Surface Science
Room 305 - Session SS-MoM

Precision On-Surface Synthesis

Moderators: Dr. Nathan Guisinger, Argonne National Laboratory, USA, **Pavel Jelinek**, Institute of Physics of the Czech Academy of Sciences

10:00am **SS-MoM-1 Porous Graphene Nanoribbons and Nanomeshes***, **Alexander Sinitskii,*** University of Nebraska-Lincoln **INVITED**

Atomically precise porous graphene nanostructures provide a versatile platform for tailoring electronic properties through controlled structural design. Here, we present a bottom-up synthetic strategy that provides access to a family of nanoporous graphene nanomaterials, including porous nanographenes, porous graphene nanoribbons (pGNRs), and extended nanoporous graphene (NPG) networks, all derived from closely related triphenylene-based molecular precursors [1]. By varying the synthetic environment, the same molecular building blocks can be directed toward distinct carbon architectures: solution-phase coupling yields cyclotrimeric porous nanographenes, whereas on-surface synthesis on Au(111) promotes linear polymerization and cyclodehydrogenation into atomically precise pGNRs. At high surface coverage and elevated annealing temperatures, these ribbons laterally fuse into extended nanoporous graphene sheets, establishing a modular and broadly tunable synthetic framework for porous carbon nanomaterials.

This platform further enables systematic investigation of how nanopore incorporation influences GNR properties [2]. By comparing a pristine N = 15 armchair GNR (15-AGNR), its periodically perforated analogue containing [18]annulene pores (15-pGNR), and the more extensively carved chevron GNR (cGNR), we track the evolution of the electronic structure with progressive pore opening. STS and ARPES measurements, as well as theoretical calculations, reveal that introducing periodic nanopores into the 15-AGNR produces a greater-than-twofold increase in bandgap, while further evolution toward the cGNR architecture results in comparatively smaller changes. These findings provide direct insight into the combined roles of geometric confinement and periodic lattice perforation in tuning GNR electronic structure.

We further expand the structural complexity of these systems by laterally fusing pGNRs into NPG networks containing periodically spaced biphenylene units, representing a novel 2D carbon allotrope [3]. STM, nc-AFM, and DFT calculations demonstrate that incorporation of biphenylene motifs into a porous graphene framework gives rise to distinct electronic behavior, including reduced and indirect bandgaps. Collectively, these studies establish a unified molecular design strategy for structurally related porous graphene nanomaterials with tunable topology and electronic functionality, spanning 0D, 1D, and 2D carbon architectures.

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10:30am **SS-MoM-3 On-surface Synthesis of Porphyrin-Based MONs: a Model System for -Artificial Spin Lattices***, Eidsa Brenda Costa Ferreira,* University of Campinas (UNICAMP), Brazil*; Rafael Reis Barreto,* university of campinas (UNICAMP), Brazil*; Otavio Rodrigues de Oliveira, Iago Aedon Silva Prior, Isabela Costa Tonon,* University of Campinas (UNICAMP), Brazil*; Vanessa Carrenõ-Diaz, Breno Santimaria Sertori,* university of Campinas (UNICAMP), Brazil*; Igor Stein Weiler, **Abner de Siervo**,* University of Campinas (UNICAMP), Brazil

Over the past decade, significant advances have been achieved in the on-surface synthesis of atomically precise one-dimensional (1D) and two-dimensional (2D) metal–organic networks (MONs) using selected molecular precursors as modular building blocks in a "molecular LEGO" approach. This strategy exploits substrate properties, precursor molecular geometry, functional groups, diffusion behavior, and thermal activation energies to steer hierarchical reactions and the formation of novel nanostructures [1]. Porphyrins have well-defined geometry, rich electronic properties, and the ability to accommodate a central metal atom within their mycrocycles, making them particularly promising building blocks. When their molecular periphery is terminated with cyano, pyridyl, carboxylic, or halogen groups, deposited or substrate-derived adatoms can be trapped to form metal–organic coordination nodes. This leads to MONs with linear, square, rectangular, hexagonal, or kagome lattices, with geometries dictated by the molecular structure and substrate registry. Such architectures serve as important model systems for two-dimensional artificial spin lattices, among other phenomena. In this work, we present recent examples of MON formation using two types of free-base porphyrins: 5,10,15,20-tetra(4-pyridyl)porphyrin (2H-TPyP) on Ag(100) [2] and 5,10,15,20-tetrakis[4'-(4-pyridyl)phenyl]porphyrin (2H-TPyPP) on Ag(111)[3]. In both cases, the introduction of Fe promotes de formation of different MONs with well-ordered and extended spin lattices. These different structures can be selectively realized by controlling the annealing protocol and the Fe deposition sequence [2,3]. These studies combine scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) experiments, supported by density functional theory (DFT) calculations.

Acknowledgements

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10:45am **SS-MoM-4 Deciphering Atomic Layer Deposition in Materials Processing: A Surface Science Perspective***, **Joerg Libuda,*** Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Atomic Layer Deposition (ALD) enables controlled growth of ultrathin films with sub-nanometer precision, making it a key technique for nanoelectronics, catalysis, and energy applications. However, its success critically depends on the early stages of nucleation, which determine film continuity, uniformity, and defect density. Achieving uniform nucleation and atomic-level control remains challenging. Among the emerging materials accessible by ALD, transition-metal dichalcogenides (TMDCs) are of particular interest due to their tunable band gaps. Besides the extensively studied MoS_2, HfS_2 is a promising candidate, offering higher carrier mobility and a suitable band gap for electronic applications.

Here, we present our work on elucidating ALD nucleation mechanisms using a surface-science approach under ultrahigh vacuum (UHV). Atomically defined films and nanoislands of transition metal oxides (CoO(100), Co_3O_4(111)) on metal single crystals (Ir(100), Au(111)) serve as model substrates. HfS_2 growth is achieved via self-limiting reactions of tetrakis(dimethylamido)hafnium (TDMAH) with H_2S (or D_2S). The nucleation and growth processes are investigated in situ by combining scanning tunneling microscopy (STM) with time-resolved and temperature-programmed infrared reflection absorption spectroscopy (TR-IRAS, TP-IRAS).

Our results reveal that initial ALD nucleation is highly complex, involving multiple mechanisms and surface species. In the presence of surface OH/H_2O, mobile OH species induce full TDMAH hydrolysis (Brønsted acid–base mechanism). With increasing exposure, nuclei evolve dynamically through reactions of partially hydrolyzed species. While OH-functionalized self-assembled monolayers reduce OH mobility, substantial stoichiometric changes persist during early growth. Notably, nucleation also occurs on oxide surfaces in the complete absence of OH groups, indicating a Lewis acid–base mechanism with ligands bound to surface Co^{2+} sites. On CoO nanoislands, STM identifies initial intermediates, providing direct evidence for the Lewis acid–base mechanism. At elevated temperatures, dehydrogenation sets in as an additional reaction channel and generates OH groups that subsequently react via the Brønsted acid–base mechanism.

Overall, nucleation involves a highly complex interplay of Brønsted and Lewis acid–base pathways and dehydrogenation processes. These findings highlight that precise control over process parameters, surface structure, OH/H_2O chemistry, and reactant purity is essential for achieving controlled ALD nucleation.

11:00am **SS-MoM-5 Iterative Organic Modification of Pt Nanoparticles for Site-Selective Surface Engineering***, **Yongju Yun**, Minji Yun,* Pohang University of Science and Technology (POSTECH), Republic of Korea

The controlled modification of surface chemical environments is important for understanding structure-sensitive reactions on metal nanoparticles. However, conventional single-step surface modification methods often lead to non-selective coverage of surface sites, limiting precise control over local surface environments. In this study, we present an iterative organic modification strategy using ethylenediamine (EDA) as a molecular modifier to tune the electronic and geometric properties of Pt/Al_2O_3 surfaces.

Successive cycles of molecular adsorption and mild thermal annealing progressively introduced N-containing surface species. X-ray photoelectron spectroscopy (XPS) showed an increase in the fraction of electron-deficient $Pt^{\delta+}$ species through Pt–N interfacial interactions. In parallel, CO diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) suggested preferential modification of under-coordinated (UC) sites, leading to a relative increase in the exposure of well-coordinated (WC) terrace sites. Compared with conventional single-step modification, the iterative approach resulted in a higher WC/UC ratio, indicating improved site selectivity. The modified catalysts exhibited enhanced enantioselective hydrogenation performance for α-keto esters, achieving an enantiomeric excess (ee) of up to 96.5%. These results demonstrate that iterative organic modification can provide an effective approach for tuning interfacial surface environments and surface-site distributions on heterogeneous catalysts.

11:15am **SS-MoM-6 Probing the Role of Anodization Leading to Improved Sn Uptake for the Creation of High-Performance Nb_3Sn SRF Cavities**, ***Jasper Brown***, *Van Do,* University of Chicago*; Liana Shpani,* Cornell University*; Helena Lew-Kiedrowski,* University of Chicago*; Matthias Liepe,* Cornell University*; Steven Sibener,* University of Chicago

One of the primary obstacles to implementing Nb_3Sn in the creation of high performance superconduction radio frequency cavities (SRF) for use with high gradient particle accelerators is the presence of film-growth inhomogeneities, which promote vortex pinning and generate localized surface hot spots that degrade cavity performance. Studies have shown that pre-anodizing Nb enhances Sn nucleation, leading to the formation of more stoichiometric and uniform Nb_3Sn coatings. Although anodized Nb surfaces have been widely investigated, there remains limited understanding of the chemical and structural evolution of these surfaces under Sn nucleation conditions. In this work, we employ in-situ X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to examine the thermal evolution of anodized polycrystalline Nb samples annealed to 773 K at heating rates of 3 K/min and 7 K/min in the absence of Sn. We find that compared to the control sample, the anodized Nb surface exhibits an RMS roughness an order of magnitude greater and displays an isotropically rough and porous morphology that persisted throughout the annealing process. Additionally, XPS measurements revealed persistent surface contamination associated with the anodizing electrolyte both prior to and following annealing. Through this study, we quantified surface roughness, chemical composition, and the oxide dissolution activation energy for both anodized and native Nb surfaces. These findings provide important insight into the role of anodization in influencing Sn nucleation behavior and the subsequent Nb_3Sn alloying process.

11:30am **SS-MoM-7 Methods and Mechanisms to Engineer Monodispersed Noble Metal Single Atoms, Dimers, Trimers, and Bi-atomic Metal–Oxygen Dimers on TiO_2(110)-(1×1) Surface for Catalysis**, ***Xiao Tong***, BNL

Monodispersion of size-selected nanoclusters supported on metal oxide is critical for catalytic activity, selectivity, and stability, but small clusters often diffuse and aggregate into 3D structures after adsorption, losing their size specificity. This study examines how oxygen vacancy density, cluster landing energy, and environmental water influence the adsorption of Au_1, Ag_n (n = 1–3), and VO clusters on TiO_2(110)-(1×1). High landing energies of clusters or elevated substrate temperatures promote monodispersion of monomers, dimers, trimers, and 2D sheet growth by creating transient defects that pin clusters while thermal dissipation heals surrounding damage, or by preserving oxygen vacancies from passivation by environmental water. Water can displace Au_1 from oxygen vacancies to nearby 5-fold Ti sites and passivate the vacancies through hydroxyl formation. VO clusters stabilize water dimer strings that act as barriers and spacers, preventing aggregation of incoming clusters and enabling control over monodispersion density by modulating string length. These findings demonstrate how tuning physical and chemical parameters can stabilize the monodispersion of size- and composition-selected clusters, advancing novel catalytic design.

11:45am **SS-MoM-8 Ni Porphyrin as a Model Single Atom Catalyst for CO_2 Adsorption**, *J. Sanchez,* The University of Texas at San Antonio*; J. Martinez, P. Sharma, H. Wang,* University of North Texas*;* ***Fang Xu***, The University of Texas at San Antonio

Metalloporphyrin is an ideal model for fundamental studies of single atom catalysis (SAC), becaues the electronic structure of the central metal atom is tunable by electron donating or withdrawing substituents.In this work, we investigate the self-assembly and electronic structure of Ni-tetraisopropylporphyrin (Ni-TIPP) and its substituent Ni-tetrabromoisopropylporphyrin (Ni-TBTIPP) for CO_2 activation on Au(111) surface. Scanning tunneling microscopy and spectroscopy (STM/STS) were employed to qualitatively probe changes in local density of states associated with variations in the porphyrin substituents and central metal environment. STS detects a large band gap associated with the strong insulating porphyrin molecules. The STM results show that Ni-TIPP forms a 2D network of porphyrin islands with an upward tilted phenyl in each molecule due to possible tension, while molecules at the edge of the islands appear relaxed and more planar to the surface. The tilt was not observed in the case of Ni-TBTIPP which self-assembles planarly and flatly to the Au(111) substrate. The assembled Ni-TIPP was subsequentially exposed to CO_2 through a direct dosing tube with enhanced pressure effect. Control experiments of STM and temperature desorption indicate the formation of formate as the intermediate of CO_2 activation. This work visualizes CO_2 activation to formate over Ni metalated porphyrins for the first time, and the fundamental understanding provides key insight toward catalytic designs of CO_2 conversions.

Surface Science
Room 305 - Session SS-MoA

Surface Electronic, Magnetic, and Optical Properties

Moderators: Prof. Abner de Siervo, University of Campinas (UNICAMP), **Alexander Sinitskii**, University of Nebraska-Lincoln

1:30pm **SS-MoA-1 Graphene Nanoarchitectonics: Exploring Dimensionality Effects from 0 to 1.X**, ***Aitor Mugarza***, Catalan Institute of Nanoscience and Nanotecnology - ICN2, Spain **INVITED**

Nanostructuring Graphene Confers Multiple Functionalities to This Material, Making It Attractive to Very Diverse Applications in Electronics, Molecular Sensing and Filtering. For Instance, Semiconducting Gaps Can Be Induced by Reducing Its Dimensions to the Nanometer Scale. At This Scale, Edges Play a Crucial Role in Determining the Physico-Chemical Properties of the Nanomaterial, with the Emergence of Magnetism Localized at Zigzag Edges, or the Capability to Add Functional Groups Being Representative Examples. on the Other Hand, Introducing Pores of Similar Sizes Turns Impermeable Graphene Into the Most Efficient Molecular Sieve Membrane. For Both the Material and Void Components, the Interesting Scale for Applications Is Below 3-5 Nm, a Regime Where Bottom-Up Synthesis Can Be Particularly Efficient.

Here I Report Different Surface-Assisted Methods to Grow *0d* Graphene Quantum Dots with Magnetic Zigzag Edges (1-4), *1d* Nanoribbons Where the Electronic Properties Are Tuned by Controlled Edge Functionalization (5,6), and Nanoporous Graphene Sheets That Combine 1nm Size Ribbons and Pores (7). The Highly Anisotropic Structure of These Weakly Coupled Ribbon Arrays and the Modular Strategy Employed for Their Synthesis Allow Us to Control Their *1.X* Dimensionality by Molecular Bridge Engineering (8), or Even the Realization of 1nm Wide Lateral Heterostructure Superlattices Where Novel Excitonic States Are Predicted (9).

the Novel Electronic States of the Synthesized Nanoarchitectures Are Correlated with the Particular Atomic Structures by Using Scanning Tunnelling Microscopy. Their Potential Application in Devices Is Illustrated by Gate Modulated Transport Measurements in Nanoporous Graphene Sheets.

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2:00pm **SS-MoA-3 Spatially Probing the Topologically Protected Surface State of Bi_2Se_3 to Local Impurities and Defects**, ***Nathan Guisinger***, Argonne National Lab

Low-dimensional materials functioning at the nanoscale are a critical component for a variety of current and future technologies. The exploration of novel quantum materials and architectures to advance quantum information science (QIS) is at the forefront of condensed matter research. There has been tremendous interest in alternative strategies that utilize topologically protected states. Because these states are robust to their local environment, topological QIS offers advantages towards longer coherence time and a more fault tolerant platforms. This talk will discuss our recent atomic-scale study of the well-known topological insulator Bi_2Se_3 that has been doped n-type with magnetic Fe atoms. Specifically, the impact of sub-surface impurities, Se vacancies, and adatoms on the two-dimensional topologically protected surface state. An ultrahigh vacuum low-temperature scanning tunneling microscope was used to perform this study with applied magnetic field up to 9T. Both topographic imaging and spectroscopy were utilized for spatial characterization. This research was performed at the Center for Nanoscale Materials (CNM) at Argonne National Laboratory, which is one of the five Department of Energy Nanoscale Research Centers.

2:15pm **SS-MoA-4 Spectro-Microscopic Characterization of Surface Magnetization in Bulk Fe_3GeTe_2**, *Trevor A. Tyson,* New Jersey Institute of Technology*; Abdullah Al-Mahboob,* ***Jerzy T. Sadowski***, Brookhaven National Laboratory

The spatial variation of the magnetic structure in Fe_3GeTe_2 has previously been investigated using scanning tunneling microscopy, magnetic force microscopy, X-ray magnetic circular dichroism (XMCD), scanning electron microscopy with polarization analysis, and Lorentz transmission electron microscopy. Here, we employ the XMCD imaging mode of X-ray photoemission electron microscopy (XMCD-XPEEM) to investigate the magnetic domain structure of Fe_3GeTe_2 in zero applied magnetic field. The observed domain configuration follows the expected pattern for thick crystals with strong uniaxial magnetic anisotropy.

To further probe the magnetic texture, we use low-energy electron microscopy (LEEM) with a tilted incident electron beam to image magnetic domain walls. Unlike spin-polarized LEEM, this method does not require specialized sample preparation or a spin-polarized electron source. Instead, magnetic contrast is generated by tilting the incident electron beam relative to the sample surface normal, or equivalently by tilting the sample itself. We demonstrate how the resulting contrast can be analyzed to determine the domain-wall type and to extract critical exponents associated with the surface magnetic behavior.

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2:30pm **SS-MoA-5 Surface Electronic Structure of $Sr_3Ir_2O_7$ (001) Thin Films**, ***Peace Adegbite***, *M. Zaid Zaz, Yuanyuan Zhang, Arjun Subedi,* University of Nebraska-Lincoln, USA*; Alpha T N'Diaye,* Lawrence Berkeley National Laboratory*; Kenya Shimada,* Research Institute for Synchrotron Radiation Science, Hiroshima University, Japan*; Takashi Komesu, Xia Hong, Peter Dowben,* University of Nebraska-Lincoln, USA

$Sr_3Ir_2O_7$ is a narrow band-gap Mott insulator and member of the Ruddlesden-Popper strontium iridates. It is a layered material with competing energy scales for strong spin-orbit coupling and Coulombic interactions. The competing energies for band width (W), correlation (U) and spin-orbit coupling affects the surface characteristics in interesting ways. In this study, we investigated the surface electronic behavior and band structure of $Sr_3Ir_2O_7$ (001) thin films, using a variety of surface-sensitive spectroscopy techniques.

Angle-resolved photoemission spectroscopy (ARPES) revealed the presence of a finite density of states at the Fermi level that is localized to the surface, indicating a metallic surface coexisting with an insulating bulk. This surface-localized metallicity is further supported by transport measurements, as the electrical conductivity of $Sr_3Ir_2O_7$ thin films increases with decreasing film thickness. X-ray photoemission spectroscopy shows no measurable band bending with increasing Au overlayer thickness on the $Sr_3Ir_2O_7$ thin film, consistent with the measured linear I-V character and indicating the absence of a Schottky barrier at the Au/$Sr_3Ir_2O_7$ interface. From the valence band dispersion in ARPES, we estimated a light effective hole mass of 0.11 m_0 along the Γ-M direction of the surface Brillouin zone. To obtain a comprehensive view of the electronic structure, the unoccupied band structure was mapped using angle-resolved inverse photoemission spectroscopy and the orbital symmetry of the unoccupied bands at the Sr L-edge was assigned through angle-resolved X-ray absorption spectroscopy.

Furthermore, low energy electron diffraction reveals an anomalous temperature dependence of the surface scattering intensity that contradicts the conventional Debye-Waller behavior. We attribute this behavior to the damping of the normal mode vibrations via thermally activated carriers with increasing temperature.

2:45pm **SS-MoA-6 Revealing the Band Structure of High Entropy Oxides with Angle Resolved Photoemission**, ***Elena Salagre***, *Elliot Fuller,* Sandia National Laboratories

Recent years have seen interest rise for materials that can be tuned beyond traditional means. Compositionally complex oxides (CCOs), also identified as High Entropy Oxides (HEOs), are a unique approach to tailor properties by introducing multiple cations (typically 4+) to a lattice site. Despite such disorder, CCOs often maintain high crystal quality and homogeneity due to entropy stabilization effects. High entropy oxides have been explored as catalyst and as materials for microelectronics, applications in which their surface band structure becomes critical. However, few works have captured

the electronic structure of these oxides. Here we reveal how electronic properties emerge due to the competing effects of compositional complexity, disorder and strong correlations. We present a combination of electronic transport and Angle Resolved Photoemission (ARPES) on ABO_3 high entropy oxides both in terms of the A-site and B-site cation substitutions. For the A site substitution by La, Sm, Nd, Gd, Y adds compositional complexity as a fraction substitution (La_{1-x}[Sm, Nd, Gd, Y]$_{x/4}BO_3$) while Sr can be used as a traditional hole dopant to tune the electronic behavior. For B site, a mixture of the transition metals Cr, Mn, Fe, Co, Ni is used to add complexity while tuning *U*, *W*, *Δ* and spin degrees of freedom. Our results present clear evidence that a unified and coherent band structure is maintained in CCOs, even when the valence band is formed by 5 transition metal oxide *d*-levels. Additionally, we explore using compositional complexity in a strongly correlated double exchange metal (LSMO), where it can be used as a tool to systematically explore how new phases emerge, including a crossover regime between correlation and disorder induced behaviors. With these new measurements of the band structure of these CCOs, a better understanding of observed transport and magnetic properties can be achieved.

3:00pm **SS-MoA-7 Unveiling the Surface Electronic and Morphological Properties of the Centrosymmetric Nano-Skyrmion Host $EuAl_4$**, ***Jarred Grant***, *David King, Nikiphoros Vlastos, Yuri Dahnovsky, Jinke Tang, TeYu Chien,* University of Wyoming

Centrally symmetric (centrosymmetric) magnets capable of hosting skyrmions have attracted intense interest because they lack the Dzyaloshinskii-Moriya interaction (DMI). In these materials, inversion symmetry is preserved, requiring alternative mechanisms beyond DMI for skyrmion formation and stabilization. Proposals include symmetry-breaking effects such as charge density waves (CDW). The interplay among possible DMI, Ruderman-Kittel-Kasuya-Yosida (RKKY), and four-spin interactions in these systems creates a rich platform for diverse magnetic textures and phases. Centrosymmetric $EuAl_4$ is a particularly promising example, owing to its exceptionally small reported skyrmion size (~3 nm). Direct visualization of these nanoscale skyrmions is highly desirable. Spin-polarized scanning tunneling microscopy (SP-STM) is ideally suited for this length scale; however, key surface properties of cleaved $EuAl_4$, including the cleavage plane, surface morphology, local electronic structure, and termination—remain largely unexplored. In this talk, I will present STM, LEED, and DFT results detailing the cleavage plane, atomic-scale surface morphology, and corresponding dI/dV spectra of cleaved $EuAl_4$(001) single crystals.

