERS has achieved Angstrom-scale spatial resolution under ultrahigh-vacuum conditions, making it a powerful tool for investigating surface-bound species. To extend this technique to soft samples in an electrolytic environment, such as *in vitro* biological samples, scanning ion-conductance microscopy (SICM) was selected as the platform for integrating TERS. In this presentation, I will provide the background and instrumentation design principles that enable SICM-TERS, along with examples of proof-of-concept systems. Additionally, the plasmonically enhanced near-field in SICM-TERS can be used to deliver intracellular cargo with single-cell precision; examples on human T-cells will be discussed. In the future, we expect this newly developed SICM-TERS platform to provide chemical information at interfaces in regimes that conventional techniques find challenging to access.

[1] **Peter Mark Memorial Award Winner**

Author Index

Bold page numbers indicate presenter