*This work was supported by: DMR- 2414748

3:15pm **SS-MoA-8 Engineering Electronic States in High-Entropy Materials: From Disorder-Induced Pseudo Gaps to Gap Tuning in Transition Metal Dichalcogenides**, ***TeYu Chien***, University of Wyoming

High-entropy materials provide a unique platform to engineer novel electronic states through extreme chemical disorder. This talk presents scanning tunneling microscopy and spectroscopy (STM/STS) investigations into local electronic structures across two distinct high-entropy systems.

First, we examine the impact of atomic-scale chemical disorder in high-entropy alloys (HEAs). Local d*I*/d*V* spectra reveal the emergence of a disorder-induced pseudo gap at the Fermi level, directly reflecting modifications to the local density of states driven by electron-electron interactions caused by random potentials seen by electron wave function in random elemental distribution environment.

Second, we demonstrate electronic tuning in high-entropy transition metal dichalcogenides (HE-TMDs). By controlling metal compositions, we show a systematic evolution of the tunneling spectrum from low entropy to medium entropy HE-TMDs. Specifically, the characteristic V-shaped d*I*/d*V* spectrum transitions into a distinct U-shaped gap structure. These findings highlight the potential of entropy-stabilized configurations to precisely tailor quantum phases and electronic behaviors at the nanometer scale.

3:30pm **SS-MoA-9 Revealing Cu-Mn Electronic Structure Interaction in Activated CuMn/Al_2O_3 Catalyst by Decoupling of Overlapping XPS Spectra**, ***Yong Yang***, Shanghaitech University, China; *Rongjia Du,* ShanghaiTech University, China; *Evgeny I. Vovk,* ShanghaiTech University, China, Russian Federation

Mn promoted Cu based catalysts demonstrate high efficiency and stability in various chemical processes including methanol synthesis. Investigation of active centers in bimetallic Cu-Mn catalysts meets certain problems: Mn oxidation state cannot be directly determined because of strong overlapping of Mn and Cu photoelectron and Auger spectra. In this study, a new approach of convoluted background subtraction was proposed to separate the net Mn photoelectron spectra from overlapping Cu signal. The structure of CuAl and CuMnAl catalysts was investigated by XPS, XRD and EXAFS. XPS data were obtained after *in situ* activation and passivation treatments. After dedicated data analysis, the XPS results indicated the interaction and charge transfter between the Cu and Mn species on the CuMnAl catalyst. This study insighted how Mn promoter can effectively tune the electronic states of Cu catalyst; while it also provided a methodology example of separating low intensity Mn photoelectron spectra from overlapped complex background signals that can be aplyed to Mn-Cu or similar multicomponent systems.

4:00pm **SS-MoA-11 Understanding of STS Maps of Strongly Correlated Molecules on Surfaces: Can We Image Molecular Orbitals?**, ***Pavel Jelinek***, Institute of Physics of the Czech Academy of Sciences, Czechia **INVITED**

Traditionally, scanning tunneling spectroscopy (STS) of individual molecules is interpreted within the formalism of one-electron molecular orbitals [1]. Although this theoretical approach gives satisfactory agreement with experiment in some cases [2], it is in direct contradiction with the basic principle of quantum mechanics, which excludes direct observation of the wave function [3].

Moreover, recent progress in on-surface synthesis has enabled the preparation of strongly correlated polyradical molecules [1], which are not available by traditional solution-phase synthetic approaches. It is not surprising that interpreting STS maps of such polyradical molecules based on standard one-electron STM theory often fails. In this talk, we will discuss a many-body theoretical framework that enables us to simulate STS maps of strongly correlated molecules accurately [3]. Namely, we will introduce the concept of Dyson orbitals [4] to interpret ionic resonances in STS maps and natural transition orbitals [5] describing spin excitations in STS maps. Finally, we will discuss Kondo orbitals [6] to understand the origin of the spatial Kondo signal in high-spin molecules on metal surfaces.

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4:30pm **SS-MoA-13 Nanoscale Characterization of Metal-Supported Ultrathin Films Using Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**, ***Nan Jiang***, University of Illinois - Chicago

Metal-supported ultrathin films exhibit unique structural and vibrational properties governed by reduced dimensionality and strong interfacial coupling. Probing these properties at the nanoscale requires techniques that combine high spatial resolution with chemical specificity under well-controlled surface conditions. Here, we utilize ultrahigh vacuum (UHV) tip-enhanced Raman spectroscopy (TERS) to investigate model two-dimensional systems with sub-nanometer resolution.

Our measurements focus on ultrathin films grown on metallic substrates, such as two-dimensional materials and metal oxides. Borophene, a polymorphic two-dimensional boron phase, presents substrate-dependent lattice configurations and anisotropic vibrational responses. UHV-TERS enables identification of distinct vibrational modes associated with different borophene polymorphs and reveals nanoscale structural heterogeneity. In parallel, ultrathin iron oxide films serve as model oxide systems with thickness- and phase-dependent properties. TERS measurements resolve localized phonon modes and provide insight into spatial variations in oxidation state and coordination at the metal–oxide interface.

The UHV environment ensures clean surfaces and reproducible tip–sample junctions, allowing direct correlation between spectroscopic signatures and atomic-scale structure. These results demonstrate the capability of UHV-TERS to probe structure–property relationships in supported ultrathin films with unprecedented spatial resolution. This approach provides a pathway for nanoscale characterization of complex oxide and low-dimensional materials relevant to catalysis and surface science.

4:45pm **SS-MoA-14 Precision Force-Volume HR-AFM Reveals Single-Molecule Reactive Sites and Reactivity Landscapes Quantitatively***, **Percy Zahl**,* Brookhaven National Laboratory*; Xinzhe Wang,* Yale University*; Jara Trujillo-Mulero, Emiliano Ventura-Macias,* Universidad Autonoma de Madrid, Spain*; Yunus Dogan, Bugrahan Guner,* Yale University*; Rubén Pérez,,* Universidad Autonoma de Madrid, Spain*; Eric I. Altman, Udo D. Schwarz,* Yale University

Studying molecular interactions at surfaces is crucial for advancing catalytic technologies and addressing numerous challenges in materials science. While three-dimensional atomic force microscopy (3D-AFM), introduced in 2009 [1], enables measurements of tip–sample interactions with sub-angstrom spatial resolution and piconewton force precision, quantitative site-specific information on molecule–molecule interactions has thus far remained inaccessible. This limitation arises because the recovered total tip–sample force contains substantial contributions from the substrate (denoted F_1 and F_2 (see below) as well as from the back part of the tip (F_4), which typically dominate the measured interaction and obscure details in the force (F_3) of interest.

Here, we demonstrate a novel post-processing correction framework that removes these unwanted F_1, F_2, and F_4 contributions. Using the interaction between cobalt phthalocyanine (CoPc)—a prototypical CO_2 reduction catalyst deposited on Ag(111)—and a CO molecule attached to the tip apex, we isolate the CoPc–CO interaction force F_3. This approach reveals site-specific reactivity landscapes and their modulation through $–NH_2$ substitution. Our advance transforms 3D-AFM into a chemically specific and quantitative tool for probing interaction forces between complex molecules, achieving an accuracy previously accessible only through theoretical modeling.

[1] B. J. Alberset al.,Nature Nanotechnology 4, 307 (2009)

[2] Xinzhe Wanget al.,ACS Nano18, 4495 (2024)

Forces assuming a CO terminated metal tip:
F_1: substrate — tip [background]
F_2: background, CO — substrate [background]
F_3: molecule — CO [the one of interest]
F_4: metal apex of tip — molecule [the main enemy]

5:00pm **SS-MoA-15 Statistical Adsorption Mapping and 3D-AFM Characterization of Cobalt Phthalocyanine (CoPc) on Au(111)***, **Bugrahan Guner**, Yunus E. Dogan,* Yale University*; Percy Zahl,* Brookhaven National Laboratory*; Xinzhe Wang,* Oak Ridge National Laboratory, USA*; Eric I. Altman, Udo D. Schwarz,* Yale University

Molecule-substrate interactions play a critical role in molecular adsorption because local atomic registry, reconstructions, and related surface strain can influence where molecules adsorb, how they orient, and how strongly they interact with the surface. Au(111) is one of the most widely used model substrates for such studies, as it is chemically stable, atomically well-defined, and exhibits the characteristic herringbone reconstruction, which creates distinct fcc, hcp, domain-wall, and elbow/kink regions. Cobalt phthalocyanine (CoPc) is also a widely studied model molecule due to its relevance in substrate-supported molecular catalysis [1].

To examine how the reconstructed Au(111) surface guides CoPc adsorption, we employ low-temperature scanning tunneling microscopy to first identify the positions and orientations of individual adsorbed CoPc molecules, followed by a statistical analysis where molecules are assigned to specific reconstruction regions while considering their distance to the nearest elbow. This allows adsorption near elbows/kinks, along herringbone/domain-wall regions, and within fcc/hcp domains to be compared systematically.

This analysis is then connected to three-dimensional atomic force microscopy (3D-AFM) measurements, where frequency-shift data collected at different tip-sample distances are used to reconstruct local interaction forces between the sample and a tip functionalized by attaching a CO molecular to its apex [2-3], which yields complementary force-sensitive information on molecule-substrate coupling and chemically relevant interactions. Together, these approaches connect surface reconstruction, molecular organization, and local interaction forces, providing a framework for understanding how structured metal substrates influence molecular catalyst behavior.

References

[1] Y. Wu et al., Nature 2019, 575, 639.

[2] X. Wang et al., ACS Nano 2024, 18, 4495.

[3] M. Z. Baykara et al., Beilstein J. Nanotechnol. 2012, 3, 637.

5:15pm **SS-MoA-16 Energy-Resolved Low-Energy Electron Microscopy as a Quantitative Metrology for EUV Photoresist Films***, **Peter Sun**, Chang-Yong Nam, Jerzy Sadowski,* Brookhaven National Laboratory

Extreme ultraviolet (EUV) lithography drives photoresists toward thinner films, smaller features, and tighter line-edge roughness (LER), placing new demands on the characterization of resist behavior. Resist chemistry is governed by low-energy secondary electrons (<20 eV) generated from 13.5 nm photons, but transient surface charging shifts the effective landing energy throughout exposure, leaving film response at these energies unresolved by existing metrology.

We address this gap with charging-compensated low-energy electron microscopy and diffraction (LEEM/LEED) as a quantitative metrology platform for next-generation EUV resist films. Using 25 nm PMMA as a model system irradiated at 5–20 eV, we monitor the diffuse diffraction response and resolve the landing energy and surface potential. A conductance-based charging model extracts the total electron yield and dissipation parameters, enabling a dynamic electron-energy ramping scheme that locks the landing energy and turns LEEM/LEED into a controllable, energy-resolved metrology for resist films.

The energy-resolved method enables studies of resist-degradation performance and efficiency, including stochastic energy diffusion correlated with LER, and supports next-generation EUV and beyond-EUV resist development.

This research is supported by the U.S. Department of Energy Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. This research used resources (XPEEM/LEEM end station of the ESM beamline) of the Center for Functional Nanomaterials and the National Synchrotron Light Source II, which are the U.S. Department of Energy (DOE) Office of Science facilities at Brookhaven National Laboratory, under Contract No. DE-SC0012704.

5:30pm **SS-MoA-17 DFT Insights into Electronic Modulation of Cobalt Sites for N_2O Decomposition on Ni-Doped Spinel Oxides***, Hyung Chul Ham, **Chi Hun Lee**,* Inha university, Republic of Korea*; Su Keun Kuk, Jong-Min Lee, Hyuk Jae Kwon,* Samsung Advanced Institute of Technology, Republic of Korea

Nitrous oxide decomposition on transition-metal oxide surfaces is controlled by the adsorption and conversion of N_2O-derived intermediates, as well as by the ability of the surface to release oxygen. In this study, we use density functional theory calculations to investigate the surface reaction mechanism of N_2O decomposition on Co_3O_4(110) and $NiCo_2O_4$(110) spinel surfaces, which serve as representative models for oxidized shells formed on Co–Ni co-exsolved nanoparticles. Particular attention is given to how Ni incorporation modifies the surface reaction energetics and the electronic structure of Co-centered active sites.

Our calculations show that N_2O activation occurs near surface octahedral Co sites on both Co_3O_4(110) and $NiCo_2O_4$(110). The reaction proceeds through a bent trans-$N_2O_2^{2-}$ intermediate, consistent with experimentally observed hyponitrite-like surface species. Compared with Co_3O_4(110), $NiCo_2O_4$(110) stabilizes adsorbed N_2O more strongly and lowers the energetic penalty for forming the trans-$N_2O_2^{2-}$ intermediate. Transition-state calculations further show that Ni incorporation reduces the activation barrier for hyponitrite decomposition into N_2 and surface oxygen species. In addition, the subsequent O_2 formation step becomes more favorable on $NiCo_2O_4$(110), which can be attributed to weaker binding of surface oxygen species.

Electronic-structure analyses reveal that the improved reaction energetics originate from Ni-induced restructuring of Co-centered active sites. Ni incorporation modifies metal–oxygen covalency and stabilizes hybridized metal 3d–N 2p states involved in N_2O adsorption, as supported by projected density of states and crystal orbital Hamilton population analyses. In addition, surface octahedral Co sites exhibit a surface-induced spin-state change, suggesting that the spin-polarized electronic structure of these sites contributes to N_2O activation and intermediate conversion.

These results indicate that Ni-modified Co_3O_4 spinel surfaces enhance N_2O decomposition by simultaneously promoting N_2O adsorption, hyponitrite intermediate decomposition, and oxygen release. More broadly, this work highlights how surface composition and electronic structure, including spin-

state effects, can be tuned to design non-noble-metal oxide catalysts for greenhouse-gas decomposition.

Surface Science
Room 305 - Session SS-TuM

Dynamics

Moderators: Sara Mason, Brookhaven National Laboratory, **Dr. Zbynek Novotny**, Pacific Northwest National Laboratory

8:00am **SS-TuM-1 Hyperthermal Atomic-Oxygen Scattering Dynamics on Representative Satellite Surfaces**, ***Timothy Minton***, *Pedro Jorge,* University of Colorado Boulder **INVITED**

There is intense interest in the utilization of very low Earth orbit (VLEO, 100 – 350 km in altitude); a few missions in this region have been flown and more are planned. Despite the advantages of VLEO satellite operation (e.g., enhanced image resolution, faster data transfer rates, reduced development and launch costs, and straightforward demise scenarios), VLEO altitudes have long been avoided because of the high density and harsh oxidizing environment of the residual atmosphere. VLEO environments contain predominantly oxygen atoms and nitrogen molecules, which collide with ram surfaces on spacecraft at relative velocities of ~7.5 km s^{-1}. Momentum exchange between these atmospheric atoms/molecules and satellite surfaces results in an aerodynamic drag force on the vehicle. For VLEO operation, the drag is significant enough to require propulsion to counteract drag and maintain orbit, resulting in increased energy and also size (typically from solar panels and propellant storage) to operate the propulsion system. Increased size results in increased drag forces and the need for more energy and propellant, creating a vicious cycle. Beyond the clear necessity of minimizing drag for feasible flight in VLEO, the quantification of drag allows for orbital path determination and collision avoidance. Thus, minimizing and predicting drag are crucial for proliferated VLEO operation.

We have conducted molecular beam-surface scattering experiments with O atoms, traveling at orbital velocities of ~8 km s^{-1}, to investigate their inelastic scattering dynamics on several realistic and ideal material surfaces as a function of both polar (*q*) and azimuthal (*f*) scattering angles. The velocity and angular distributions of scattered O atoms depend strongly on the incident angle of the impinging atoms and the roughness of the surface in ways that are not *a priori* predictable. Using on the scattering dynamics data, a new gas-surface scattering model has been formulated, based on a washboard approach which uses a gamma function roughness model and a coupled Cercignani-Lampis (CL) model to describe the local atom-surface scattering dynamics. When parametrized to give the optimum fit to the molecular beam-surface scattering data, the model may be used for the determination of overall energy and momentum accommodation and for simulations of satellite drag.

8:30am **SS-TuM-3 Beyond the Binary Collision Approximation: Approximate Modeling of Low-Energy Impingement Events Using Classical Molecular Dynamics**, ***Carson Mize***, *Jörg Meyer,* Leiden University, Netherlands

Since their development in the 1970s, Binary Collision Approximation (BCA) models are widely applied tools to help validate ion and atom implantation processes on materials, such as deposition, diffusion, and damage in good agreement with experimental data at high incidence energies (> 1 MeV). BCA codes are practical and useful due to their computational efficiency to account for nuclear and electronic contributions to the stopping of the impinging particles, however, the approximations are expected to break down completely within the low energy regime (< 1 keV). Considering recent advances in molecular dynamic (MD) models commonly used in gas-surface dynamics, we aspire to answer the following two questions: 1) Do BCA models have any validity in the low energy regime? 2) Can we develop a classical-MD based model that still is computationally inexpensive for common applications with considerably improved accuracy?

To this end, we focus on bombarding a tungsten surface with low energy hydrogen atoms (5 – 100 eV) as a showcase system due to the availability of an EAM potential designed to model H absorption in W and the associated defects caused by H.[1] While our dynamical models based on a "grand-canonical"-like MD are still a work in progress due to the modeling challenge of accounting for energy dissipation to electrons and phonons, here, we mimic the respective approximations inherent to the BCA to reduce the model comparison into the respective binary and many-body approaches. Our additive MC calculations provide us with high resolution snapshots, allowing us to capture surface evolution effects like implantation and damage, which are typically neglected in BCA models. Additionally, the model establishes a framework for future improvements such as replacing electronic stopping with a more robust electronic friction description or additional ability to describe the evolution of the surface at increasing exposure.

References

[1] D. R. Mason, D. Nguyen-Manh, V. W. Linblad, F. G. Granberg, M. Y. Lavrentiev J. Phys.: Condens. Matter 2023, *35*, 495901.

8:45am **SS-TuM-4 Influence of Subsurface Oxygen on the Energetics of CO Oxidation on Planar and Stepped Rhodium Surfaces**, ***Dan Killelea***, Loyola University Chicago; *Tim Schäfer,* Georg-August Universität, Göttingen, Germany

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

I will discuss our observations of the influence of subsurface oxygen on CO oxidation on both Rh(111) and Rh(332) and how the velocity distributions of the product CO_2 shifts when O_{sub} is present. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

9:00am **SS-TuM-5 Unexpectedly Weak Vibrational Energy Transfer in O_2/Au(111) Collisions**, ***Igor Rahinov***, The Open University of Israel; *Itai Kallos,* Ben Gurion University Be'er Sheva, Israel; *Kerim Benfreha,* University of Goettingen, Germany; *Joshua Baraban,* Ben Gurion Uni. Be'er Sheva, Israel; *Tim Schäfer,* University of Goettingen, Germany; *Alexander Kandratsenka, Alec Wodtke,* Max Planck Institute for Multidisciplinary Sciences, Germany

Vibrationally inelastic scattering of molecules from metal surfaces provides a sensitive probe of electronically nonadiabatic energy transfer accompanying breakdown of the Born–Oppenheimer approximation. Previous studies established an intuitive semi-quantitative framework in which vibrational excitation and relaxation probabilities approximately scale with the energetic accessibility of transient electron transfer between molecule and metal. Within this framework, O_2 has long been an intriguing missing case: because of its high electron affinity, and the relatively small image-charge stabilization energy required for transient-anion-formation-driven vibrational energy transfer upon collision with Au(111), it should be among the strongest electronically nonadiabatic scatterers [1]. Yet this expectation could not be tested directly because effective quantum-state-resolved detection schemes for O_2 were not available.

Here we report quantum-state-resolved measurements of vibrational excitation in O_2(v = 0-->1) scattering from Au(111), enabled by a recently developed REMPI detection scheme for vibrationally excited O_2 [2]. Rotationally resolved detection of scattered O_2(v = 1) was achieved via two-color REMPI through the 3dπ Rydberg states, allowing direct determination of O_2(v = 0 → 1) vibrational excitation probabilities under direct scattering conditions.

Contrary to expectations based on electron affinity/work function considerations and trends established for NO, CO, and HCl scattering from noble metals [1], the measured vibrational excitation probabilities for O2/Au(111) are remarkably low. We discuss a physical picture in which O_2/Au(111) represents a frustrated strong-coupling system: although only modest image-charge stabilization is required to transiently access the anion formation, the repulsive interaction potential prevents the molecule from approaching sufficiently close to the surface for efficient electron-transfer-mediated vibrational energy uptake.

[1] I. Rahinov et al., Phys. Chem. Chem. Phys. 26, 15090 (2024).
[2] I.S. Kallos et al., J. Chem. Phys. 162, 051103 (2025).

9:15am **SS-TuM-6 High Temperature Annealing Dynamics and Surface Recovery of (3x1)-O Nb(100) Elucidated by Helium Atom Scattering**, ***Michael Van Duinen***, University of Chicago; *Cristobal Mendez, Tomas Arias,* Cornell University; *Steven Sibener,* University of Chicago

Superconducting radio frequency (SRF) cavities are the fundamental accelerating components of linear particle accelerators. Niobium is the material of choice for SRF cavities due to its high malleability, thermal conductivity, and superconducting critical temperature (T_C). Despite Nb having a T_C of ~9 K, the practical operating temperature of a Nb SRF cavity is ~2 K, below the boiling point of He and consequently quite expensive to operate. The improvement of Nb SRF cavities and the lowering of operating costs has focused primarily on the development of new materials on the Nb

surface. One of the primary limitations to both Nb SRF cavities and the new materials under study is the presence of a thermally stable and robust oxide. Understanding the formation, stability, and dynamics of the oxide and its effects on the operation of Nb SRF cavities requires study of atomic-scale surface material chemistry. Helium atom scattering (HAS) is a surface diffraction technique that has the ability to probe surface structure, bonding, and dynamics. The chemically inert He and an ultra-high vacuum (UHV) environment make HAS an ideal probe for the chemically reactive and sensitive Nb surface. High-temperature HAS studies have revealed that the (3x1)-O NbO phase that forms readily on Nb(100) is stable and intact for surface temperatures as high as 1100 K. This phase of the oxide forms readily from high-temperature dissolution of the Nb_2O_5 pentoxide phase and forms optimally when annealed at 1900 K. However, little is known about the dynamics of the formation of the (3x1)-O, annealing timescales, or the effectiveness of annealing temperatures below 1900 K. The studies presented seek to take an in-depth look at the recovery of (3x1)-O surfaces that have been sputtered to disorder. High-surface-temperature helium diffraction allows for a closer look in to the temperatures relevant to the recovery of the (3x1)-O surface from sputtered defects. High-temperature diffraction also reveals the kinetics and activation energy of (3x1)-O recovery. Auger and LEED further explore the extent that elemental composition and structure influence (3x1)-O recovery from sputtering. These studies overall strengthen our understanding of the dynamics of oxides on the Nb surface that will assist in the development of new materials formed on Nb SRF cavity surfaces.

9:30am **SS-TuM-7 Isotopic, Structural, and Surface Dependencies in Non-Equilibrium Gaseous Condensation***, **Francisco Lizano**, Elizabeth Jamka, Steven Sibener,* University of Chicago

Gas-surface interactions mediated by adsorption dynamics are key to many necessary formation reactions in both astrophysical and terrestrial environments. This dynamic process of gas molecules colliding with a surface and losing energy through adiabatic and non-adiabatic interactions, however, remains poorly understood, especially regarding the mechanisms that govern the energy exchange between the impinging molecules and the interface. Factors such as the kinematics of the incident molecules, molecular structure, and surface phonon density of states can affect the rate of condensation and molecular formation efficiencies. This is especially important within the interstellar medium (ISM), where reactions between gaseous species and dust grains or ice mantles are necessary to explain the chemical evolution and formation of molecules in the ISM. Accurate simulations of the chemical evolution of ISM environments require accurate binding energies and adsorption probabilities from experimental data. Discrepancies in the $^{12}C/^{13}C$ abundance ratio between the solar system and the ISM can possibly be attributed to mass-dependent adsorption or desorption of CO that leads to isotope fractionation. It has been shown that CO molecules are known precursors to many complex organic molecules detected in the ISM, the formation of which requires both gaseous CO and solid CO adsorbed onto a dust grain. Our work employs molecular beams to study the dynamics of gas-surface interactions and adsorption probabilities of a wide range of systems. In situ spectroscopic characterization of the surface via reflection-absorption infrared spectroscopy (RAIRS) coupled with the King and Wells mass spectrometry technique allows us to determine sticking probabilities of impinging molecules onto a well-characterized surface. This has allowed for the investigation of isotopic dependencies in non-equilibrium gaseous condensation for systems such as $^{12}CO_2/^{13}CO_2$ and $^{12}CO/^{13}CO$, as well as structural dependencies using isomers of butene, at a wide range of incident energies. Ongoing work is investigating the impact surface phonon modes have on the sticking of these molecules. Understanding the factors that influence the propensity of a gas molecule to adsorb to the surface will improve models of interstellar events and further our knowledge of non-equilibrium condensation in fields such as heterogeneous catalysis, thin film growth, and aircraft icing in cold environments.

9:45am **SS-TuM-8 Effects of Subtle Temperature Fluctuations on Surface Mobility of Atomic Steps and Oxidation Dynamics in High-Temperature Alloys***, **Shyam Patel**,* Brookhaven National Laboratory*; Chaoran Li,* Binghamton University*; Abdullah Al-Mahboob, Jerzy Sadowski,* Brookhaven National Laboratory*; Guangwen Zhou,* Binghamton University

In contrast to the traditional perspective that minute thermal fluctuations are inconsequential in surface dynamics, here we report the remarkable impact of subtle temperature changes on altering surface oxidation behavior. Using real-time low-energy electron microscopy imaging of the initial-stage oxidation process on NiAl(100), we investigate the interplay between minute temperature variations and surface reaction dynamics at the atomic scale. Our findings reveal that even minor fluctuations in temperature can exert significant influence on the dynamic process of oxide formation and surface mobility of atomic steps. Specifically, these nuanced temperature changes induce the nucleation of oxide islands, which subsequently locally pin the surface migration of atomic steps, leading to the lengthening of surface steps. Furthermore, our results demonstrate that persistent temperature variations have the ability to counteract the pinning effect imposed by oxides on the migration of atomic steps. These results underscore the profound effect of minute temperature changes in inducing significant alternations to surface reaction dynamics and highlight the critical importance of considering thermal fluctuations in understanding and dynamically manipulating surface processes.

11:00am **SS-TuM-13 Theoretical Investigation of the Adsorption and Diffusion of Co and Ni on Ceria***, Nusrat Jahan Rifat, Md. Saeedur Rahman, **Ye Xu**,* Louisiana State University **INVITED**

Transition metal nanoparticles supported on ceria are widely studied to catalyze technologically important reactions such as three-way catalysis, water-gas shift, and hydrocarbon reforming. There is ample evidence in the literature that base metals such as Co and Ni exhibit unique, superior catalytic activity when supported on ceria compared to other oxides. This is generally explained in terms of bifunctionality, interfacial effects involving metal-oxygen and metal-vacancy sites as well as charge transfer, and spillover / reverse spillover of surface species between the metals and oxide. Understanding the configuration and stability of nanoparticles of these catalytic metals on ceria is therefore of importance in heterogeneous catalysis.

We theoretically study and analyze the energy, geometry, and electronic configuration of Co and Ni clusters of up to several dozen atoms adsorbed on the $CeO_2(111)$ surface based on density functional theory (DFT) calculations. Furthermore, potential diffusion mechanisms of small Co and Ni species up to tetramers on $CeO_2(111)$ are investigated, and additional factors that enhance or hinder the diffusion of these metals on ceria are explored. The broad similarities and subtle differences between the two metals are revealed and discussed. The implications of the stability and diffusivity of the clusters to particle size distribution, stability, and growth are discussed in the context of mathematical and kinetic models. The totality of these findings is used to rationalize the findings of recent surface science studies, including STM and XPS, of Co and Ni deposited on model ceria thin film surfaces. Our work provides fundamental insights to the understanding of ceria-supported Co- and Ni-catalyzed reactions and guidance to improved catalyst design based on the Co- and Ni-ceria materials systems.

11:30am **SS-TuM-15 Stimulus-Driven Catalysis: Surface Reactions under Oscillatory Pressure Conditions***, Esteban Fornero,* Instituto de Desarrollo Tecnológico para la Industria Química, Argentina*; Gengnan Li,* Brookhaven National Laboratory*; Zubin Darbari, Eliseo Perez Gomez, Jay Shukla, Ignacio Vargas,* Brookhaven National Laboratory and State University of New York at Stony Brook*; Dario Stacchiola, Qin Wu, **J. Anibal Boscoboinik**,* Brookhaven National Laboratory

Periodic external stimuli provide a promising route for manipulating catalytic activity and accessing reaction pathways unavailable under steady-state conditions. Here, I present an in-situ experimental approach that combines synchronized pressure-wave perturbations with fast time-resolved spectroscopy to investigate catalytic dynamics on well-defined surfaces. Using CO oxidation on Pt(111) as a model system, we demonstrate how square-wave modulation of the CO partial pressure drives periodic changes in surface coverages and reaction kinetics. Infrared reflection absorption spectroscopy (IRRAS) and online mass spectrometry with millisecond time resolution directly track transient CO_2 production and reveal how controlled perturbations of the reaction environment can dynamically overcome CO poisoning. The measurements expose the formation of non-equilibrium surface states associated with enhanced catalytic turnover and provide direct insight into the coupling between gas-phase forcing and surface reaction dynamics. Beyond CO oxidation, this methodology is readily extendable to other catalytic systems and operando spectroscopic techniques, particularly to reactions governed by competitive adsorption processes where dynamic modulation of surface populations can strongly influence catalytic performance, reactivity, and selectivity.

11:45am **SS-TuM-16 Dynamic Metal–Support and Bimetallic Interactions in Ru Catalysts during Ammonia Decomposition***, **Soomin Kim**,* Korea Advanced Institute of Science and Technology, Republic of Korea*; Yujin Jeon,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Kwangjin An,* Ulsan National Institute of Science and Technology, Republic of Korea*; Mu-Hyun Baik,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Jeong Young Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Ammonia decomposition is a cornerstone of the green hydrogen economy, requiring highly active and durable catalysts. Ruthenium (Ru) is recognized as the most efficient catalytic candidate; however, its high cost, scarcity, and sensitivity to surface electronic structure necessitate precise optimization of Ru-based systems. To achieve this, fine-tuning the metal-support interface and surface composition is paramount. In this study, we investigate two distinct surface engineering strategies: leveraging facet-dependent Strong Metal-Support Interactions (SMSI) in Ru/TiO_2 and exploring bimetallic synergy in RuCo/MgO catalyst.

For Ru/TiO_2 catalysts, anatase TiO_2 supports exposing predominantly (101) or (001) facets were employed to regulate SMSI during ammonia decomposition. In situ ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and in situ DRIFTS reveal that NH_3 induces temperature-dependent formation of a TiO_x overlayer on Ru nanoparticles, accompanied by substantial modulation of Ru electronic states. The Ru/bipyramid-TiO_2 forms a thinner and partial TiO_x overlayer that preserves accessible Ru surface sites while generating an electron-rich Ru–TiO_x interfacial structure favorable for NH_3 dehydrogenation and N≡N recombination. In contrast, the Ru/nanosheet-TiO_2 undergoes more extensive encapsulation, resulting in reduced surface accessibility and lower catalytic activity. Complementary DFT calculations demonstrate that the oxide–metal interfacial sites lower the activation barriers for N–H bond cleavage through oxygen-assisted dehydrogenation pathways. In parallel, RuCo/MgO catalysts exhibit enhanced catalytic stability and reactivity arising from dynamic bimetallic surface interactions. The incorporation of Co modifies the electronic environment of Ru, stabilizing the surface ensembles under ammonia decomposition conditions and suppressing sintering while promoting NH_x activation and nitrogen recombination.

Our findings reveal that ammonia decomposition relies on dynamic surface and interfacial changes in Ru-based catalysts. In situ techniques uncover SMSI evolution, interfacial charge transfer, and bimetallic synergy, providing actionable design principles to optimize Ru-based catalyst efficiency for hydrogen production from ammonia.

12:00pm **SS-TuM-17 Vibrational Excitation in Plasma Catalysis: How Important Are Dynamical Effects?***, **Floris van den Bosch**, Jörg Meyer,* Leiden University, Netherlands

Plasma catalysis offers to be a promising alternative to current ammonia production processes, due to the combination of high selectivity of heterogeneous catalysis and efficient activation of nitrogen in the plasma. However, the theoretical understanding of how various plasma processes contribute to efficiency improvements remains limited. The pioneering work of Metha et al. [1] extended the standard formulation of transition state theory by making it vibrational state-specific through the use of the Fridman-Macheret α model [2]. The resulting microkinetic model accounted for vibrational contributions under the non-equilibrium conditions of a plasma reactor. In this work, we critically examine the prototypical chemical process of activated N_2 reactivity on ruthenium through explicit rate coefficient calculations using state-of-the-art molecular dynamics, based on a potential energy surface previously validated against molecular beam experiments. Our findings reveal that vibrational activation is significantly more effective in promoting surface reactivity than predicted by the Fridman-Macheret α model, which fails to capture the full complexity of state-specific contributions. Furthermore, our calculations indicate that vibrational activation is also the primary driver of highly activated thermal catalytic reactions. These results provide a valuable benchmark to guide the development of future state-specific microkinetic models for heterogeneous and plasma catalysis.

[1] Metha, P., et al. Nat. Catal., 2018. 1: p. 269-275
[2] Fridman, A. Plasma Chemistry. Cambridge University Press, 2008. ISBN: 978-0-521-84735-3

Surface Science
Room 305 - Session SS-TuA

Chemical Reactions

Moderators: Fang Xu, The University of Texas at San Antonio, **Prof. Ye Xu**, Louisiana State University

2:15pm **SS-TuA-1 Atomic-Scale Insights Into Reactivity and Excitations at Oxide Surfaces**, ***Camilla Ferreira de Sá Codeço,*** Federal University of Rio de Janeiro, Brazil **INVITED**

Oxide surfaces exhibit a strong interplay between local electronic structures, chemical reactivity, and collective excitations, governing processes relevant for catalysis, energy conversion, and infrared nanophotonics. In this work, we investigate how oxidation state, structural disorder, and local coordination affect both surface reactivity and light–matter interactions in model oxide systems.

The reactivity of transition-metal oxide surfaces was investigated considering CO_2 hydrogenation and hydroxylation conditions. On α-Fe_2O_3(012), near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) and low-energy electron diffraction (LEED) were used to correlate surface structure and Fe charge state with CO_2 activation pathways. Exposure of the reconstructed (2×1) surface to CO_2 + H_2 induces partial surface reduction and the formation of electronically enriched Fe^{2+} sites, which stabilize activated CO_2^- intermediates. Complementary studies on MnO(001) and Mn_3O_4(001) surfaces show that hydroxylation by water strongly depends on the oxidation state of surface Mn cations, with Mn^{2+} sites acting as active centers for hydroxyl formation. Together, these results demonstrate that oxide surface reactivity is directly governed by local electronic structure and cation valence.

Beyond surface reactivity, oxide interfaces also support collective excitations that are highly sensitive to local chemical environments. Using synchrotron infrared nanospectroscopy (SINS), we investigated surface phonon polaritons (SPhPs) in amorphous SiO_2 films after fluorine-ion irradiation. The dominant SPhP associated with the asymmetric stretching mode exhibits a pronounced reduction in intensity, revealing modifications in the local dielectric response induced by ion-generated disorder. Finite dipole model calculations indicate that the measured response originates from an effective medium composed of mixed SiO_2 and SiO_x regions, demonstrating how nanoscale chemical heterogeneity modifies polaritonic excitations at oxide surfaces.

Together, these results show how local electronic structure and chemical heterogeneity govern both catalytic activation pathways and confined light–matter interactions at oxide interfaces.

2:45pm **SS-TuA-3 In Situ AP-STM and AP-XPS Studies of CO_2 Activation on Oxide-Tuned PdIn(111) Surfaces**, ***Jiwon Park,*** Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *Jeongjin Kim,* Pohang Light Source II, Pohang University of Science and Technology (POSTECH), Republic of Korea; *Jeong Young Park,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

The catalytic conversion of CO_2 into value-added products, such as methanol, presents a promising strategy towards carbon neutrality. Palladium-Indium (Pd-In) intermetallic alloys have emerged as a highly selective and effective catalyst for CO_2 hydrogenation. However, their surface structures and interactions with CO_2 at the solid-gas interface require further understandings. In this study, the CO_2 activation pathways on the oxide-tuned PdIn(111) single crystal alloy surfaces were investigated in situ, using ambient pressure scanning tunneling microscopy (AP-STM) and synchrotron-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS).

Under ultra-high vacuum (UHV), the metastable PdIn(111) surface adopts unique surface structure consisting of clusters, atomic protrusions and ordered superstructure domains. Exposure to ambient pressure O_2 or CO_2 drives dramatic morphological transformations, as dissociated atomic oxygen triggers indium-selective oxidation, and upward segregation of InO_x. Such surface restructuring generates interfacial Pd-In-O_x nanostructures with defect-rich oxygen vacancies, serving as highly active sites for CO_2 activation and the formation of carbonate intermediates. In contrast, the elevated O_2 pressure and temperatures accelerate the dealloying of the Pd-In lattice and the growth of passivating indium oxide overlayer with significantly lower CO_2 activation capabilities.

These in situ observations provide fundamental insights into the active role of the metastable PdIn(111) intermetallic alloys surface in CO_2 activation. Furthermore, they demonstrate that precisely tuning the PdIn(111) surface oxide structures to maintain active interfacial sites is essential for the rational design of robust Pd-In intermetallic catalyst for CO_2 conversion.

3:00pm **SS-TuA-4 Growth, structure and surface chemistry of Pd/In surface alloys and InOx thin films on Pd(111)**, ***Aditya Patidar,*** *Om Amar Zavare, Shubham Ravan, Jason F. Weaver,* University of Florida

Growth, structure and surface chemistry of Pd/In surface alloys and InO_x thin films on Pd(111)

Thermo-catalytic conversion of carbon dioxide (CO_2) to methanol (CH_3OH) is important for mitigating CO_2 emissions and producing fuels and value-added products. Indium oxide (In_2O_3) has emerged as a promising catalyst for activating CO_2 and selectively converting it to methanol while suppressing competing reactions. Adding transition metals (TMs), such as Pd, improves catalytic performance, presumably by promoting efficient H_2 dissociation. Under reducing conditions and during CO_2 hydrogenation, TMs supported on In_2O_3 can transform into TM-In intermetallic compounds, giving rise to complex couplings between surface chemistry and coexisting metal and metal-oxide structures. These effects motivate fundamental studies using model systems.

In this talk, I will first discuss the structural evolution of Pd-In alloys grown on Pd(111) as a function of In coverage and temperature. Temperature-programmed X-ray photoelectron spectroscopy (TP-XPS) demonstrates that Pd-In intermixing produces In-rich surface alloy phases at room temperature and that the surface In concentration decreases with increasing temperature as In dissolves into the bulk Pd. XPS fitting identifies distinct Pd 3d and In 3d components associated with In-poor and In-rich Pd-In phases, whose compositional regimes correlate with the extent of Pd-Pd connectivity within the intermetallic structures. We further show that an ordered ($\sqrt{3} \times \sqrt{3}$)R30° surface alloy (Pd_2In) forms upon heating 2 ML In/Pd(111) to 600 K, while InPd(110) domains develop on an initial 6 ML In/Pd(111) surface between ~400 and 525 K.

I will also discuss the formation and structure of InO_x thin films on Pd(111), characterized using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). STM shows that InO_x film growth follows the Stranski–Krastanov mechanism, in which InO_x initially forms a well-connected wetting layer up to an oxide coverage of 1 ML (monolayer), after which multilayer InO_x islands develop. Both the wetting layer and thicker oxide islands exhibit (5 × 5) periodicity relative to Pd(111), characteristic of bixbyite In_2O_3(111). Lastly, I will discuss cooperative interactions between InO_x islands and the exposed Pd surface regions. XPS and TPD measurements show that H_2 dissociates readily on Pd domains, and that a substantial fraction of the resulting H-atoms migrates to neighboring InO_x domains, driving InO_x hydrogenation rather than recombinative H_2 desorption. These findings provide molecular-level insights into cooperative metal/oxide interactions to CO_2 hydrogenation chemistry.

3:15pm **SS-TuA-5 Activation and Selective Hydrogenation of CO_2 on Inverse MgO/Cu(111) Surface**, ***Arephin Islam,*** Brookhaven National Laboratory; *Jose Rodriguez,* Brookhaven National Laboratory and State University of New York at Stony Brook

Industrial CO_2 emissions remain a major driver of climate change, motivating the development of efficient capture and conversion materials. Magnesium oxide (MgO) is an earth–abundant, thermally stable oxide having the capacity of CO_2 capture and conversion, yet the role of nanoscale structure and metal–oxide interfaces in governing its reactivity remains insufficiently understood. Here, we investigate morphology–dependent CO_2 activation and hydrogenation pathways on MgO nanostructures supported on metal substrates using a combined experimental and theoretical approach. Scanning tunneling microscopy (STM), ambient–pressure X–ray photoelectron spectroscopy (AP–XPS), low–energy ion scattering (ISS), temperature–programmed desorption, and catalytic measurements reveal that sub–monolayer MgO clusters (0.3–1.8 nm) dispersed on CuO_x/Cu(111) are 4–5 times more reactive toward CO_2 than bulk MgO and enable selective hydrogenation to methanol at moderate temperatures (500–550 K). MgO forms nano–islands rich in low–coordinated sites at the oxide–metal interface, producing adsorption and activation patterns distinct from bulk MgO(001), Cu(111), or Cu_2O/Cu(111). Spectroscopy indicates hydroxyl formation during H_2 activation and carbonate–like CO_2 binding. Density functional theory (DFT) shows that while isolated MgO motifs enhance CO_2 and H_2 activation, they are limited in promoting complete CO_2 → CH_3OH conversion. In contrast, the MgO/Cu(111) inverse catalyst exhibits a substantially smoother reaction

landscape, with a highest barrier of only 0.98 eV compared to 1.49 eV on unsupported MgO clusters. The MgO–Cu interface stabilizes CO_2–derived intermediates and lowers hydrogenation barriers, enabling both strong CO_2 trapping and selective conversion. Together, these findings demonstrate that MgO nanostructuring on Cu creates cooperative interfacial sites that integrate efficient CO_2 activation with tunable reactivity, offering a promising route for sustainable CO_2 utilization.

4:00pm **SS-TuA-8 Interpreting Composition-Dependent Oxygen Vacancy Mechanisms in Layered Oxides Through Machine Learning Residuals and Electronic Structure Analysis***, **Sara E. Mason**,* Brookhaven National Laboratory **INVITED**

Layered transition metal oxides underpin a wide range of functional materials, including intercalation electrodes and oxide catalysts, where oxygen activity strongly influences stability, reactivity, and electronic behavior. Understanding oxygen vacancy formation across compositionally complex chemistries remains challenging due to the interplay between local coordination, electronic structure response, and redox behavior. Here, we investigate oxygen vacancy energetics across layered oxide chemistries using density functional theory (DFT), random forest tree (RFT) models, and electronic structure analysis.

RFT models successfully capture composition-dependent trends in pristine layered oxide formation enthalpies using physically motivated descriptors, demonstrating that bulk thermodynamic properties remain transferable across chemistries. In contrast, prediction accuracy decreases for oxygen vacancy formation energetics, where systematic residual patterns emerge as a function of both local coordination environment (LCE) and host composition. These structured residuals suggest that defect-driven redox behavior introduces mechanistic complexity not fully represented within generalized descriptor-based models.

To probe the origin of these deviations, we analyze charge redistribution following oxygen vacancy formation. Vacancy accommodation mechanisms vary significantly with composition and extend beyond purely local bonding effects. Ni-rich environments preferentially stabilize vacancies through metal-centered reduction and localized electron accommodation, whereas Mn-rich systems exhibit more heterogeneous redistribution pathways. Co-rich and electronically inactive cation environments suppress conventional transition-metal redox, promoting increased oxygen-centered or delocalized compensation behavior.

Together, these results demonstrate that oxygen vacancy energetics in layered oxides arise from a continuum of composition-dependent electronic response mechanisms that are fundamentally more complex than the pristine-state properties used to describe the host lattice. More broadly, this work highlights an important limitation of transferable ML models for complex oxides: while generalized descriptors can successfully predict bulk thermodynamic properties, defect-mediated redox processes depend sensitively on emergent electronic structure effects that require more mechanistically informed representations. These findings demonstrate how structured ML residuals can serve as physically meaningful indicators of unresolved chemical complexity, providing a pathway for integrating interpretable machine learning with physics-based electronic structure analysis.

4:30pm **SS-TuA-10 Adsorption of Carbon Monoxide on the r-cut Hematite Fe_2O_3(012)-(1×1) Surface***, **Moritz Eder**, Johannes Filzmoser, Faith J Lewis, Adam Vavrecka, Maosheng Hao, Tun Sinner, Florian Kraushofer, Margareta Wagner, Christian Schäfer, Jiři Pavelec, Florian Libisch, Gareth S Parkinson,* TU Wien, Austria

Understanding CO adsorption on well-defined metal oxide surfaces provides critical benchmark data for interpreting catalytic processes and infrared spectroscopy on complex powder materials. We present a multi-technique study of CO on the Fe_2O_3(012)-(1×1) r-cut surface, which has a structurally homogeneous array of equivalent Fe^{3+} and O^{2-} sites. Nevertheless, temperature-programmed desorption (TPD) reveals three distinct desorption peaks (58, 100, 125 K) despite the homogeneous surface. We attribute this finding to lateral repulsive interactions between CO molecules. Infrared reflection absorption spectroscopy (IRAS) shows blue-shifted CO frequencies relative to the gas phase (>2143 cm^{-1}) at low coverage that red-shift with increasing coverage. This is consistent with electrostatic interaction between CO and cationic Fe^{3+} sites. Light polarization-dependent measurements provide direct evidence for tilted CO orientation. Non-contact atomic force microscopy (nc-AFM) reveals protrusions consistent with adsorption atop surface Fe^{3+} sites, with distinguishable static and mobile CO populations. Our multi-technique approach establishes adsorption energetics, vibrational signatures, spatial ordering, and bonding geometry, providing a molecular-level foundation for interpreting complex powder catalyst systems.

4:45pm **SS-TuA-11 A Closer Look at Oxygen Reconstructions of Rh Single Crystals** *, **Elizabeth Serna-Sanchez**, Alexis Gonzalez, Dan Killelea,* Loyola University Chicago

Heavy transition metals such as Rh are commonly used for catalysis and have been heavily studied for oxidative reactions. The fundamental understanding of an oxidized Rh surface is widely investigated on low index single crystals however; limited information is available on the behavior of oxygen on high index surfaces. Using a bi-faceted Rh(111)/(322) crystal, we were able to analyze how oxidation of the two facets compared using scanning tunneling microscopy (STM) to characterize the reconstruction oxidation by surface defects and step width. Alongside with the STM, other techniques such as temperature programmed desorption, and low energy electron diffraction are used to identify the various species of oxygen present on the surface and the structures those oxygen species form.

5:00pm **SS-TuA-12 Desorption Characteristics of CO on Oxidized Rh Surfaces***, **Alexis Gonzalez**, Dan Killelea, Elizabeth Serna-Sanchez,* Loyola University Chicago

Heterogeneous catalysis plays an important role in energy production, environmental remediation, and chemical manufacturing, where reactions occur on solid surfaces. Understanding how oxygen interacts with catalytic metal surfaces is necessary for improving catalytic performance. In this study, we investigate oxygen adsorption on two Rh single-crystal surfaces: the flatRh(111) surface and a bifaceted surface with a flat (111) surface and a stepped (322) surface, which contains a high density of under-coordinated sites. Using Reflection Absorption Infrared Spectroscopy, different oxygen prepared surfaces were exposed to CO to examine how surface structure influences CO adsorption behavior. Comparisons between the two crystal single crystals revealed differences in CO vibrational peak positions, peak shifts, and relative intensities, suggesting the presence of distinct CO adsorption species. The results demonstrate that oxygen pre-coverage and surface morphology affect CO adsorption on Rh surfaces. This study provides understanding into structure sensitive adsorption behavior relevant to catalytic oxidation processes.

5:15pm **SS-TuA-13 CO on a Rh/Fe_3O_4 Single-Atom Catalyst: High-Resolution Infrared Spectroscopy and Near-Ambient-Pressure Scanning Tunnelling Microscopy***, **Nail El Hocine Barama**, Chunlei Wang, Panukorn Sombut, David Rath, Adam lagin,* Institute of Applied Physics, TU Wien, Austria*; Martin Ormos,* Department of Surface and Plasma Science, Charles University in Prague, Czechia*; Lena Puntscher, Faith Lewis,* Institute of Applied Physics, TU Wien, Austria*; Zdenek Jakub,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czechia*; Florian Kraushofer, Moritz Eder,* Institute of Applied Physics, TU Wien, Austria*; Matthias Meier,* Faculty of Physics and Center for Computational Materials Science, University of Vienna, Austria*; Michael Schmid, Ulrike Diebold,* Institute of Applied Physics, TU Wien, Austria*; Cesare Franchini,* Dipartimento di Fisica e Astronomia, Università di Bologna, Italy*; Peter Matvija,* Department of Surface and Plasma Science, Charles University in Prague, Czechia*; Jiri Pavelec, Gareth Parkinson,* Institute of Applied Physics, TU Wien, Austria

Infrared (IR) spectroscopy is one of the most powerful techniques in heterogeneous catalysis and remains the most widely used optical spectroscopy in the field. Its various experimental modes enable the investigation of a broad range of samples, from powders studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to flat single crystals examined by infrared reflection–absorption spectroscopy (IRAS or IRRAS). Owing to this versatility, IR spectroscopy is widely regarded as a bridging technique that connects fundamental surface science with applied catalysis.

In this work, we use a newly developed IRAS setup optimised for dielectric single crystals to investigate CO adsorption on the model single-atom catalyst Rh/Fe_3O_4(001).[1] Our spectra resolve three distinct Rh–CO species: monocarbonyls on isolated twofold-coordinated Rh adatoms, monocarbonyls on fivefold-coordinated Rh atoms incorporated into the surface, and gem-dicarbonyls on isolated twofold-coordinated Rh adatoms.[2] These assignments are established unambiguously by combining isotope-substitution experiments (^{12}CO, ^{13}CO, and mixed $^{12}CO/^{13}CO$) with precise control of Rh coverage and surface preparation. The interpretation is further supported by our previous SPM, XPS, and TPD studies, as well as DFT calculations.[3]

Under UHV conditions, monocarbonyls at Rh adatom sites are the predominant species. Gem-dicarbonyl formation is kinetically hindered, occurring primarily through CO-induced dissociation of Rh dimers rather than sequential CO adsorption on isolated adatoms. However, NAP-STM shows that the sequential adsorption pathway becomes accessible at millibar CO pressures, linking the behaviour observed under UHV to that expected under realistic reaction conditions. Although DFT provides qualitative insights, it does not quantitatively reproduce the experimental frequencies and is highly sensitive to the computational parameters, underscoring the need for robust experimental benchmarks. The spectroscopic fingerprints established here provide benchmark reference spectra for oxide-supported single-atom catalysts and a reliable basis for assigning Rh coordination environments in practical catalysts and for evaluating theoretical predictions.

1 D. Rath, *et al.*, *Rev. Sci. Instrum.*, 2024, **95**, 065106.

2 N. E. H. Barama, *et al*., https://arxiv.org/abs/2512.15194v2,.

2 C. Wang, *et al.*, *Angew. Chem. Int. Ed.*, 2024, **63**, e202317347.

5:30pm **SS-TuA-14 Well-Defined Cu-Delafossite Catalysts***, **Dario Stacchiola***,* BNL

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 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.

Surface Science
Room 305 - Session SS-WeM

Heterogeneous Catalysis

Moderators: Gengnan Li, Argonne National Laboratory, **Joerg Libuda**, Friedrich-Alexander-University Erlangen-Nürnberg (FAU)

8:00am **SS-WeM-1 Molecular Systems for Reversible Hydrogen Storage: Atomistic-Level Insights*, Swetlana Schauermann,*** Kiel University, Germany **INVITED**

Heterogeneous catalysts based on bimetallic single atom alloys (SAA) play a significant role in numerous technical processes. The fundamental working principles of these systems, however, remain poorly understood, especially the aspects related to the nanoscopic nature of bimetallic particles and the associated structure-reactivity relationships. In this study, we developed well-defined SAA catalysts consisting of Pd atomically dispersed in Cu nanoparticles prepared under ultra-high vacuum conditions on model Al_2O_3/NiAl(110) support.[1] Employing a unique combination of surface sensitive techniques – scanning tunning microscopy (STM), infrared reflection absorption spectroscopy (IRAS), molecular beams – and density functional theory (DFT) calculations, we performed detailed structural characterization of these systems at the microscopic level. We demonstrate that Pd disperses atomically in Cu nanoparticles and becomes partly negatively charged. Importantly, these Pd/Cu nanostructured systems show an outstanding catalytic performance in selective dehydrogenation of butanol and exhibit 100 % selectivity toward butanal over a broad range of Pd loadings – the property that cannot be reproduced employing simplified single crystalline Pd/Cu(111) counterparts.

In the second part, the catalytic decomposition of 2-propanol to acetone over Co_3O_4(111) catalyst will be addressed with the specific focus on the role of water and its derivatives in the reaction mechanism and the overall catalytic activity.[2] Pre-treatment of this catalyst with water at elevated temperatures (573 K) was shown to result in a substantial increase in the acetone formation rate. Combined STM and IRAS studies revealed that this procedure leads to the formation of isolated hydroxyls involving a lattice oxygen atom, which play a key role in H abstraction, both from molecular 2-propanol and from the propoxy reaction intermediate, leading to efficient formation of the target product acetone. Our results suggest that the isolated O_sH group is substantially more efficient hydrogen acceptor than the adsorbate-free lattice oxygen O_s.

1. *"Pd/Cu single atom alloys for selective alcohol dehydrogenation: from single crystalline to nanostructured model catalysts"*, P. A. Fredersdorff et al, Angew. Chem. Int. Edit. **(2026)** 65, e21885
2. *"Promoting role of isolated surface hydroxyls on selective dehydrogenation of 2-propanol to acetone over Co_3O_4 catalyst: a mechanistic study."*J. Smyczek et al, ACS Catalysis **(2025)** 15, 19268

8:30am **SS-WeM-3 When Interfaces Break Scaling: Metal–Ceria Catalysts for Selective Methane Conversion*, Maria Veronica Ganduglia-Pirovano, Pablo G. Lustemberg, Estefanía Fernández-Villanueva,*** Instituto de Catálisis y Petroleoquímica-CSIC, Spain

The selective activation of methane under mild conditions remains one of the central challenges in heterogeneous catalysis. Metal–oxide interfaces, particularly those formed between transition metals and ceria (CeO_2), provide a unique platform to control both activity and selectivity by coupling metal reactivity with the redox flexibility of the oxide support.

In this contribution, we present recent advances in the understanding and design of metal–ceria catalysts for methane conversion, combining DFT+U simulations with operando and in situ characterization (AP-XPS, XRD, XAFS) and catalytic testing. We show that low metal loadings (Ni, Co, Pt, Pd) on ceria generate highly active interfacial sites, where electron transfer to Ce 4f states stabilizes oxidized metal species, enabling methane activation at unusually low temperatures and efficient methane dry reforming under mild conditions. These systems deviate from conventional linear scaling relationships, demonstrating that nanostructured metal–oxide interfaces can overcome intrinsic activity–selectivity limitations.[1]

Building on this concept, we highlight recent results on the direct conversion of methane to methanol under mild conditions. In particular, PdAu/CeO_2 catalysts enable selective methane oxidation using water as the sole oxidant, achieving high methanol selectivity (~80% at 500 K). The alloy–oxide interface plays a decisive role: isolated Pd sites at the PdAu–ceria interface promote methane activation and water dissociation, while Au suppresses over-oxidation pathways leading to methanol decomposition. This synergistic interplay effectively tunes Pd reactivity, balancing activity and selectivity.[2]

These findings establish a unifying picture in which metal–oxide and alloy–oxide interfaces act as tunable active sites that decouple elementary steps and break traditional scaling constraints. This provides a rational framework for designing catalysts capable of selectively converting methane into value-added chemicals under technologically relevant conditions.

This work builds on a close and highly fruitful collaboration with José A. Rodriguez and his team at Brookhaven National Laboratory.

References

[1] Lustemberg, P. G. et al. *J. Phys. Chem. Lett.* **11**, 9131−9137 (2020)

[2] Fernández-Villanueva, E. et al. *Angew. Chem. Int. Ed.* **127**, e202505716 (2025)

8:45am **SS-WeM-4 Supported Ni-Cu Catalysts for the Selective Dehydrogenation of Liquid Organic Hydrogen Carriers*, Donna Chen, Nirmal Phuyal, Mengxiong Qiao, Biplab Budhathoki,*** University of South Carolina

Hydrogen is a promising source of clean and renewable energy, but a major challenge lies in its storage and transportation. The use of liquid organic hydrogen carriers (LOHC) enables hydrogen storage in organic molecules that are liquids at room temperature and therefore suitable for transportation through existing petroleum infrastructure. The methylcyclohexane (MCH) toluene pair has been used for the catalytic cycle of hydrogenation to store hydrogen and dehydrogenation to release hydrogen. While inexpensive and efficient catalysts are already available for hydrogenation, there is still the need for the development of selective dehydrogenation catalysts that inhibit deactivation due to carbon fouling. In this work, Cu-Ni clusters deposited on a rutile TiO_2(110) support are studied as catalysts for selective dehydrogenation. Methylcyclohexene (MCE) is used as a surrogate probe molecule to investigate the surface chemistry of MCE in ultrahigh vacuum since MCE adsorbs more strongly on Ni surfaces than MCH. Temperature programmed desorption (TPD) experiments for MCE on pure 2 ML Ni clusters show that nonselective decomposition to H_2 and surface carbon is the main reaction pathway; the evolution of CO at high temperature from the recombination of surface carbon and lattice oxygen from the titania support is used to quantify the extent of nonselective decomposition. In contrast, MCE reaction on 2 ML Cu clusters results in little overall dehydrogenation activity although a small amount of toluene is evolved. For 2 ML Ni clusters modified by the deposition of 0.25 ML of Cu, the amount of toluene produced is increased by a factor of 3 compared to pure Cu, but the extent of nonselective decomposition is still comparable to what is observed on pure Ni, indicating that Cu-Ni alloying and site blocking do not completely suppress MCE decomposition. However, the deposition of a small coverage of Ni (0.1 ML) on 2 ML Cu clusters results in 100% selectivity to toluene and a toluene yield that is seven times greater than on pure Cu. Increasing the Ni coverage to 0.25 ML lowers toluene production and leads to the initial onset of nonselective decomposition.The high toluene selectivity for the 0.1 ML Ni on 2 ML Cu clusters is attributed to the formation of a dilute alloy in which the Ni ensembles are not large enough to promote nonselective decomposition, but the desired reaction pathway of dehydrogenation to toluene is facilitated. These results demonstrate that controlling Ni ensemble size in Cu–Ni dilute alloys is an effective strategy for developing selective, coke-resistant dehydrogenation catalysts.

9:00am **SS-WeM-5 Surface Structure, Stability, and Catalytic Reactivity of Metal Nanoparticles Supported on Tantalum Oxide*, Ravi Ranjan, Francisco Zaera,*** University of California - Riverside

The surface structure, thermal stability, and catalytic behavior of copper (Cu) and platinum (Pt) nanoparticles (NPs) supported on tantalum oxide (TaO_x/Ta) thin films have been investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD), with carbon monoxide (CO) as the probe molecule.

Cu NPs were prepared by vapor deposition at room temperature and under ultrahigh vacuum (UHV) conditions, and characterized by following the adsorption of CO at 77 K. Increasing deposition of Cu led to the growth of nanoparticles exhibiting distinct adsorption sites associated with the metal-oxide interface and different Cu surface facets. The Cu NPs remained stable under both UHV and high-pressure CO environments over a broad range of

temperatures.

Pt deposition onto TaO_x/Ta resulted in the gradual formation of NPs with predominantly one major CO adsorption feature. In contrast to the case of Cu, Pt NP growth was less structurally distinct, as indicated by the CO vibrational signatures. Pt nanoparticles remained stable in UHV up to approximately 500 K, above which subsurface migration into the oxide support was observed.

The catalytic properties of the Pt/TaO_x/Ta surfaces were further examined using acrolein hydrogenation as a model reaction. Reaction studies under atmospheric pressures, using a so-called high-pressure cell to directly transfer the surfaces from UHV to the catalytic reactor, revealed the formation of propanal, propanol, and allyl alcohol, demonstrating competing hydrogenation pathways involving both C=C and C=O. These findings provide molecular-level insights into how nanoparticle structure, stability, and metal-support interactions influence catalytic selectivity and reactivity under catalytic conditions.

9:15am **SS-WeM-6 CO Oxidation on Plasma-Activated Pd and PdAg Surfaces**, ***Pablo de Oliveira***, *Camilla Codeço, Marcos G. Menezes,* UFRJ, Brazil*; J.Anibal Boscoboinik,* BNL

Plasma-assisted surface treatments offer an attractive alternative to conventional sputter/annealing cycles for surface cleaning and activation, particularly in alloyed materials where preferential sputtering or thermal segregation may alter the near-surface stoichiometry. Here, we investigate how sequential oxygen and hydrogen plasma cycles modify the surface chemistry and CO oxidation activity of Pd-based systems. By combining ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), ambient-pressure infrared reflection–absorption spectroscopy (AP-IRRAS), and density-functional theory (DFT) calculations, we compare the reaction pathways on a Pd foil and a PdAg alloy under near-ambient conditions. While both systems exhibit CO oxidation even slightly above room temperature (373 K), they reveal a dependence on the CO:O_2 composition. On Pd foil, CO oxidation is mainly observed under balanced feeds (p_{CO} = p_{O2}), whereas the PdAg alloy sustains activity even under oxygen-rich conditions (p_{O2} = 2 x p_{CO}). This enhanced tolerance is attributed to the formation of hydride-like Pd species during the in situ, room temperature hydrogen plasma. DFT calculations further confirm that hydrogen dissociation is energetically favored on the PdAg alloy compared to Pd foil. The presence of hydride prevents the formation of PdO layers, enabling alternative low-energy pathways for CO oxidation. These results demonstrate that sequential plasma treatments can do more than clean Pd-based surfaces, actively tuning the active sites that govern CO oxidation in alloy catalysts.

9:30am **SS-WeM-7 Catalysis with Liquid Gallium Alloys**, ***Christian Papp***, Freie Universität Berlin, Germany **INVITED**

Recently, Supported Catalytically Active Liquid Metal Solutions (SCALMS) were shown to surpass conventional alkane dehydrogenation catalysts in both activity and stability, due to their liquid nature and the presence of catalytically active single atom sites. SCALMS consist of a liquid metal matrix (Ga) that dissolves a catalytically active transition metal (Pt, Rh, Pd, Ni). Binary SCALMS systems are the subject of extensive research on the fundamental level with the aim to reach optimal performance.

Here, we present an operando NAPXPS study of the dehydrogenation of simple alkanes on gallium-platinum SCALMS (Supported Catalytically Active Liquid Metal Solutions) catalyst systems. As an industrially relevant test reaction, the dehydrogenation reaction of propane was used. In the study we compare the activity of oxidized GaPt SCALMS and liquid / metallic GaPt SCALMS surfaces, using Near-Ambient Pressure X-ray Photoelectron Spectroscopy. From the study, we conclude that the oxide shows a lower activity as compared to the metallic liquid GaPt SCALMS model systems. Further, the gallium matrix reduces under reaction conditions and coke residues disappear.

Our study thus underscores the practical value of NAPXPS in tracking surface changes and electronic states during catalytic reactions. By exploring these differences, the study sheds light on the role of oxides on the catalytic performance. These findings contribute essential insights for optimizing catalyst design and improving effectiveness, offering a pragmatic approach to catalytic enhancement.

Acknowledgement:

The research is funded by the DFG through SFB 1452 (Project number: 419654270).

11:00am **SS-WeM-13 Ni as a Promotor for Ethylene Epoxidation: Computation, Surface Science, and Reactor Studies**, ***Matthew Montemore***, Tulane University **INVITED**

Single-atom alloys have shown strong catalytic performance for several types of reactions, including hydrogenation reactions and alkane conversion. However, single-atom alloys have not been extensively studied for oxidation reactions, despite the critical importance of these reactions. The possibility that single-atom alloys could easily activate molecular oxygen but bind O relatively weakly makes them intriguing, as weakly bound O is likely to be quite reactive. In this work, we computationally designed single-atom alloys for oxidation, focusing on surfaces that can easily activate O_2 but give relatively weak O binding. We found several Ag-based single atom alloys that are predicted activate O_2 with very low barriers, in some cases near 0, while still binding O relatively weakly. In particular, NiAg stood out as a case with a very low barrier but relatively weak binding. Subsequent experimental synthesis and testing of single-crystal single-atom alloy surfaces shows that NiAg can activate O_2 and create relatively weakly bound O. Characterization with X-ray photoelectron spectroscopy, scanning tunneling microscopy, and temperature-programmed desorption gives strong fundamental insight into the interaction of these materials with oxygen and their state when exposed to oxygen and a reductant. Finally, NiAg nanoparticles were synthesized and tested, and show excellent performance for ethylene epoxidation. This work demonstrates the utility of integrated computational-experimental studies, and opens up the possibility of high-performance single-atom alloy catalysts for many oxidation reactions.

11:30am **SS-WeM-15 Tuning Oxygen Activation on Gold with RhAu Single-Atom Alloys**, ***Dennis Meier***, *Vinita Lal, E. Charles H. Sykes,* Tufts University

Selective oxidation reactions, such as olefin epoxidation and alkane oxidation, are large-scale industrial processes and are key to the more efficient conversion of natural gas into value-added products. Given the ongoing challenge of optimizing industrial chemical processes, there is a great need for highly selective catalysts. We investigated Au, which is known to be exceptionally selective for many oxidation reactions, but whose inability to efficiently activate O_2 limits reaction rates.

Density functional theory (DFT) predicted that small amounts of Rh guest atoms could overcome the low intrinsic activity of Au toward oxygen activation while preserving its high selectivity. We prepared RhAu single-atom alloys (SAAs), in which Rh atoms remain isolated in the Au surface, and probed their reactivity using a combination of temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). At comparable O_2 pressures and sample temperature, the RhAu systems show a significantly higher amount of Au-associated oxygen than clean Au, providing strong evidence that O_2 is activated at Rh sites and subsequently spills over onto the Au surface, which is the initial step for selective oxidation on Au. We further studied how the coordination environment of the guest atoms influences reactivity by comparing the (111) and (110) facets. The latter forms a (1×2) reconstruction that gives rise to undercoordinated surface sites. Using AP-XPS, we investigated the stability of RhAu SAAs at different temperatures and during exposure to CO and O_2. Together, these findings show that RhAu SAAs can overcome the low oxygen-activation activity of pure Au while retaining the potential for highly selective oxidation chemistry.

11:45am **SS-WeM-16 Reaction Product and Single-Atom Promotion of Acetylene Cyclotrimerization and Cross-Coupling on Ag(111)**, ***Nipun Kahagalla Dewage***, Tufts University*; Santu Biswas,* Tulane University*; Volkan Cinar, Dennis Meier,* Tufts University*; Matthew Montemore,* Tulane University*; Charles Sykes,* Tufts University

Benzene (C_6H_6) and toluene (C_7H_8) are irreplaceable chemical feedstocks used to produce pharmaceuticals, polymers, and materials. These aromatics are currently produced primarily through petroleum cracking and reforming processes, which require high energy input, harsh operating conditions, and lack full selectivity. As hydrocarbon feedstocks increasingly shift from oil to shale gas, alternative catalytic routes for the selective synthesis of aromatics are of significant interest. Acetylene (C_2H_2) cyclotrimerization is one promising pathway because it uniquely produces C_6H_6 with 100% selectivity on Ag(111). However, this reaction requires more than one monolayer (ML) of C_2H_2 on Ag(111) to initiate C_6H_6 formation, necessitating high reactor pressures that limit its practical applicability.

To understand and overcome this limitation, C_2H_2 cyclotrimerization on Ag(111) was investigated using Temperature-Programmed Desorption

(TPD), 12 K Scanning Tunneling Microscopy (STM), and Density Functional Theory (DFT). Coadsorption experiments with isotopically labeled benzene (C_6D_6) reveal that C_6D_6 promotes acetylene conversion to 20% at coverages of ≥0.6 ML. STM and DFT show that attractive C_2H_2-C_6D_6 interactions and increased molecular packing stabilize the key C_4 transition state involved in the rate-limiting step, making C-C coupling competitive with C_2H_2 desorption. In addition, coadsorption of C_2H_2 and propyne (C_3H_4) was examined to explore heterocoupling pathways for toluene (C_7H_8) formation. While coupling occurs at ≥1 ML total coverage with higher C_3H_4:C_2H_2 ratios, reaching a maximum at 1.5:1, C_6H_6 remains the dominant product (95%), with C_7H_8 forming only in minor quantities (5%). Guided by mechanistic insights from DFT, we further demonstrate that introducing chromium (Cr) dopant atoms into Ag(111) to form a Cr single-atom alloy dramatically alters the free energy landscape of C_2H_2 cyclotrimerization. This enables C_6H_6 formation at C_2H_2 coverages below 0.1 ML while maintaining the 100% selectivity of Ag(111) at Cr coverages ≤2%.

Together, these findings provide mechanistic insight into product-promoted C_2H_2 cyclotrimerization and C_2H_2-C_3H_4 coupling on Ag(111). They also demonstrate that CrAg(111) single-atom alloys can enable selective aromatic formation, offering a potential pathway for upgrading shale-gas-derived $C_{2,3}$ hydrocarbons into high-value aromatics without requiring high reactor pressures.

12:00pm **SS-WeM-17 Selective Hydrogenation of Styrene to Ethylbenzene Over a Pd/Cu(111) Single Atom Alloy Surface***, Mohammad Rahat Hossain, Michael Trenary,* University of Illinois - Chicago

Selective hydrogenation of alkynes and alkenes is central to industrial catalysis, yet direct spectroscopic identification of surface intermediates under realistic pressure conditions remains challenging. Here, we investigate styrene hydrogenation on a Pd/Cu(111) single-atom alloy (SAA) surface using polarization-dependent reflection absorption infrared spectroscopy (PD-RAIRS), Auger electron spectroscopy (AES), and kinetic analysis under ambient-pressure conditions. A 0.03 ML Pd/Cu(111) surface selectively hydrogenates styrene to ethylbenzene while suppressing aromatic ring hydrogenation. Time-resolved RAIRS measurements reveal the disappearance of styrene vibrational features at 909, 991, 1018, and 1637 cm^{-1} and the growth of ethylbenzene bands at 1033, 1066, 1329, 1385, and 1462 cm^{-1}, accompanied by aliphatic C–H stretching modes below 3000 cm^{-1}. A transient surface feature at ~1385 cm^{-1} is assigned to a benzylic σ-bound intermediate, consistent with β-selective hydrogenation of the vinyl group. Kinetic measurements show approximately first-order dependence on H_2 and near-zero-order dependence on styrene, supporting a Langmuir–Hinshelwood-type mechanism involving facile styrene adsorption and kinetically relevant hydrogenation steps. Repeated reaction cycles lead to carbon accumulation detected by AES, with carbon coverage increasing from ~45% to ~65%; however, catalytic activity persists despite the formation of a thin carbonaceous overlayer. These findings demonstrate that Pd/Cu(111) SAAs provide atom-efficient and highly selective hydrogenation catalysts while enabling molecular-level insight into hydrocarbon hydrogenation and carbon overlayer formation under elevated-pressure conditions.

Surface Science
Room 305 - Session SS-WeA

Somorjai

Moderators: David Castner, University of Washington, **Prof. Jeong Park**, Korea Advanced Institute of Science and Technology (KAIST)

2:15pm **SS-WeA-1 Professor Somorjai's Impact on the Evolution of Surface Science**, ***Miquel Salmeron***, Lawrence Berkeley National Laboratory **INVITED**

The surface of materials usually exhibits unique chemical and electronic properties determined by their atomic structure, which is largely determined by their interaction with the external phases of vacuum, gas, liquid or solids. The current scientific foundation of the field of Surface Science was the result of the work of several Pioneers of which Professor Somorjai was a prominent one, who provided new concepts on the role of the surface structure that determine their properties. andthe development of new instruments. In this review I will highlight the evolution of surface science in the last 40 years, and the important role of the development of new instruments and the discoveries they brought, to the scientific and engineering communities.

2:45pm **SS-WeA-3 Professor Somorjai's Impact on my Journey from Single Crystals to Biomaterials**, ***David Castner***, Depts of Bioengineering & Chemical Engineering

Surface science plays an important role in a wide range of research and development areas such 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 50 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. I am extremely grateful for the training I received during my PhD studies with Professor Somorjai as well as his continued mentorship and support throughout my career. This talk will discuss my adventures as a surface scientist starting from chemisorption and reactivity studies of small molecules on single crystal surfaces at UC Berkeley followed by industrial catalysis research at Chevron and eventually moving to biomedical surface analysis at the University of Washington. It has been an exciting journey and I will use it to provide some examples of the multidisciplinary nature of surface science embraced by Prof. Somorjai and his students, post-docs and staff. 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. However, even with the advances that have been achieved with these powerful surface science techniques, there 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.

3:00pm **SS-WeA-4 Surface Chemistry at the Sliding, Solid-Solid Interface**, ***Wilfred Tysoe***, University of Wiscosin-Milwaukee

Somorjai realized that the action of lubricants was inherently a surface science problem and, in 1995, was instrumental in launching Tribology Letters. The focus of the journal was to be on the science, rather than the engineering, of tribology, the study of friction and wear, and this is still its guiding principle today. Furthermore, the ultrahigh vacuum approach to understanding surface chemistry pioneered by Somorjai can be adapted to studying sliding-induced reaction pathways and this approach is illustrated here by studying a simple model tribochemical reaction consisting of the lubrication of copper by dialkyl disulfides. For example, this approach identifies a tribochemical reaction cycle, analogous to a catalytic reaction mechanisms, which includes shear-induced adsorbate decomposition and a mixing processes that causes adsorbates to be transported into the subsurface region to form a friction-reducing film. These model systems are sufficiently simple so that they are amenable to being analyzed using first-principle density-functional theory calculations that allow a deep understanding of the physical principles that underpin stress-induced reactions on surfaces to be obtained.

3:15pm **SS-WeA-5 Structural Evolution and Stability of Rh/TiO_2 Catalysts under CO_2 Hydrogenation Conditions**, ***Simon R Bare***, SLAC National Accelerator Laboratory; *Greg Barber,* Penn State University; *Xiaobo Chen, Judith Yang,* Brookhaven National Laboratory; *Robert Rioux,* Penn State University

At low temperatures (< 400°C), single atoms of Rh supported on rutile TiO_2 ($rTiO_2$) are responsible for the formation of CO during the reverse water gas shift (RWGS), while methane production is associated with the Rh-TiO_2 interface due to the observed correlation between methane formation rates and the volume-averaged Rh nanoparticle diameter.As the temperature is increased to >540°C, there is a notable increase in CO selectivity as the methane production rates tend towards zero.At 600°C and > 4 h time on stream, the catalytic behavior becomes completely agnostic to the initial Rh structure as well as weight loading, and the catalysts are highly selective for the RWGS reaction.Post-reaction HR-TEM image analysis confirms Rh nanoparticles crystallize/order during the reaction; at 400°C, most of the Rh particles are disordered, while at 600°C, they are more ordered. Infrared spectroscopy of CO adsorption on Rh nanoparticles supports the appearance of defined facets after annealing in nitrogen at high temperatures.will be referenced to the pioneering research of Gabor Somorjai in the 1980's where he showed the ability of Rh(111) surfaces and the Rh(111) terraces of stepped Rh single crystal surfaces to dissociate CO_2.

3:30pm **SS-WeA-6 Origins of Lipid Asymmetry in Supported Biomembranes**, ***Paul Cremer***, *Ruofei Wang, Ella Gregory,* Penn State University

Biological membranes show remarkable asymmetry in living systems. Phospholipids, such as phosphatidylethanolamine (PE) and phosphatidylserine (PS), primarily reside on the inner leaflet, while others, like phosphatidylcholine (PC) and sphingomyelin (SM), are more abundant on the outer leaflet. While maintaining this asymmetry in vivo requires significant energy from ATP-hydrolyzing enzymes, we show—using a novel lipid bilayer unzipping assay—that an uneven lipid distribution exists at equilibrium solely due to differences in the hydrogen-bonding environments between the leaflets. Specifically, a remarkable degree of asymmetry was generated using planar glass supports rich in hydrogen-bond acceptors that form stronger hydrogen bonds with PE and PS lipids than with water. Protein-coated substrates yielded nearly identical results. These findings have important implications for in vivo systems, where distinct hydrogen-bonding gradients naturally exist between the inner (cytoskeletal) and outer (glycocalyx) leaflets.

4:15pm **SS-WeA-9 Behavior of Cu-Pt Single-Atom Alloy Catalysts Under Realistic Conditions**, ***Francisco Zaera***, Dept. Chemistry **INVITED**

There has been some recent interest in the use of so-called single-atom catalysts, whereby one catalytic metal is isolated within a second to add a key but otherwise unavailable functionality, to control selectivity during the hydrogenation of organic reactants. We have recently shown that metal alloys consisting of Pt single atoms diluted within Cu nanoparticles selectively promote the hydrogenation of C=O bonds in unsaturated aldehydes, a reaction of interest in fine chemical manufacturing. Our rationale, that Cu surfaces may favor C=O over C=C hydrogenation steps with atomic hydrogen but may require Pt sites to promote the initial activation of molecular hydrogen, was corroborated by kinetic catalytic experiments. However, fundamental surface-science studies and quantum mechanics calculations showed a more nuanced picture. Specifically, IR titration experiments using carbon monoxide failed to identify Pt atoms accessible on the surface of the catalysts, suggesting that their catalytic contribution may involve indirect electronic changes on neighboring Cu atoms. Additional *in situ* x-ray absorption (XAS) data have indicated a preference for the Pt atoms to locate at the metal/support interface. DFT calculations also support the preference for the Pt atoms to be placed at the metal nanoparticle/silica boundary, and explain how they can still facilitate H_2 activation, remotely. These results have led us to reinterpret the way that single-atom alloy catalysts operate.

4:45pm **SS-WeA-11 Plasmonic Hot Carrier-Driven Catalytic and Photoelectrochemical Processes**, ***Jeong Y. Park***, Department of Chemistry, Republic of Korea

The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community. The earlier works in Berkeley indicate hot electron flow generated on a gold thin film by photon

absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance. In addition, it has been found that the hot electron flux generated under photon absorption and exothermic chemical reaction is the major mediator of energy conversion process [1-3]. In this talk, I highlight the research direction to attempt to detect the surface plasmon driven hot carrier at the nanometer scale by using scanning probe microscopy. To detect and utilize the hot electron flows at the macroscale level, the metal-semiconductor nanodiodes were constructed. At the nanometer scale, we utilized photoconductive atomic force microscopy to observe photoinduced hot electrons on a triangular Au nanoprism on n-type TiO2 under incident light. This is the direct proof of the intrinsic relation between hot electrons and localized surface plasmon resonance. We observed surface plasmon induced hot hole by using the system of Au nanoprism on p-type GaN [4]. I will discuss the impact of hot carriers in the photocatalytic activity under photoelectrochemical water splitting by using Au-based plasmonic nanostructures [5] an AuPd bimetallic nanoparticles [6]. Plasmon-driven hot carriers provide new mechanistic insight into light–matter interactions at catalytic interfaces and offers a pathway toward designing highly efficient plasmonic energy conversion systems.

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5:00pm **SS-WeA-12 2D Ising Model for Enantiomer Adsorption on Achiral Surfaces: L- and D-Aspartic Acid on Cu(111)***, **Andrew Gellman**,* Carnegie Mellon University, USA

The 2D Ising model is well-formulated to address problems in adsorption thermodynamics. It is particularly well-suited to describing the adsorption isotherms predicting the surface enantiomeric excess, *ees*, observed during competitive co-adsorption of enantiomers onto achiral surfaces.

Herein, we make the direct one-to-one correspondence between the 2D Ising model Hamiltonian and the Hamiltonian used to describe competitive enantiomer adsorption on achiral surfaces. We then demonstrate that adsorption from racemic mixtures of enantiomers and adsorption of prochiral

molecules are directly analogous to the Ising model with no applied magnetic field, i.e., the enantiomeric excess on chiral surfaces can be predicted using Onsager's solution to the 2D Ising model. The implication is that enantiomeric purity on the surface can be achieved during equilibrium

exposure of prochiral compounds or racemic mixtures of enantiomers to achiral surfaces.

Surface Science
Room 305 - Session SS-ThM

Reduced Dimensional Systems

Moderators: Dr. Rachael Farber, University of Kansas, **Prof. Nan Jiang**, University of Illinois - Chicago

8:00am **SS-ThM-1 Large Moiré Potential in a Weakly Interacting Organic/2D Material Heterostructure*, Oliver Monti,*** University of Arizona **INVITED**

Layered materials provide an exceptional platform for manipulating electronic states and spin properties, with examples ranging from the emergence of strongly correlated phases to exciton condensates and the appearance of multiferroicity. Key to these advances in creating a sandbox for materials “synthesis” is the concept of proximitization of two materials. Conventionally, this is achieved by few-layer heterostructures of 2D materials to create moiré potentials by lattice mismatch and twist angle. The depth of this potential is often restricted to some tens of meV. Achieving deeper moiré potential would enable the control of correlated phenomena to significantly higher temperatures, expanding the utility of moiré heterostructures and potentially revealing new phenomena. In this presentation, I will discuss how this can be achieved in a hybrid organic/van der Waals layered material heterostructure, with the case of C_{60}/T_d-WTe_2. We employ angle-resolved photoemission spectroscopy and scanning tunneling microscopy to reveal that the interface forms a quasi-periodic moiré potential owing to a lattice mismatch between C_{60} and T_d-WTe_2. The C_{60} rotational orientation on the surface establishes a quasi-periodic superlattice locked to the moiré pattern, which in turn modulates the molecular bandgap. This manifests as a moiré potential with an unusually deep modulation depth of 130(20) meV.

This discovery reveals a new path for creating highly tunable moiré heterostructures that lend themselves for creating flatband systems that may enable the study of correlated physics at elevated temperatures. The wide space of available organic molecules in combination with the growing library of 2D materials makes this a promising new avenue to pursue, with the potential to afford larger wavelength moiré structures with fewer defects than conventional 2D/2D heterostructures fabricated by exfoliation and transfer can provide.

8:30am **SS-ThM-3 Epitaxial Moiré-Graphene for Resonance Excitonic Energy Transfer in Moiré -Graphene-TMDC Heterostructures*, Abdullah Al-Mahboob,*** *Asish Kundu, Dario Stacchiola, Jerzy T. Sadowski,* Brookhaven National Laboratory

Two-dimensional (2D) quantum materials, specifically, Moiré-Graphene (MGr) and Van der Waals heterostructures (HSs) of quantum materials have attracted great interest because of their exotic quantum properties and having promises in novel optoelectronic and photonic applications. HSs made of stacking atomically thin layers of transition-metal dichalcogenides (TMDCs) allow us to manipulate the optical and spintronic properties. In TMDC HSs of monolayers having the resonance between dark excitonic states, recently, we observed unconventional energy transfer (ET) process massively enhancing photoluminescence (PL) and valley polarization (VP) [1]. In-order to elucidate underlying mechanism, we synthesized scalable epitaxial MGr (EMGR) in ultra-high vacuum system and fabricated HSs of WSe_2-hBN-EMGr in Ar-atmosphere. We employed in-situ, low-energy electron microscopy and X-ray photoemission electron microscopy (LEEM/XPEEM) for in-situ growth study and electronic/structural characterization of both EMGR and HSs, high-resolution ARPES for obtaining band-structure of EMGR and series of optical, microscopy and spectroscopy techniques for the study of the resonant excitonic exchange in HSs. The electronic band structure of EMGR revealed that the energy of optical transition between Moiré Dirac-cone to Van Hove Singularity states across M-point in EMGr has matching with resonance excitation energies in WSe_2. The observed optical data could be understood via vvacuum-fluctuation-mediated phonon-bypass mechanism suppressing non-radiative recombination of exciton and valley depolarization in Van der Waals HSs.

Research was carried out at the Center for Functional Nanomaterials and the National Synchrotron Light Source II at Brookhaven National Laboratory under Contract No. DE-SC0012704.

[1] Arka Karmakar, Abdullah Al-Mahboob, Natalia Zawadzka, Mateusz Raczyński, Weiguang Yang, Mehdi Arfaoui, Gayatri, Julia Kucharek, Jerzy T. Sadowski, Hyeon Suk Shin, Adam Babiński, Wojciech Pacuski, Tomasz Kazimierczuk, Maciej R Molas, Twisted MoSe2 Homobilayer Behaving as a Heterobilayer, Nano Lett. 24, 31, 9459–9467 (2024).

8:45am **SS-ThM-4 Can the Binding Energy of H_2O Admolecules on the Ice Ih(0001) Surface Exceed the Bulk Cohesive Energy?*, Jörg Meyer,*** Leiden University, Netherlands

The adsorption of water molecules on ice surfaces is of significant importance in many respects, in particular for gaining a deeper understanding of ice crystal growth. There is a wide distribution in the binding energy of the admolecule on the ice Ih surface due to the proton disorder, and previous theoretical calculations have indicated that it can even exceed the cohesive energy of the crystal at certain sites [1]. While the accuracy of those calculations has been contested [2] and direct measurement of these binding energy remains elusive, such strong binding sites have been tentatively brought up to rationalize experimental observations [3].Here, we study the adsorption of a water molecule on the ice Ih(0001) surface using recently developed polarizable many-body interaction potential functions [4,5], which provide high accuracy for a number of ice properties. We show that sites with binding energy larger than the cohesive energy are found on surfaces with a wide range of proton ordering. Although the binding energy is dominated by electrostatics, it is also significantly influenced by dispersion interactions. Furthermore, we show how the local environment at the binding site affects the binding energy, and propose a descriptor that serves as a predictor of the binding energy at a given site.[1] E. R. Batista and H. Jónsson, Comp. Mater. Sci. 20, 325 (2001).[2] C. Thierfelder, A. Hermann, P. Schwerdtfeger, and W. G. Schmidt, Phys. Rev. B 74, 045422 (2006).[3] M. Mehlhorn and K. Morgenstern, Phys. Rev. Lett. 99, 246101 (2007).[4] E. Ö. Jónsson, S. Rasti, M. Galynska, J. Meyer, and H. Jónsson, J. Chem. Theory Comput. 18, 7528 (2022).[5] G. R. Medders, V. Babin and F. Paesani, J. Chem. Theory Comput. 9, 1103 (2013); V. Babin, C. Leforestier and F. Paesani, ibid. 9, 5395 (2013); V. Babin, G. R. Medders, and F. Paesani, ibid. 10, 1599 (2014).

9:00am **SS-ThM-5 Templated Growth and Intercalation Pathways of Nickel Nanoclusters on Graphene/Ir(111)*, Shilpa Choyal,*** University of Illinois at Chicago*; Nan Jiang, Michael Trenary,* University of Illinois Chicago

Two-dimensional graphene moiré superlattices on transition-metal substrates provide periodic templates for organizing metal adatoms into size- and shape-controlled nanostructures with tailored catalytic and magnetic properties. Despite extensive studies of other transition metals, the growth and thermal evolution of nickel on graphene/Ir(111) have remained largely unexplored. Here, we report a comprehensive scanning tunneling microscopy (STM) investigation of Ni nanocluster nucleation, growth, and intercalation on the Gr/Ir(111) moiré superlattice under ultra-high vacuum.

At room temperature, Ni deposition produces well-defined triangular nanoclusters with edges aligned along the ⟨110⟩ direction of Ir(111), reflecting the templating effect of the moiré. Site-resolved STM analysis reveals strong selectivity: 77% of clusters nucleate at fcc regions, 23% at atop sites, and none at hcp sites — a preference attributed to local rehybridization of graphene toward sp^3-like bonding upon Ni adsorption. By comparing stepwise and continuous deposition, we identify two distinct growth regimes: continuous deposition produces uniform triangular islands with narrow size distributions, whereas stepwise growth yields broader, irregular morphologies governed by uphill diffusion, Ostwald ripening, and Ehrlich–Schwoebel barriers.

Annealing to ~900 K drives complete intercalation of Ni beneath graphene. STM reveals two distinct inverted moiré contrasts "round" and "clover-like" corresponding to site-selective Ni occupation within the supercell. The intercalated Ni grows pseudomorphically, adopting the Ir(111) in-plane lattice and preserving the original (10×10)/(9×9) moiré periodicity. The random spatial distribution of intercalated islands beneath an intact graphene monolayer, combined with Ni's strong C-binding affinity, supports an exchange-intercalation mechanism in which transient Ni–C bonding enables atom-by-atom penetration followed by graphene self-healing. Stepwise annealing up to 1500 K shows partial Ni desorption while the moiré remains intact.

These findings elucidate registry-controlled growth and demonstrate a viable route for fabricating low-roughness graphene-based heterostructures, with implications for spintronics, heterogeneous catalysis, and graphene-based device engineering.

9:15am **SS-ThM-6 Probing local structural variations in metal–organic framework thin films using nano-FTIR**, ***Tomoko Shimizu***, *Yukihiro Matsumoto, Kento Takenaka,* Keio University, Japan*; Hiromasa Sato,* Institute for Molecular Science, Japan*; Yuto Fujita,* Keio University, Japan*; Toshiki Sugimoto,* Institute for Molecular Science, Japan

Precise control over coordination structures and orientation is crucial for integrating metal–organic framework (MOF) thin films into functional devices.Structural defects, such as missing metal ions or unbound functional groups leading to incomplete coordination, can markedly impact the pore architecture and alter material properties. Therefore, techniques capable of probing local bonding states and defect distributions are essential for understanding and ultimately controlling structural irregularities in MOF films.

In this study, we employed infrared scattering-type scanning near-field optical microscopy (IR s-SNOM), which combines atomic force microscopy (AFM) with nano-Fourier transform IR spectroscopy (nano-FTIR), to definitively characterize local coordination bonding in a representative MOF thin film, NAFS-1, fabricated at the air/liquid interface and transferred to Si substrates[1].

Variations in structural features and nano-FTIR spectra revealed inhomogeneities in coordination bonding and orientation. In NAFS-1 prepared by the conventional method, which incorporated a water-rinsing step after each film transfer cycle, peaks attributed to uncoordinated carboxyl groups (COOH) were found to be distributed throughout the film,indicating incomplete coordination. In contrast, certain sparse features, such as particle-like aggregates and large, elevated features, exhibited enhanced coordination, as evidenced by the increased intensity of the carboxylate (COO^-) vibrational peaks. Notably, while omitting the post-transfer water-rinsing step increased structural inhomogeneities at the nanoscale, macroscopic spectroscopies, such as the transmission-mode FTIR and UV-Vis absorption spectroscopy, suggested more effective coordination and expanded conjugation.

Our findings emphasize the necessity of integrating nanoscale imaging with spatially resolved spectroscopy to identify the local crystallinity and orientation of MOF thin films. This approach provides a crucial framework for evaluating and optimizing the structural integrity of this class of materials, preventing misinterpretation of macroscopic data that would otherwise obscure irregularities due to averaging effects.

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9:30am **SS-ThM-7 Spatially Resolved Understanding of Electronic-Metal Support Interactions on Pristine and Defected Cu/TiO_2(110)**, ***Lindsey Penland***, The University of Kansas*; Hirushan Arachchige, Nadith Dissanayake,* The University of Kansas, Sri Lanka*; Rachael Farber,* The University of Kansas

Oxide-supported metal nanoparticle catalysts are commonly used in heterogeneously catalyzed chemical transformations due to their high selectivity, efficiency, and stability. There is a unique interplay between the metal nanoparticles and oxide support which results in strong metal support interactions (MSI). These MSI lead to observed changes in catalytic activity. Electronic metal-support interactions (EMSI), a subcategory of MSI characterized by electronic perturbations attributed to charge transfer across a metal/support interface, have a direct influence on the physicochemical properties of oxide supported metal nanoparticles. There are, however, several coexisting factors that can influence the degree of EMSI in a system such as the identity, size, and morphology of the nanoparticles and the Lewis acidity and oxygen defect density of the oxide support. Consequently, the coexisting nature of these factors makes it difficult to distinguish their respective effect on EMSI. As such, there is a need to develop a thorough understanding of the material properties leading to EMSI in a controlled and isolated way. In this work, insight into how the electronic landscape of a Cu/TiO2(110) model catalyst evolves as a function of EMSI was obtained through the use of low-temperature scanning tunneling microscopy (LT-STM) and spectroscopy (STS). It was found that the local density of states (LDOS) of clean rutile TiO2(110) has subtle variations in the valance region depending on the exact surface reconstruction of the TiO2(110) substrate. STM characterization post sub-monolayer Cu deposition highlighted variations in Cu morphology induced by thermal aggregation. LDOS measurements taken atop, near, and away from Cu particles show that electronic perturbations occur not only at the immediate metal/support interface but also extend into the near-interfacial region surrounding the Cu particles. Distinct variations in the LDOS perturbation radius and intensity suggest the degree of EMSI is correlated to nanoparticle size and morphology. These findings not only highlight how the presence and morphology of metal nanoparticles have direct influence on the electronic structure of the support but also opens the door to determining how electronic heterogeneity may play a role in heterogeneously catalyzed transformations. Ongoing and future work is focused on expanding these findings to structurally heterogeneous surfaces to understand how the inherent electronic heterogeneity of defected TiO2(110) influences the EMSI between Cu and TiO2(110).

9:45am **SS-ThM-8 Engineering Surface Confinement and Isolated Active Sites for Selective C–C Cleavage in Polyolefin Upcycling**, ***Wenyu Huang***, Iowa State University

Transforming polyolefin waste into uniform, high-value chemicals is a significant challenge in catalytic surface science. Most heterogeneous catalysts lack the necessary spatial control over polymer chain conformations, leading to statistical C–C bond scission and the formation of undesirable gases. This work demonstrates a catalyst design strategy that suppresses non-selective reactivity by integrating isolated transition-metal sites into structurally well-defined porous architectures. By manipulating the interplay between surface-active sites and nanoscale confinement, we create a catalytic environment capable of guiding long hydrocarbon chains through a processive mechanism. This design facilitates controlled adsorption and activation while utilizing geometric constraints to favor the production of liquid-range hydrocarbons over terminal scission products. We characterize the relationship between pore topology and catalytic selectivity, providing fundamental insights into how engineered surface environments can unlock new reactivity patterns. These findings offer a scalable framework for developing highly selective catalysts tailored for sustainable polymer upcycling and circular chemical manufacturing.

11:00am **SS-ThM-13 Structure and Electronic Properties of Two-Dimensional Iron-Based Oxides on Silver**, ***Lindsay R. Merte***, Malmö University, Sweden **INVITED**

Reduced dimensionality can stabilize oxide structures, coordination environments, and electronic states that differ substantially from those of bulk materials. Two-dimensional iron oxides grown on silver surfaces exemplify this, forming structures distinct from both bulk iron oxides and from strongly bound wetting layers observed on more reactive substrates such as platinum. In particular, a 2D-Fe_3O_4 phase forms with mixed Fe^{2+}/Fe^{3+} valence and both tetrahedral and octahedral coordination, analogous to bulk magnetite but composed exclusively of close-packed layers. Incorporation of cobalt or nickel is expected to modify the electronic structure and catalytic behavior of these oxides, making them attractive model systems for energy-conversion materials. Here we present structural and electronic characterization of pure and mixed Fe–Co and Fe–Ni two-dimensional oxide phases prepared by co-evaporation on Ag surfaces using STM, synchrotron XPS and NEXAFS, surface X-ray diffraction, and anomalous diffraction techniques. Complementary DFT calculations are used to explore the atomic structure and electronic properties of the observed phases. We further demonstrate anomalous surface X-ray diffraction measurements under ambient-pressure conditions, enabling element-selective structural characterization of these complex multicomponent 2D oxide phases during exposure to reactive environments.

11:30am **SS-ThM-15 A Multiscale Framework for Oxygen Adsorption, Surface Reconstruction, and Reactivity on Ag(111)**, ***Bright Daniel***, University of Tennessee Knoxville*; Braden Penuel,* University of Tennessee, Knoxville*; Carson Mize,* Leiden University, Netherlands*; Lonnie Crosby, Sharani Roy,* University of Tennessee Knoxville

Understanding oxygen behavior on Ag(111) is central to improving silver-based catalysts for ethylene epoxidation, yet capturing this behavior across realistic length and time scales remains a fundamental challenge. While density functional theory (DFT) provides atomic-level insight, its limited system size restricts direct exploration of coverage effects, subsurface oxygen formation, and surface reconstruction under catalytic conditions.

In this work, a multiscale framework was developed to bridge this gap by integrating DFT, lattice-gas modeling, and Monte Carlo (MC) simulations. First, DFT calculations were used to systematically study oxygen adsorption on Ag(111), including adsorption energetics, coverage-dependent surface saturation, subsurface oxygen formation, and pairwise interaction energies. The computed trends were consistent with experimental observations and prior theoretical studies, providing a reliable foundation for model development.

These DFT-derived interactions were then used to construct a lattice-gas model, enabling efficient exploration of large surface models beyond DFT-

accessible scales. Monte Carlo simulations in both canonical (NVT) and grand canonical (μVT) ensembles were employed to probe oxygen adsorption behavior as a function of temperature and chemical potential. This approach captures coverage-dependent ordering, subsurface incorporation, and thermodynamic stability of oxygen populations. Building on this framework, the model was extended to investigate surface reconstruction by incorporating Ag–Ag and Ag–O interactions. Co-adsorption of oxygen and silver adatoms reveals emergent restructuring phenomena driven by oxygen coverage and local coordination environments, providing insight into dynamic surface evolution under reaction-relevant conditions. Finally, configurations derived from these studies were used to examine ethylene epoxidation pathways with and without chlorine promotion, linking surface structure directly to catalytic performance.

Overall, this work establishes a unified, physics-based framework that connects atomistic energetics to mesoscale surface behavior, offering a pathway to rationally design and control catalytic surfaces under realistic conditions.

11:45am **SS-ThM-16 Atomic-Scale Study of Boron Nanostructure Growth on Platinum***, **Nozomi Shirato**,* Argonne National Laboratory

Low-dimensional boron nanostructures have attracted significant attention due to their intricate structural polymorphism, unique electronic states, and catalytic relevance. Despite growing interest, the growth mechanisms governing boron nanostructure formation on metal substrates remain poorly understood. Here, we investigate the growth of boron on an Pt(111) single crystal surface, aiming to understand the complex interplay between surface geometry, boron-boron interactions, and boron-platinum binding that collectively drives polymorph selection and structural evolution. Low-temperature scanning tunneling microscopy (LT-STM) is employed to characterize the intricate surface structures at atomic resolution, revealing the detailed morphology of the resulting nanostructures. X-ray photoelectron spectroscopy (XPS) measurements provide insight into the chemical states of boron and its bonding conditions with the substrate. Combined, the techniques reveal structural and chemical states of boron growth on Pt(111) and lay the groundwork for tailoring boron nanostructures for catalytic applications.

12:00pm **SS-ThM-17 Differentiable Multivariate Curve Resolution for X-Ray Absorption Spectroscopy***, **Changhae Kim**, Jennifer Bjorklund, Brian Lee,* Brookhaven National Laboratory*; Esteban Fornero,* Instituto de Desarrollo Tecnológico para la Industria Química, Argentina*; Dario Stacchiola, Xiaohui Qu, Sara Mason,* Brookhaven National Laboratory

Time-resolved *in situ* X-ray absorption spectroscopy (XAS) is a premier technique for probing atomic structure and reaction dynamics. Deconvolving spectral sequences into invariant components and relative concentrations can draw direct connections between spectroscopic data and chemical kinetics. However, chemically meaningful deconvolution remains challenging. Multivariate curve resolution (MCR) is widely used for this purpose, but conventional implementations offer limited flexibility for incorporating prior knowledge. Here, we present a differentiable optimization framework inspired by machine learning fields that enables simultaneous regression of spectra and concentration profiles, with flexible, chemically informed constraints. We demonstrate this approach on XAS measurements of redox reactions at the $CuGaO_2$ (011) surface. The method can isolate small surface signals from the dominant bulk contributions and can distinguish catalytically active species by leveraging coupled multi-species kinetics, capabilities which are challenging to achieve with conventional approaches. In addition, preprocessing with a blind-spot denoising network can improve robustness. These results highlight the potential of differentiable MCR for analyzing complex, multi-dimensional spectroscopic data.

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.

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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.

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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.

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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**

Surface Science
Room Ballroom A - Session SS-ThP
Surface Science Poster Session

SS-ThP-1 Development of Machine-Learned Models for Understanding Oxygen Adsorption on Silver Surfaces, ***Bright Daniel***, University of Tennessee, Knoxville; *Carson Mize,* Leiden University, Netherlands; *Lonnie Crosby, Sharani Roy,* University of Tennessee Knoxville

The interaction of atomic oxygen with silver surfaces plays a critical role in surface oxidation, oxygen-induced restructuring, and selective oxidation catalysis such as ethylene epoxidation. Capturing these phenomena across multiple adsorption environments, coverages, and subsurface regions using density functional theory (DFT) alone remains computationally prohibitive. In this work, machine-learned (ML) adsorption models were developed to accelerate and extend the study of oxygen adsorption on Ag(111) surface using periodic DFT datasets spanning surface and subsurface adsorption configurations across multiple oxygen coverages.

Coverage-aware SchNetPack models were trained to predict adsorption energetics with near-DFT accuracy at substantially lower computational cost. The optimized models achieved low RMSD values (0.047 eV/O) and strong generalization performance ($R^2 > 0.95$), while successfully capturing coverage-dependent stabilization, subsurface oxygen incorporation, and complex local and nonlocal oxygen interactions. Hyperparameter optimization, reproducibility testing, and learning-rate scheduler benchmarking were systematically performed to improve model robustness and transferability. Beyond the default ReduceLROnPlateau scheduler, additional learning-rate schedulers were implemented directly within SchNetPack workflows, with cosine annealing scheduling reducing RMSD by approximately 74–82% relative to alternative approaches.

In parallel, pretrained MACE foundation models were evaluated as transferable machine-learned interatomic potentials (MLIPs) through direct inference on DFT-generated O/Ag (111) configurations without additional retraining. Notably, the OC20-trained multi-head MACE variants demonstrated superior transferability and predictive performance relative to general-purpose MACE-MP models, highlighting the importance of surface-chemistry-focused pretraining for catalytic adsorption applications. These results demonstrate the promise of physically informed DFT–ML frameworks for scalable modeling of surface and subsurface oxygen chemistry relevant to catalytic surface science and rational catalyst design.

SS-ThP-2 Chemically Programmable Hole Migration on TiO2(111) Revealed by Time-Resolved Atomic Force Microscopy, *Nuray Basaran, Mohammad Safikhani-Mahmoudi,* École de technologie supérieure, University of Quebec, Canada; *Bugrahan Guner,* Yale University; ***Omur E. Dagdeviren,*** École de technologie supérieure, University of Quebec, Canada

Charge migration in metal-oxide semiconductors is often treated as a thermally activated process controlled by fixed energetic barriers. However, reactive oxide surfaces can reorganize carrier transport through facet-dependent defect chemistry, irradiation history, and adsorbate-mediated charge transfer. Here, we use time-resolved atomic force microscopy (TR-AFM) to directly probe hole-migration dynamics on single-crystal rutile TiO_2(111), a highly reactive facet relevant to photocatalysis and surface redox chemistry. Measurements were performed as a function of temperature under pristine conditions, after high-energy ultraviolet (UVC) irradiation, and following exposure to ethanol or methanol.

The temperature-dependent relaxation dynamics reveal that pristine TiO_2(111) does not follow a conventional positive activation barrier. Instead, the surface exhibits an apparent negative effective migration barrier of −313 ± 40 meV in the dark. UVC irradiation shifts this value to −55 ± 8 meV, indicating that photoinduced surface oxygen vacancies reorganize the carrier-defect landscape rather than simply accelerating a fixed migration pathway. Alcohol adsorption further reshapes the response. Ethanol preserves a negative-barrier regime that is nearly insensitive to UVC irradiation, with barriers of −123 ± 8 meV in the dark and −114 ± 11 meV under UVC. Methanol produces a stronger negative-barrier response, changing from −208 ± 21 meV in the dark to −263 ± 42 meV under UVC. These results show that methanol and ethanol, although often treated as comparable hole scavengers, are dynamically distinct modifiers of hole migration on TiO_2(111). The negative apparent barriers indicate that the measured relaxation dynamics are not governed by simple thermally activated hopping, but by coupled migration, trapping, detrapping, and temperature-dependent redistribution among surface and near-surface defect states. More broadly, this work establishes TiO_2(111) as a dynamically distinct metal-oxide surface whose charge-transport behavior cannot be inferred from TiO_2(100). The results demonstrate that charge migration in TiO_2 can be programmed through facet selection, high-energy irradiation, and adsorbate chemistry, providing a surface-science framework for engineering carrier dynamics in photocatalytic and photoactive oxide materials.

SS-ThP-3 Controlling Catalytic Surface Chemistry and Interfacial Water Transport in CO-Based Oxidative Carbonylation, ***Yeonsong Lee,*** KITECH, SKKU, Republic of Korea; *Min-zy Kim,* KITECH, Republic of Korea; *Ji Man Kim,* Sungkyunkwan University (SKKU), Republic of Korea; *Tae Yong Kim,* KOREATECH, Republic of Korea; *Yong Jin Kim, Jayeon Baek,* KITECH, Republic of Korea

The oxidative carbonylation of alcohols with CO and O_2 is an attractive phosgene-free route for producing dialkyl carbonates, but the reaction is strongly affected by the local liquid–solid reaction environment. In the synthesis of bis(2-methoxyethyl) carbonate (BMEC) from 2-methoxyethanol (MEG), water is formed as a by-product and limits equilibrium conversion. In addition, selenium-based catalytic species can undergo structural and chemical changes during continuous operation, including formation and leaching of soluble selenium–carbonyl species. These coupled issues indicate that control of both catalytic surface chemistry and interfacial mass transport is required for stable liquid-phase carbonylation.

In this study, we developed a recirculating packed-bed membrane reactor that combines a Se/Al_2O_3 catalyst bed with a hydrophilic LTA zeolite membrane supported on tubular α-Al_2O_3. The reactor was designed to regulate the liquid-phase catalytic environment by selectively removing water while retaining MEG, BMEC, and selenium-containing species within the recirculating phase. The LTA membrane provided water-selective transport through strong hydrophilicity and molecular sieving, whereas the recirculation configuration reduced net selenium loss from the catalytic zone. Thus, the membrane functioned not as a downstream separator but as an interfacial component that continuously modified the reaction environment during carbonylation.

The membrane showed preferential water permeation in H_2O/MEG and H_2O/BMEC mixtures, with effective retention of organic reactants and products. Molecular dynamics simulations using a machine-learned interatomic potential indicated that water molecules could enter the LTA pore structure, whereas MEG and BMEC were hindered near the pore entrance. Under CO/O_2 oxidative carbonylation conditions, in-situ water removal increased MEG conversion and BMEC selectivity compared with a conventional fixed-bed reactor. The effects of temperature, pressure difference, solvent dilution, and liquid flow rate showed that membrane performance was governed by water activity, concentration polarization, and interfacial mass transfer.

These results demonstrate that CO-based oxidative carbonylation can be improved by controlling both catalytic surface chemistry and interfacial molecular transport. By coupling selenium-mediated carbonylation with water-selective zeolite transport, this study provides a surface-science-based strategy for regulating the local reaction environment in liquid-phase heterogeneous catalysis.

SS-ThP-4 Revisiting MOF-Based Encapsulation for CO_2 Hydrogenation to Methanol: Metal–Oxide Interface Design in Cu-Based Catalysts, ***Yerin Lee,*** Korea Institute of Industrial Technology, University of Science and Technology, Republic of Korea; *Yesub Keum,* Korea Institute of Industrial Technology, Republic of Korea; *Vu Nguyen,* Korea Institute of Industrial Technology, University of Science and Technology, Viet Nam; *Huiwon Jung,* Korea Institute of Industrial Technology, Konkuk University, Republic of Korea; *Yong Jin Kim, Jayeon Baek,* Korea Institute of Industrial Technology, University of Science and Technology, Republic of Korea

Metal–oxide interfaces are critical in CO_2 hydrogenation to methanol because they govern CO_2 activation, hydrogenation of surface intermediates, and the oxidation state of Cu active sites. In our previous work with Prof. Gabor A. Somorjai, Cu nanocrystals encapsulated in the Zr-based metal–organic framework UiO-66 showed enhanced methanol formation and high methanol selectivity. This behavior was attributed to strong interaction between Cu and the Zr-oxide secondary building units of UiO-66, indicating that MOF-derived oxide clusters can act as chemically active interfacial promoters rather than simple porous supports.

Here, we revisit this MOF-based encapsulation concept by designing a MOF-derived Cu–oxide hybrid catalyst for CO_2-containing C1 gas hydrogenation. An oxide-containing framework was constructed around Cu nanoparticles to increase metal–oxide interfacial contact while maintaining accessibility of reactants to Cu-based active sites. This architecture was designed to retain the advantages of encapsulation while introducing reducible oxide domains near Cu, which can contribute to CO_2 activation, intermediate stabilization, and methanol formation.

The structure and composition of the catalyst were examined by X-ray diffraction, inductively coupled plasma analysis, and scanning electron microscopy with elemental mapping. Continuous-flow hydrogenation of CO_2-containing C1 gas was conducted and compared with a conventional $Cu/ZnO/Al_2O_3$ catalyst. The MOF-derived Cu–oxide hybrid catalyst showed promising methanol formation activity, suggesting improved utilization of interfacial Cu sites. These results indicate that rational construction of Cu–oxide interfaces can be an effective strategy for enhancing methanol synthesis from CO_2-containing C1 gas streams.

This work connects the earlier Cu⊂UiO-66 encapsulation strategy with a new MOF-derived interfacial catalyst design. By revisiting MOF-based encapsulation from a surface and interface perspective, this study provides a route for developing Cu-based catalysts in which metal–oxide contact, redox functionality, and active-site accessibility are controlled for CO_2 hydrogenation to methanol.

SS-ThP-5 Plasmonic TiN/$BiVO_4$ Photoanodes for Enhanced Photoelectrochemical Water Oxidation, ***Minseok Lee***, *Hyewon Park,* Korea Advanced Institute of Science and Technology, Republic of Korea*; Dae Han Wi,* Chungnam National University, Republic of Korea*; Jeong Young Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Photoelectrochemical (PEC) water oxidation on $BiVO_4$ photoanodes is limited by inefficient charge transport, recombination, and sluggish surface reaction kinetics. Localized surface plasmon resonance (LSPR)-based strategies can address these limitations by enhancing light harvesting and enabling hot-carrier and photothermal energy conversion.[1] Here, titanium nitride (TiN) nanocubes were introduced onto $BiVO_4$ as refractory plasmonic components to promote hot electron transfer and local photothermal effects. TiN combines metallic conductivity, chemical/thermal robustness, and broadband visible-to-near-infrared absorption, making it a promising alternative to noble-metal plasmonic nanostructures.[2] TiN/$BiVO_4$ photoanodes with different TiN loadings were examined using structural, optical, and vacuum-based surface-sensitive analyses, and their PEC performance was evaluated under simulated solar illumination. Scanning electron microscopy and elemental mapping confirmed TiN integration on $BiVO_4$. UV–vis absorption showed enhanced broadband absorption, suggesting a TiN-derived broad plasmonic feature.X-ray photoelectron spectroscopy identified an ultrathin TiO_xN_y/TiO_x surface layer on TiN, indicating surface oxidation/passivation. PEC measurements showed loading-dependent photocurrent enhancement, with optimized TiN/$BiVO_4$ outperforming pristine $BiVO_4$. Incident photon-to-current efficiency, wavelength-selected chopped chronoamperometry, and electrochemical impedance analysis suggest that the enhanced response isassociated with local photothermal effects and hot electron transfer from broadband TiN plasmonic absorption, along with reduced surface charge-transfer resistance. These results provide insight into designing refractory plasmonic photoelectrodes that efficiently transfer plasmonic energy to semiconductor materials for PEC water splitting.

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SS-ThP-6 Surface Electronic Modulation in Au-Based Bimetallic Nanostructures for Photoelectrocatalysis, ***Dasol Kim***, *Hyosun Lee,* University of Seoul, Republic of Korea

Abstract

Bimetallic nanostructures have received considerable attention in catalysis because the integration of distinct physicochemical properties of different metallic constituents enables catalytic functionalities beyond those attainable with monometallic systems. In this regard, Au-based bimetallic nanostructures constitute a promising class of photoelectrocatalytic materials, where coupling between Au and catalytically active secondary metals enables simultaneous modulation of surface electronic structures, enhancement of catalytic activity, and efficient separation of plasmon-generated hot charge carriers. In this study, Au@Pd and Au@Ni core–shell nanoparticles with controlled Pd and Ni contents, respectively, were synthesized via seed-mediated shell growth on preformed Au seeds and integrated with TiO_2 and $BiVO_4$ photoelectrodes to evaluate their photoelectrochemical activity toward the oxygen evolution reaction (OER). Au@Pd nanoparticles formed well-defined core–shell structures with sub-monolayer-to-monolayer-level Pd shell coverage on Au seeds, and X-ray photoelectron spectroscopy (XPS) analysis revealed electronic interactions between Au and Pd through Pd-content-dependent spectral changes. Similarly, Au@Ni nanoparticles were synthesized with ultrathin Ni surface layers below the monolayer level, and successful Ni incorporation was confirmed by Inductively coupled plasma mass spectrometry (ICP-MS) and XPS analysis. When integrated with semiconductor photoelectrodes, these Au-based bimetallic nanostructures enhanced photoelectrochemical performance under light irradiation. In particular, Au@Pd/TiO_2 exhibited improved visible-light-driven OER activity with increasing Pd shell coverage, while Au@Ni-modified TiO_2 and $BiVO_4$ photoelectrodes showed enhanced photocurrent responses under visible light irradiation. Overall, this study highlights the potential of Au-based bimetallic nanostructures as multifunctional photoelectrode modifiers that simultaneously promote plasmonic light harvesting, charge separation, and surface catalytic reactions within a single nanoscale architecture.

SS-ThP-7 Plasmonic 3D Au Mesh Gas-Diffusion Electrode for Photo-Assisted CO2 Electroreduction, ***hyunwoo Jeong***, *Yeneul Lim, Hyosun Lee,* University of Seoul, Republic of Korea

Abstract

The electrochemical CO_2 reduction reaction (ECO_2RR) driven by renewable energy is a promising strategy for mitigating CO_2 emissions and producing value-added chemicals. For plasmonic metals such as Au and Ag, photo-assisted ECO_2RR can provide an attractive route to facilitate surface reactions through localized surface plasmon resonance (LSPR)-induced hot-carrier transfer to adsorbates, local electromagnetic field enhancement, and localized heating effects. However, conventional Au nanoparticles (Au NPs) often suffer from limited plasmonic enhancement of primitive plasmon modes and insufficient utilization of photo-activated surface sites. Herein, we fabricate a multilayered three-dimensional mesh Au structure (3D-mesh Au) on gas-diffusion electrodes (GDEs) with different widths (20 - 200 nm) and pitches (80 nm - 1.2 μm). Under AM 1.5G illumination, the 3D-mesh Au exhibits significantly enhanced CO faradaic efficiency (FE) compared to both dark conditions and conventional Au NPs. This superior performance originates from a large electrochemically active surface area provided by abundant edges, junctions, and interconnected nanostructures, alongside enhanced plasmon effects. Furthermore, we demonstrate that tuning the geometric parameters of the 3D-mesh Au enables modulation of LSPR wavelengths, thereby giving rise to distinct CO selectivity. This work elucidates the mechanism governing the selectivity of surface reactions in plasmonic photoelectrochemical catalysis via precise surface structure control, while validating the feasibility of large-scale electrode utilization within a GDE system for practical photo-assisted ECO_2RR.

SS-ThP-8 Facet-Controlled Au-Cu2O Heterostructures for Selective Electrochemical CO2 Reduction, ***Yeneul Lim***, *Gangbin Ryoo, Hyosun Lee,* University of Seoul, Republic of Korea

The electrochemical CO2 reduction reaction (ECO2RR) provides a promising pathway for converting CO_2 into valuable chemical products. However, its reaction pathway is highly sensitive to the local surface and interfacial environment of the catalyst. In particular, metal-oxide interfaces can create distinct reaction environments by modulating electronic interactions and intermediate adsorption at the catalyst surface. In this study, we investigate facet-controlled Au-Cu_2O heterostructures as surface-engineered metal-oxide interfaces for selective CO_2 electroreduction. Au nanoparticles (NPs) were deposited on to cubic and octahedral Cu_2O particles with well-defined morphologies, exposing the {100} and {111} facet, respectively. These facet-controlled Cu_2O structures were used to investigate the influence of Cu_2O surface structure on the catalytic effects of Au incorporation. Compared with bare Cu_2O, Au-loaded catalysts exhibited enhanced electrochemical activity and improved CO selectivity, indicating that Au modifies the interfacial reaction environment and promotes the CO-formation pathway. Among the catalysts examined, Au-deposited octahedral Cu_2O showed the most significant enhancement in CO Faradaic Efficiency (FE) and CO partial current density, suggesting that the Au-Cu_2O interface formed on the {111}-faceted octahedral surface is more effective in directing CO_2 reduction

toward CO production. Computational simulation results further revealed the same facet-dependent trend, supporting the critical role of interfacial surface structure in determining CO_2RR selectivity. These results highlight facet-dependent metal-oxide interface engineering as an effective strategy for regulating CO_2RR selectivity and emphasize the importance of surface structure in the design of heterogeneous electrocatalysts.

SS-ThP-9 DFT Study of Ru–Co Bimetallic Synergy in Ammonia Decomposition, ***Yujin Jeon***, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Soomin Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea; *Mu-Hyun Baik,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Jeong Young Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Ammonia decomposition is a key reaction for hydrogen production and NO-$_x$ emission control. Among transition metal catalysts, Ru exhibits high activity for ammonia decomposition, while Co is a cost-effective non-noble metal with promising catalytic performance. In addition, Co and Ru share the same hcp crystal structure, making Ru–Co bimetallic catalysts a promising platform for enhancing catalytic activity through alloying effects. Experimentally, Ru_3Co_1/MgO exhibited higher ammonia conversion than monometallic Ru/MgO, indicating pronounced bimetallic synergy. In this study, density functional theory calculations were performed to elucidate the origin of the enhanced activity of Ru–Co bimetallic nanoparticles supported on MgO. To model the Ru_3Co_1 hcp(0001) surface, 2 × 2 × 1 supercells with different atomic configurations were optimized, and the most stable structure was selected based on formation energy. The calculations reveal that Ru–Co alloying substantially lowers the N–N recombination barrier relative to bare Ru. This enhancement cannot be explained solely by N* adsorption strength. Instead, Bader charge and PDOS analyses show charge transfer from Co to Ru in the Ru_3Co_1 alloy, generating electron-deficient Co sites. These Co sites serve as active centers for N–N bond formation, lowering the activation barrier for recombination. These results provide molecular level insight into the bimetallic synergy of Ru_3Co_1 catalysts and offer design principles for improved ammonia decomposition catalysts.

SS-ThP-10 Ligand Field and Spin-Orbit Competition in a Pb-π System, *Fahri Alkan,* Bilkent University, Turkey; *Paul Bagus,* University of North Texas; ***Sefik Süzer***, Bilkent University, Turkey

There has been a strong recent interest in the large spin-orbit coupling (SOC), a relativistic effect, in Pb moieties adsorbed on graphene and related 2D materials. Since the SOC is inherently an atomic property, a conceptually simple and bold approach might have been pursued to relate the underlying physical/chemical origin of the large SO splitting to the lead atom's outermost valence 6p atomic level. To examine this possible origin at the most fundamental level, we investigated a minimal heavy-adatom–π model system consisting of a single Pb atom positioned at various distances above the center of a benzene (C_6H_6) molecule. In order to analyze the evolution of the electronic structure of this model system, fully relativistic four-component Dirac–Hartree–Fock (4c-DHF) calculations, which took account of the angular momentum coupling of the open shell, Pb 6p, electrons, as well as quasi-relativistic approaches are used. Our results show that the ligand field effects exerted by benzene on the excited states of Pb are comparable in magnitude to the intrinsic 6p SOC of the Pb atom when it is at short distances above the C_6H_6. Indeed, in this regime, the SOC and ligand-field interactions cannot be cleanly separated. In addition, single-determinant and quasi-relativistic SOC treatments are shown to overestimate the Pb–benzene interaction and the associated SOC transfer to the π system, whereas the inclusion of multiconfigurational effects significantly reduces SOC within the open-shell space. A key result of our findings is that the SOC in heavy-adatom–π systems is not a simple projection of atomic SOC, but rather a consequence of hybridization, which depends critically on the correlated description of the heavy-atom valence shell.

SS-ThP-11 Inelastic Electron Tunneling Through Adatoms and Molecular Nanomagnets, *Daria Kývala,* ***Jindrich Kolorenc***, Institute of Physics (FZU), Czech Academy of Science, Prague, Czechia

The inelastic electron tunneling spectra (IETS) measured in a scanning tunneling microscope (STM) have repeatedly proved very useful for investigation of spin excitations in transition-metal adatoms placed on various surfaces. More recently, more complex STM-IETS measurements were achieved, involving tunneling through multiple coupled magnetic centers (multiple partially filled atomic shells). These measurements include a sequential tunneling through a magnetic molecule (nickelocene) attached to the STM tip and through another magnetic nanosystem placed on the surface [1,2], or a tunneling through multiple partially filled shells located at a single adatom [3]. To model the inelastic spectra measured in these arrangements, we employ a variant of the cotunneling theory [2,4,5] with the magnetic nanosystems being represented by means of a cluster Hubbard model [6]. In the case of an iron adatom probed by a nickelocene-terminated STM tip [1], we show that our model reproduces the experimentally observed bias asymmetry of the inelastic spectra without introducing the apparent spin polarization of the surface electrode as a fitting parameter as done in [1]. In the case of tunneling through the 6s shell that is exchange coupled to the partially filled 4f shell in a rare-earth adatom [3], we demonstrate that our theory faithfully captures not only the spectral features corresponding to relative reorientation of the 6s and 4f spins, but also the features corresponding to the crystal-field excitations of the 4f magnetic moment. Finally, we discuss the exchange between the spin of the tunneling electron and an adatom that carries a large orbital moment, and we show that this exchange is richer than the usually assumed Heisenberg form. This richer exchange induces more features in the inelastic tunneling spectra than would be expected with the Heisenberg exchange [5].

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SS-ThP-12 Interfacial Electronic and Optical Responses in Au-Based Bimetallic Systems, ***Sieun Yang***, *Hyosun Lee,* University of Seoul, Republic of Korea

In plasmonic nanostructures, the interplay between plasmonic light absorption and interfacial electronic structure plays an important role in controlling optical and catalytic functionalities. Au nanoparticles (NPs) are attractive plasmonic cores because of their strong localized surface plasmon resonance (LSPR) in the visible-light region. However, their relatively inert surface chemistry can limit catalytic functionality. Coupling Au with another metal in a core–shell geometry offers an effective strategy to integrate plasmonic light-harvesting with interfacial electronic modulation and enhanced surface reactivity. Herein, we investigate the interfacial electronic and optical responses of Au-based bimetallic core–shell NPs (i.e., Au@Pd NPs and Au@Ni NPs) with sub-monolayer shell coverage. The surface coverage of the metal shell modulates the Au LSPR response, leading to attenuation and broadening of the plasmonic absorption band, while X-ray photoelectron spectroscopy (XPS) analysis suggests interfacial electronic interactions between the Au core and the surrounding metal shell. Furthermore, femtosecond transient absorption measurements of core–shell NPs reveal accelerated hot-carrier relaxation dynamics, highlighting the role of the metal shell in regulating plasmon-driven carrier behavior. These findings provide insight into how metal-shell formation modulates the coupled optical responses and interfacial electronic properties in Au-based bimetallic nanostructures and provide design insight for plasmonic photocatalytic systems.

SS-ThP-13 Visible-Light-Driven Metal/Cu2O/Fe2O3 Janus Micromotors with Engineered Interfacial Charge Transfer, ***Park Yijun***, University of Seoul, Republic of Korea; *Son Jihan, Lee Hyosun,* University of Seoul, Republic of Korea

Microplastics have emerged as a critical global pollution issue, and micromotors are increasingly recognized as promising tools for their efficient collection and degradation in aquatic environments. Among them, metal-oxide-based Janus micromotors exhibit high photocatalytic activity; however, the risks of secondary contamination, such as corrosion of noble metal caps, remain a practical concern. To address this challenge, we develop α-Fe_2O_3-based heterostructure micromotors incorporating Cu_2O semiconductor shells and metallic caps (Cu, Au, Pt). Compared with

conventional TiO_2-based micromotors, α-Fe_2O_3-based micromotors exhibit enhanced visible-light-driven propulsion and photocatalytic activity, while the introduction of Cu_2O further improves micromotor performance through heterostructure-assisted charge separation and interfacial charge transfer. Among the metallic caps examined, Cu-capped micromotors show the highest propulsion efficiency and photocatalytic activity under visible-light irradiation. In addition, methylene blue degradation is examined as a model reaction to evaluate the pollutant-removal capability of the micromotors under light irradiation. The enhanced performance of Cu-capped micromotors isattributed to the synergistic effect of Cu-based redox cycling, which efficiently activates H_2O_2 to sustain reactive oxygen species (ROS)-mediated oxidative degradation and self-diffusiophoretic propulsion, combined with favorable interfacial charge transfer at the Cu/Cu_2O junction. These findings highlight that interfacial band alignment and catalytic synergy are critical determinants of micromotor performance and provide design principles for eco-friendly photocatalytic micromotors for environmental remediation, including microplastic removal.

SS-ThP-14 Exploring a New Functionality for Surface Modifications, Organo-Azides, ***John R. Mason***, *Andrew V. Teplyakov,* University of Delaware

Organo azides are a reactive nitrogen containing species that have been puzzling chemists for almost 200 years. These species readily eliminate molecular nitrogen, and can insert an organo-nitrene, and have been studied for various applications in click chemistry of clean surfaces, but very little work has been done on modified (terminated) semiconductor substrates, that are currently more industrially applicable as compared to ultra-high vacuum surfaces that these compounds have been studied on. This work aims to look at liquid organic azides, and their ability to functionalize a wide range of semi-conductor surfaces including silicon and metal oxides, to attempt to elucidate the reaction mechanism of the azide on the surface, and what surface products are formed after the reaction, through the use of Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). This work could then be used in area-selective atomic layer deposition to attempt to further explore a new class of small molecule inhibitors from this underexplored molecular species.

SS-ThP-15 Facet-Engineered Cu Nanocatalysts for Efficient Nitrate Electroreduction to Ammonia, ***Zhen Meng***, *Xiaofeng Feng,* University of Central Florida

Electrochemical nitrate reduction reaction (NO_3RR) shows great potential for the recycling of nitrate from wastewater sources for the denitrification of wastewater and sustainable ammonia production. Development of this technology requires electrocatalysts that can enable high activity and selectivity for nitrate conversion to ammonia. Here we report a Cu nanoflake electrocatalyst with tunable morphology and exposed crystal facets, synthesized directly on a Cu foam substrate. Compared with their Cu nanowire counterparts, the Cu nanoflakes showed a 5-fold increase in the NO_3RR activity with 81% Faradaic efficiency for ammonia production at a low overpotential of +0.15 V vs RHE. Furthermore, the surface-area-normalized NO_3RR activity of the Cu nanoflakes remains three-times higher than that of the Cu nanowires, which is attributed to the synergistic exposure of Cu(100) and Cu(111) facets. The Cu nanoflake electrode was further evaluated in a single-pass flow cell for continuous nitrate electrolysis, which achieved high activity and >90% Faradaic efficiency for nitrate-to-ammonia conversion at 0 V vs RHE cross a wide range of nitrate concentrations, while maintaining stable performance over ~100 h of continuous operation. Our work provides insights into the rational design of NO_3RR electrocatalysts for practical nitrate remediation and sustainable ammonia production.

SS-ThP-16 Monte Carlo Simulation of Dynamic CO Oxidation on Pt(111), ***Ignacio Vargas***, *Eliseo Pérez,* Brookhaven National Laboratory and State University of New York at Stony Brook*; Qin Wu,* Brookhaven National Laboratory*; J. Aníbal Boscoboinik,* Brookhaven National Laboratory and State University of New York at Stony Brook

This project presents a Python-based kinetic Monte Carlo (kMC) simulation developed to model catalytic CO oxidation on a Pt(111) surface under dynamically varying reactant conditions. The catalyst surface is represented as a two-dimensional lattice that captures the nearest-neighbor interactions characteristic of the Pt(111) crystal structure. The model incorporates the elementary surface processes involved in CO oxidation, including CO adsorption/desorption, dissociative O_2 adsorption, and surface reactions leading to CO_2 formation, with the stochastic evolution of the system governed by temperature-dependent rate constants within a kinetic Monte Carlo framework. A key aspect of this work is the implementation of time-dependent CO partial-pressure pulses in the presence of a constant O_2 background, enabling the investigation of non-steady-state catalytic behavior. The simulation is designed to reproduce experimentally measured transient CO_2 signals obtained under pulsed conditions, and the simulated transient responses are directly compared with experimental data, including CO_2 production profiles and temperature-dependent kinetic regimes such as CO-poisoned and oxygen-rich surface states. Particular attention is given to understanding how dynamic forcing influences the interplay between adsorption, reaction kinetics, and surface coverage evolution. Simulation outputs include time-resolved surface coverages, transient CO_2 production rates, and evolving surface configurations, providing insight into how stochastic surface processes contribute to experimentally observed catalytic behavior under dynamic conditions. This work establishes a computational framework that can be further refined to improve agreement with experiment and extended to investigate larger surface models, more realistic catalytic environments, and additional kinetic processes relevant to dynamic heterogeneous catalysis.

SS-ThP-17 Methanol Dehydrogenation and Combustion Pathways on Oxidized Cu (111), ***Vishwa Don Lokugan Hewage***, *Michael Trenary,* University of Illinois - Chicago

Methanol dehydrogenation is an industrially important reaction for the production of formaldehyde and hydrogen as valuable chemical feedstocks. Previous studies on oxidized copper surfaces have identified methoxy as the dominant intermediate in the formation of formaldehyde and hydrogen at elevated temperatures. More recent investigations of alcohol oxidation on Cu surfaces have also revealed competing combustion and hydration pathways that produce ethylene, CO_2, and H_2O through oxygen-assisted surface reactions. In addition, prior studies have suggested that CO_2 formation may proceed through a minor formate intermediate at elevated temperatures. In this study, methanol reactions on oxygen-precovered Cu(111) surfaces were investigated under ultrahigh vacuum (UHV) conditions using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction spectroscopy (TPRS) to elucidate reaction pathways and surface intermediates.TPRS experiments showed the formation of both CO_2 and H_2O at elevated temperatures on oxygenated Cu(111), while clean Cu(111) surfaces remained largely inert under identical conditions. Although previous studies reported only a single CO_2 desorption feature near 466 K, our TPRS results at higher oxygen coverages (100 L O_2) exhibited four distinct CO_2 desorption peaks at 359 K, 373 K, 403 K, and 466 K, with the lower-temperature features contributing the highest CO_2 yield. A single H_2O desorption feature was observed near 375 K and shifted to higher temperatures with increasing oxygen exposure. Methane formation was also detected near 320 K on both oxygenated and clean Cu(111) surfaces and is attributed to methanol fragmentation to surface methyl species followed by hydrogenation by adsorbed hydrogen atoms. RAIRS measurements identified a formate intermediate with a characteristic OCO stretching feature at 1343 cm^{-1} that formed near 200 K and remained stable on the surface up to 360 K together with the dominant methoxy intermediate. The formate yield reached a maximum at approximately 150 L oxygen exposure before decreasing at higher coverages. The persistence of surface formate over the temperature range associated with CO_2 desorption suggests that formate acts as a precursor to CO_2 formation on oxygenated Cu(111). These findings demonstrate that methanol on oxygenated Cu(111) proceeds through coupled dehydrogenation and combustion pathways involving dominant methoxy and minor formate intermediates, while no significant dehydration products were observed.

SS-ThP-18 Atomic-Scale Studies of Electron- and Hole-Induced Desorption at Single-Atom Alloy Active Sites, ***Nima Rajabi***, Tufts University*; Phillips Hutchison,* Princeton University*; Kai Shen,* UC Santa Barbara*; Charles Sykes,* Tufts University*; Emily Carter,* Princeton University*; Phillip Christopher,* UC Santa Barbara

Single-atom alloys (SAAs) have attracted significant attention as thermo-, electro-, and more recently plasmonic photocatalysts due to their unique electronic and chemical properties. Unlike thermal catalysis, plasmonic photocatalysis enables energy-efficient and selective molecular activation via localized surface plasmon resonances. However, the mechanisms governing adsorbate reaction and desorption remain unclear. Here, we explore how charge injection contributes to bond weakening, leading to more efficient CO removal – a major challenge in catalytic processes where CO acts as a poison. Using scanning tunneling microscopy (STM) and spectroscopy (STS), we investigate the geometric and electronic structure of four different SAA surfaces—NiAg(100), PtAg(100), PdAg(100), and RhAg(100)—and their role in electron-stimulated CO desorption. STS and

density functional theory (DFT) allow correlation of local densities of states with electron/hole energies to help probe the mechanism of desorption. Specifically, we probe charge injection induced desorption, often postulated to involve transient negative ion (TNI) states formed by plasmon-induced charge transfer. Our results indicate that SAAs exhibit drastically different CO desorption rate dependence on electron energy than would be expected solely from their CO binding energies. To further support our experimental findings, we employed nanoparticle studies, DFT, and embedded correlated wavefunction (ECW) theory. These studies provide insight into electronic structure modifications induced by charge transfer during the induced desorption process. Specifically, ECW reveals similar charge transfer mechanisms – involving intermetallic excited states - for RhAg, PtAg, and PdAg, with NiAg alone indicating possible TNI formation. Our findings provide deeper insights into the electronic and catalytic properties of SAAs and offer guidance for designing more efficient and sustainable photocatalysts that minimize the use of precious metals.

SS-ThP-19 Pulsed Dosing of Platinum Topography Effects in CO Oxidation and ZIF Film Diffusion, ***Eliseo Perez Gomez,*** Stony Brook University/Brookhaven National Laboratory*; Esteban L. Fornero,* Universidad Nacional del Litoral (UNL), Argentina*; J. Anibal Boscoboinik,* Stony Brook University/Brookhaven National Laboratory

A comprehensive understanding of surface reactions requires isolating the distinct contributions of chemical kinetics, surface topology, and mass transport. This study utilizes a pulsing valve system to precisely control dosing parameters, including valve opening/closing intervals and cycle repetitions, to drive transient surface reactions. By coupling this controlled dosing framework with simultaneous in situ infrared spectroscopy and mass spectrometry, we are able to monitor the resulting surface phenomena and gas-phase products with millisecond-scale time resolution. By systematically modifying these experimental parameters, we investigate two distinct regimes: defect-driven catalysis and framework-confined diffusion. First, we explore the impact of surface morphology on CO adsorption and oxidation kinetics by comparing flat, annealed Pt (111) against rough, sputtered Pt (111) and Pt films (deposited by sputtering). Enhanced CO_2 production on rougher surfaces indicates a key role of undercoordinated active sites. Second, we extend this pulsing methodology to evaluate molecular transport and gas diffusion resistance through porous zeolitic imidazolate framework (ZIF) overlayers synthesized on both inert (Au) and active (Pt) substrates. Together, these parallel investigations showcase the exceptional utility of transient pulse systems to precisely monitor reactions, map surface coverage, and decouple the intricate relationships between physical surface roughness, catalytic activity, and localized molecular diffusion.

SS-ThP-20 Next-Generation Momentum Microscopy, *Andreas Janzen,* Scienta Omicron GmbH, Germany*; Gerd Schönhense, Olena Tkach,* Johannes Gutenberg-Universität, Institut für Physik, Germany*; Andrew Yost, Xin Zhang,* ***Daniel Beaton,*** Scienta Omicron Inc.

Momentum Microscopy (MM) offers an alternative to performing ARPES and photoelectron diffraction (PED) for energies from the VUV to hard X-rays. MM captures (k_x,k_y) momentum images with diameters ranging from 2 to 12 $Å^{-1}$, easily covering a full Brillouin zone in parallel for virtually all materials.

In this contribution, we present a new momentum microscope that combines a single high-resolution hemispherical energy analyser with a photoelectron microscopecolumn that can easily be switched between generating real and reciprocal space images from a selected region of interest. The key ingredient is the versatile objective lens that enables several operation modes.

With the novel objective lens design [1], the electric field at the sample surface can be shaped from strongly accelerating (similar to a conventional PEEM) to zero-field and retarding. Retarding fields effectively reduce the space-charge interaction by redirecting slow electrons back to the sample. The 'repeller mode' is useful for ARPES at high energies and time-resolved experiments involving intense pump pulses. Space-charge suppression has been proven at the free-electron laser FLASH [2] and at high-harmonic-generation sources [3].

We present first experimental results demonstrating the ultimate energy resolution of the instrument in gas-phase electron spectroscopy.

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SS-ThP-21 Investigating the Properties of Transition Metal-Doped Ceria Thin Films Grown by Pulsed Laser Deposition, ***Rosa Virginia Melinda,*** *Nishan Paudyal, David King, Jinke Tang, Jing Zhou,* University of Wyoming

Ceria ($CeO_{2-\delta}$, $0<\delta<0.5$) has attracted increasing attention for a wide range of important catalytic applications due to its reversible Ce^{3+}/Ce^{4+} redox pairs and tailorable oxygen vacancy concentrations. The incorporation of transition metal dopants in ceria has been reported to cause modifications in the lattice structures and electronic properties of the material, thereby enhancing its catalytic performance. Additionally, doped ceria has been reported to exhibit improved thermal stability, further extending its applicability in high-temperature catalytic environments. In this study, transition metal-doped ceria ($Ce_{1-x}M_xO_{2-\delta}$, $0<x<0.5$, M=Ti, Ni, Co, Fe) thin films were synthesized on Si(111) substrates using the pulsed laser deposition (PLD) technique under an O_2 environment. X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) data revealed that the resulting thin films are polycrystalline and stoichiometric with respect to the intended metal-dopant concentrations. Atomic force microscopy (AFM) images showed that the synthesized thin films have flat surface morphologies with roughness of about 130 ± 30 pm and are composed of nanostructures with a width average of 28 ± 3 nm. X-ray photoelectron spectroscopy (XPS) was used to examine the chemical state of the incorporated metal dopants. Ti exhibits the +4 state, while Ni and Co are in the +2 state. Based on the analysis of the Ce 3d region in XPS, the thin films grown without O_2 are highly reduced. The presence of O_2 during deposition is effective for tuning the degree of reduction of ceria thin films. Our studies demonstrate that PLD offers a straightforward approach for tailored growth of transition metal-doped ceria thin films with controlled composition, thickness, and structure, which can be used as model systems of ceria to elucidate the effect of dopants on its redox properties and catalytic activity.

SS-ThP-22 Molecular Adsorption of CO at 110 K on the ZrB2(0001) Surface, ***Cosmic Gober,*** University of Illinois at Chicago

Zirconium diboride (ZrB_2) is a candidate material for extreme-environment applications such as for aerospace and hypersonic vehicles due to its ultra-high melting point and high hardness.[1] Yet a significant gap exists in the literature regarding its surface chemistry: specifically, no prior work has investigated carbon monoxide (CO) adsorption on ZrB_2(0001) at cryogenic temperatures. For many other metals, the adsorption of CO is often used to characterize the chemistry of the metal's surface. The adsorption of CO on the ZrB_2(0001) surface at 110 K was investigated with reflection absorption infrared spectroscopy (RAIRS). While CO undergoes dissociative adsorption at room temperature,[2] it is molecularly adsorbed at 110 K. It reaches saturation coverage after exposures of 0.2–0.3 Langmuir (L) with a characteristic C-O stretching frequency of 2098–2100 cm^{-1} and a narrow peak width (FWHM) of ~8.5 cm^{-1}. A saturation coverage of oxygen achieved after an O_2 exposure of ~20 L reduces the CO peak area by over 60% and increases the C-O stretch FWHM to ~15 cm^{-1} ,indicating a transition to a more disordered adlayer. However, the C-O stretching frequency remains nearly constant, suggesting that the electronic nature of the binding sites is largely unaffected by co-adsorbed oxygen. These results provide new experimental data on the surface chemistry of ZrB_2 relevant to its application in the oxidizing environments of hypersonic flight.

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SS-ThP-23 Ultrafast Photodissociation Dynamics of CH_2I_2 on SiO_x, ***Keith Blackman,*** University of Central Florida

Diiodomethane (CH_2I_2) remains an important molecule for use as a model system in gas-phase and gas-solid spectroscopic studies. In particular, the dissociation of the C-I bond provides a useful probe of the diverse reaction pathways of CH_2I_2 upon UV photoexcitation. Despite this, the overall ultrafast dynamics of CH_2I_2 is still not fully understood.

In this work, the ultrafast reaction dynamics of CH_2I_2 adsorbed on a SiO_x thin film is investigated.Temperature programmed desorption is used to investigate the interaction of CH_2I_2 with the SiO_x surface, while the photoinduced reaction of CH_2I_2 is investigated using mass spectrometry in combination with ultrafast pump-probe laser spectroscopy. In these

experiments, low intensity 266 nm pump laser pulses initiate the dissociation of the CH_2I_2 molecule, while precisely delayed, high intensity 266 nm probe pulses ionize the reaction intermediates and final products, which are subsequently analyzed by a time-of-flight mass spectrometer.

Results indicate a complex photodissociation pathway, in which intermediates such as H^+, CH_2^+, and I^+ are detected at the surface. Interestingly, I_2^+ is detected in the gas phase, likely originating from recombination of iodine atoms generated during photodissociation at the surface, followed by desorption into the vacuum.

Additionally, $H_2^+$is detected at the surface, while reaction products such as CH_3^+ and $C_2H_4^+$ indicate the likely presence of hydrogenation and carbon-carbon bonding at the surface. While not detected at the surface, $CH_2I_2^+$ and CH_2I^+ are observed as gas-phase products, likely resulting from ionization and excitation into cationic dissociative states of the parent molecule, respectively. Time-resolved data for the ultrafast dissociation and subsequent reactions at the surface will be presented.

These findings provide a framework for future investigations of the ultrafast dynamics of CH_2I_2 across a range of surfaces, including semiconductors and metal particles and clusters, where stronger adsorbate–surface interactions are expected to significantly influence the reaction dynamics.

SS-ThP-24 Self-limiting Oxidation of $Li_xAg(111)$ Surface Alloys, ***Yuchen Niu***, *Janice Reutt-Robey,* University of Maryland, College Park

The environmental stability of Li-Ag alloys is of immense interest due to their wide-ranging technological applications. Their stability against oxidation is particularly noteworthy, as the alloy pairs an extremely O_2-reactive metal with one of much lower chemical reactivity. This difference suggests a pathway for Li surface segregation in Li-Ag surface alloys, which will lead to facile oxidation on heterogeneous alloy films via oxidation of lithium component.

Despite the great potential of Li-Ag alloys in solid-state battery applications, the atomic structures of Li-Ag alloy surfaces and the site-specific reactivity of different Li-Ag alloy phases to O_2 remain largely unexplored. In this study, $Li_xAg(111)$ and Li/Li_xAg surfaces were prepared via lithium deposition on an Ag(111) substrate under UHV conditions. The chemo-structural evolution of alloy surfaces under oxidative conditions was studied *in situ* with scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). At 5 Langmuir(L) of O_2 exposure, $Li_xAg(111)$ surfaces underwent negligible oxidation, indicating low reactivity to oxygen. At high (200 L) O_2 exposure, structural evidence for oxidative transformation emerged, where atomically smooth Li surfaces on $Li_xAg(111)$ developed a corrugated and particulate morphology. Such oxidation was self-limiting, which is attributed to a sub-stoichiometric Li_xO_y surface passivation layer. Further oxidation of Li_xO_y islands could be driven by a strong local electric field from the STM tip, in accordance with the Cabrera-Mott-type oxidation mechanism. A model for Li_xAg surface evolution during the oxidation is proposed.

SS-ThP-25 Insight Into Subsurface Adsorption Behavior Over the Material Pressure Gap, ***Carson Mize***, Leiden University, Netherlands*; Sharani Roy,* University of Tennessee Knoxville

Transition metals are heavily utilized in catalytic reactions due to their ability to participate in a variety of reactions. While the fundamental focal point has been on deciphering the processes happening on the surface, the role subsurface adsorbed species play in the evolving chemical environment is less understood. It is suspected subsurface adsorption influences a variety of material effects, such as corrosion, metal oxidation, and even reconstruction, making characterizations in this region important in understanding the full properties of a material. However, to properly study subsurface adsorption, one must think of the concerted coadsorption of many atoms or molecules, as high coverage surface atoms promote diffusion into the subsurface, suggesting the demand to capture the adsorption behavior over a large coverage regime. To this end, we have developed an *ab initio*, lattice-gas model designed to include surface and subsurface adsorption in a solid[1]. We applied our model study the adsorption of atomic oxygen on Ag(111) over a wide range of coverages and O_2 pressures, representing experimental pressures (high vacuum) and industrial applications (high pressures)[2]. The coadsorbate interactions in the model are treated in a pairwise manner and all parameters of the model are calculated using density functional theory. This study demonstrates modelling this coadsorption behavior provides insight into the fundamental issue of the "pressure gap" that exists when studying adsorption and reactions at surfaces.

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SS-ThP-26 Investigating the Ultrafast Dynamics of CH_2I_2 on Metal Oxides, ***Sebastian Cimino***, *Lucas Macri, Keith Blackman, Mihai Vaida,* University of Central Florida

As a model system, CH_2I_2 is a molecule that has highly documentable dissociation and recombination behaviors. While the gas-phase ultrafast dynamics have been extensively characterized throughout previous femtochemistry research efforts, surface-aligned CH_2I_2 is still a relatively novel topic that is yet to be fully explored. One of the most significant dissociation products of CH_2I_2 is CH_2, since it has been theoretically determined that it is aligned towards the gas phase as opposed to the iodine in the compound which forms bonds with the surface. Therefore, dosing a metal oxide substrate such as titanium oxide or silicon oxide with both CH_2I2 and O_2, or ozone, leads to the creation of one of the simplest Criegee intermediates, CH_2OO or formaldehyde oxide. In current physical chemistry research, there is very little understood about the surface-aligned ultrafast dynamics of CH_2OO. While purely gas-phase formaldehyde oxide is the most prevalent form of this molecule in the environment, CH_2OO molecules in the air frequently adsorb to dust particles and unbound metal oxide matter. Understanding how CH_2OO interacts with a surface substrate can greatly assist current environmental efforts to reduce the amount of CH_2OO in the Earth’s atmosphere, since its highly reactive nature leads to the creation of several harmful compounds found in the air.

SS-ThP-27 First-Principles Study of CF_4 and C_2F_6 Hydrolysis Pathways on $ZnAl_2O_4$ and Al_2O_3 Catalysts, ***Chi Hun Lee***, *Sang Hyeon Ju, Gyeong Won Seo,* Inha University, Republic of Korea*; Hyuk Jae Kwon, Jong-Min Lee, You-Hwan Son, Jeong Yun Kim,* Samsung Advanced Institute of Technology, Republic of Korea*; Hyung Chul Ham,* Inha University, Republic of Korea

Growing environmental regulations on the semiconductor industry have placed urgent demands on the development of effective abatement technologies for perfluorocompounds (PFCs) emitted from FAB exhaust streams. In particular, carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6) are regarded as exceptionally challenging targets due to their outstanding thermochemical stability and extremely long atmospheric lifetimes. Against this backdrop, spinel-structured zinc aluminate ($ZnAl_2O_4$) and gamma alumina (γ-Al_2O_3) has emerged as a promising catalytic platform for PFC decomposition, owing to its superior thermal and chemical robustness. However, transition states — the highest-energy species along the reaction coordinate — are spectroscopically silent and thus fundamentally inaccessible through experimental observation alone, imposing inherent limitations on the elucidation of precise reaction mechanisms and catalyst deactivation pathways. To address this challenge, density functional theory (DFT) calculations are employed to systematically investigate the major reaction pathways of CF_4 and C_2F_6 on a $ZnAl_2O_4$ and γ-Al_2O_3 slab models with the most stable surface termination determined by surface energy calculations, considering both direct dissociation and hydrolysis routes. Our DFT calculation identified the most critical step that can simultaneously maximize the hydrolysis of both CF_4 and C_2F_6. In addition, the transition metal-doped $ZnAl_2O_4$ catalyst was examined to tune the surface reactivity toward CF_4 and C_2F_6 hydrolysis. The findings of this study are expected to provide molecular-level mechanistic insights into PFC hydrolysis on metal oxide surfaces and offer practical design principles for the rational development of next-generation catalytic abatement systems targeting FAB exhaust emissions.

SS-ThP-28 X-Ray Photoelectron Spectroscopy of Organo-Metallic Compounds Designed for Homogeneous Catalysis, ***Farzad Bastani***, University of Virginia*; Daniel Ess,* Brigham Young University*; T. Brent Gunnoe, Petra Reinke,* University of Virginia

Organo-metallic compounds where one or several metal or metalloid centers are surrounded by organic ligands are highly efficient homogeneous catalysts. This toolbox for optimization is limited by the “synthesizability” of an imagined compound. Our focus here is on XPS which has the advantage of quantitative elemental analysis but brings the complications of final state effects which influence chemical shifts and spectral shapes.

Compound functionality relies on the distribution of charge between ligands and metal center(s) and functionalization with strongly electronegative groups, F, O, Cl and combinations thereof modulates said charge distribution. XPS offers, via the chemical shift of core level peaks,

insight in the charge on the metal, and as an extension on other elements within the compound. We propose that XPS characterization can be used to map the relative changes in bonding and oxidation state within and between related compounds.

We have analyzed a set of 20 organo-metallic compounds which include Cu, Sb, Pt and Ag as single or double metal centers with a wide range of ligands and electronegative groups [1]. We developed a workflow to test for compound stability, and will discuss the choice of reference energy for these insulating substances. The chemical shift for core levels relies on the modulation of the oxidation state, respectively the charge state of the element. However, the shift is element and core level specific. We developed a calibration method based on data of inorganic materials, type and electronegativity of the bonding partner. We will discuss this benchmarking and its limits of transferability between inorganic and organic compounds. The relative shifts are compared to results from DFT calculations for the respective compounds. All elements within each compound are included, and fitting of the core levels is used to identify bonding configurations and corresponding ligand induced shifts. We will discuss several examples with various ligands and metal centers and develop from there a general approach to use XPS and construct a charge distribution map of the respective compound.

One of our examples are quinoline-based Sb ligands coordinated to Pt which are modified by attachment of Cl, F and $C_6Cl_4O_2$ to Sb or Pt. The charge distribution between Pt and Sb is modulated and explained with a next nearest neighbor interaction. However, changes in the Cl atom bonding and charge is traced back to a long range interaction enforced by the ligand geometry. Surprisingly switching Cl for F next to the Sb center is inconsequential to the Pt and all other oxidation states.

[1] Webber et al. Organometallics **45**, 438 (2026)

SS-ThP-29 Evaluating MLIP Representation of Reaction Mechanisms on Ni-Based High-Entropy Alloy Surfaces*, **Chiezugolum Odilinye**, Liney Arnadottir,* Oregon State University*; Gregory Herman,* Argonne National Laboratory, USA

Understanding reaction mechanisms on complex alloy surfaces remains a key challenge in catalyst design. In this work, we investigate how Machine Learning Interatomic Potentials (MLIPs) capture adsorption energetics and reaction pathways for CO_2 hydrogenation reaction on a Ni-based High Entropy Alloy (HEA). Using the Universal Model for Atoms (UMA) MLIP, we evaluate adsorption properties of key intermediates (CO, O, and H). Nudged Elastic Band (NEB) calculations are used to probe the CO hydrogenation step (CO + H >CHO). MLIP predictions are benchmarked against Density Functional Theory (DFT) calculations and ML-NEB implementations (eOn and CatLearn) to assess their ability to represent reaction energetics on multi-element surfaces. Results show that UMA systematically overestimates adsorption energies, leading to deviations in predicted activation barriers. It also reveals composition-dependent trends in adsorption energetics and activation barriers across the HEA surfaces. These findings highlight both the potential and limitations of MLIPs in capturing surface reaction physics in high-dimensional compositional spaces and provide insight into their role in AI-driven materials discovery.

SS-ThP-30 Topology-Directed Silicide Formation: An Explanation for the Growth of C49-$TiSi_2$ on the Si(100) Surface*, Lukas Hückmann,* Leiden University, Netherlands*; Jonathon Cottom,* ARCNL*; **Jörg Meyer**,* Leiden University, Netherlands*; Emilia Olsson,* ARCNL

The optimization of metal-semiconductor (MS) junctions is a fundamental prerequisite for advancing electronic device performance. Titanium disilicide ($TiSi_2$) is a widely used material due to its low electrical resistivity, good chemical stability, and low Schottky barrier height at the MS interface [1]. In practice, the existence of multiple polymorphs makes it challenging to grow phase-pure films. Among these, the C54-$TiSi_2$ phase exhibits the desired beneficial properties; yet it is the metastable, high-resistivity C49-$TiSi_2$ modification that preferentially nucleates on Si substrates. The origin of C49-selective nucleation, however, remains debated [2]. We present a first-principles atomistic model of Ti adsorption on the c(4x2) Si(100) surface that highlights the key role of surface symmetry and reconstruction for the initial stages of the interfacial TiSi2 formation process [3]. Based on DFT calculations ranging from the dilute limit to a coverage of two monolayers, we identify the energetically most stable configuration as a Ti-Ti dimer pair consisting of a surface adatom and a first-subsurface interstitial. This specific pairing coincides with the local reversal of the Si(100) surface reconstruction, which creates a characteristic low-symmetry adsorption pattern that is unique to the C49-$TiSi_2$ phase and thereby serves as a nucleation template for C49.This model aligns with experimental observations like the Stranski-Krastanov growth mode, the preferential formation of C49-$TiSi_2$ despite being less favorable than the competing C54 phase, and why disrupting the surface structure via amorphization removes the nucleation template and restores thermodynamically driven growth of the latter. This atomistic perspective on phase-selective growth suggests that such surface pre-treatment could obviate the need for the C49 to C54 transformation, thereby minimizing the thermal budget in the fabrication of next-generation nanoelectronic devices.

[1] S.-L. Zhang, U. Smith, J. Vac. Sci. Technol. A 22, 1361-1370 (2004).

[2] R. W. Mann, L. A. Clevenger, J. Electrochem. Soc. 141, 1347 (1994).

[3] L. Hückmann, J. Cottom, J. Meyer, E. Olsson, *submitted*.

Surface Science
Room 305 - Session SS-FrM

Photo- and Electrochemical Energy Conversion

Moderators: Prof. Ashleigh Baber, James Madison University, **Matthew Montemore**, Tulane University

8:15am **SS-FrM-1 Real-Time Control of Interfacial Dynamics Enables Electrocatalytic C-H and C-C Bond Transformation and Fuel Formation**, ***Marcel Schreier***, University of Wisconsin-Madison **INVITED**

Producing fuels and chemicals using electricity has drawn considerable interest in recent decades. However, research in electrocatalysis, which allows us to link electricity to chemical transformations, remains strongly focused on the electricity-driven transformation of small inorganic molecules such as CO_2, H_2O, N_2, as well as oxygen containing molecules derived from biomass. Yet, comprehensive industrial electrification will require electrocatalytic methods that can promote the reactions that make up the core of the chemicals and fuels industry: n–alkane transformations.

In this presentation, I will show that using electricity to promote n-alkane transformations opens entirely novel avenues of reactivity with the potential to address long-standing challenges in reactivity and selectivity plaguing catalytic alkane chemistry. Specifically, I will show how our group combined fundamental understanding of the interfacial processes occurring in electrocatalytic reactionswith *in-situ* product analysis using electrochemical mass spectrometry, to gain independent control over the elementary steps of complex alkane transformation reactions in real-time. Using the real-time modulation of the electrode potential applied to an electrocatalyst, we were able to independently control the *adsorption* of n-alkanes to electrocatalyst surfaces, initiate the *transformation* of adsorbates while they are bound to the catalyst, and *selectively desorb* desired products, while leaving others bound. These methods allowed us to demonstrate the room-temperature fragmentation of ethane and butane into shorter chain fragments, achieve the dehydrogenation of n-alkanes at room temperature, open pathways towards the oxidation of n-alkanes in fuel cells, and achieve other industrially relevant hydrocarbon transformations at mild conditions. I will discuss the fundamental science behind these pathways and show how they may chart a path towards more targeted transformation of chemical compounds than is possible with current chemical technologies.

8:45am **SS-FrM-3 Exploring Non-Thiol DDQ Self-Assembly on Au(111) through Cyclic Voltammetry, AmbientSTM, and XPS**, ***Nazila Hamidi***, *Cara Plaisance, Alyssa Nanneman, Soumick Naskar, Sanwu Wang, Erin Iski,* University of Tulsa

Redox-active organic molecules on noble-metal surfaces provide model interfaces for studying molecular ordering, interfacial charge transfer, and surface-confined electrochemistry. In this study, the non-thiol adsorption and self-assembly of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a strongly electron-accepting quinone, on Au(111) were investigated. Clean Au(111) substrates were immersed at room temperature in a saturated DDQ solution prepared in 0.1 M $HClO_4$ for selected immersion periods, allowing the time-dependent evolution of DDQ adsorption and surface assembly to be valuated. The resulting surfaces were characterized by Cyclic Voltammetry (CV) and ambient Scanning Tunneling Microscopy (STM), while X-ray Photoelectron Spectroscopy (XPS) is being used to evaluate surface composition. CVs showed reproducible DDQ-related redox features after immersion, indicating that electroactive DDQ species are retained at the Au interface after air exposure. The redox peak currents increase systematically with immersion time, consistent with progressive adsorption and increasing surface coverage. Scan-rate-dependent measurements support a surface-confined redox process, as the peak current scales linearly with scan rate rather than with the square root of scan rate. These results indicate that immersion time provides a direct way to tune the density of DDQ molecules on the Au(111) surface. Ambient STM was used to probe Au(111) after DDQ exposure. Compared with clean Au(111), DDQ-modified surfaces show clear changes in surface appearance, suggesting adsorbed molecular features and molecule-induced restructuring of the Au surface. The time-dependent STM observations indicate that DDQ adsorption evolves from early-stage surface modification toward more developed, linear assemblies at longer immersion times. Initial analysis suggests that the molecules tilt at elevated coverages, which allows the assemblies to be stabilized through possible pi-pi stacking and H-bonding. Because DDQ contains electron-withdrawing cyano groups and quinone carbonyl groups, adsorption may involve interactions between DDQ functional groups and Au surface atoms, including cyano-mediated binding or adatom-assisted adsorption. Ongoing XPS analysis will clarify the chemical composition of the DDQ-modified Au(111) surfaces and identify changes in the local chemical environment associated with adsorption. Complementary density functional theory calculations are planned to support plausible adsorption geometries and DDQ–Au interaction pathways.

9:00am **SS-FrM-4 Substrate Electrochemical Inertness as a Prerequisite for Reliable Electrocatalytic Characterization: Cu-Doped CNT Films Assessed by SECCM**, ***Miguel Bernal***, *Dario Stacchiola,* Brookhaven National Laboratory

Substrate selection is a decisive factor in the accurate electrochemical evaluation of active materials, as the support itself can obscure or distort the measured response. An ideal substrate combines electrical conductivity with chemical and electrochemical inertness under experimental conditions, ensuring that all measured signals are unambiguously ascribed to the material under investigation. In practice, however, true electrochemical neutrality is rarely achieved, since most conductive supports introduce parasitic contributions arising from double-layer capacitance, surface phase transitions, or residual catalytic activity.

In this context, we present copper-doped multi-walled carbon nanotube (Cu-CNT) films synthesized via spray pyrolysis using α-pinene as a renewable carbon precursor and ferrocene as catalyst, followed by microwave-assisted treatment to promote uniform copper incorporation at the nanotube surface. Films were deposited onto ITO substrates and characterized using scanning electrochemical cell microscopy (SECCM) coupled with cyclic voltammetry, enabling spatially resolved mapping of local electrochemical activity across thousands of discrete surface sites.

Systematic SECCM mapping of bare ITO first established its electrochemical profile as a reference baseline. CNT/ITO surfaces exhibited featureless voltammetric profiles with negligible background current, confirming that the nanotube overlayer effectively cover the ITO surface and yields a well-defined, electrochemically featureless support interface. Cu-CNT/ITO surfaces displayed a well-resolved anodic feature attributable to surface copper oxidation, clearly distinguishable from ITO contributions, alongside characteristic hydrogen and oxygen evolution onset potentials. Strikingly, statistical analysis of spatially resolved voltammograms revealed exceptional surface homogeneity across the Cu-CNT film, with markedly lower site-to-site variability in peak potential and current density than typically observed for heterogeneous metal–carbon interfaces.

These results demonstrate that spray pyrolysis combined with microwave treatment produces Cu-CNT surfaces with uniform electroactive site distribution and reproducible interfacial behavior. The electrochemical cleanliness of the CNT support, confirmed through rigorous substrate mapping, positions Cu-CNT films as model platforms for mechanistic studies of copper-mediated electrocatalysis.

9:15am **SS-FrM-5 Atomic-Scale Investigation of Li/Ag(111) Interfaces: New Phases, Li-Ag Alloy Formation and Lithiophilicity**, ***Yuchen Niu***, *Janice Reutt-Robey,* University of Maryland, College Park

Bimetallic Li alloys are very promising for solid-state battery applications, particularly as thin film interlayer in next-generation Li metal anodes. Exceptional lithiophilicity and Li-transport properties derive from the structure and reversible formation of Li-Ag alloys across a range of compositions. However, atomic-scale knowledge of the structure and Li-transport dynamics of Li-Ag alloy surfaces is limited.

We present an atomically detailed investigation of the formation and evolution of surface and near surface $Li_xAg(111)$ alloys. Lithium is vapor deposited on a well-characterized Ag(111) single crystal substrate under UHV conditions. Lithium films, from sub-monolayer to multilayer thickness, spontaneously form surface alloys at room temperature. Surface alloys, in turn, support and stabilize lithium metallic islands, reflecting their lithiophilicity. The atomic-scale structures, energetics and evolution of Li-Ag surface alloys are mapped with scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low energy electron diffraction (LEED). Unreported Li-Ag phases are revealed, including a $Li_xAg(111)$ solid solution wetting layer (which supports Li islands) and local $Li_1Ag_1(111)$-($\sqrt{3}\times1$) and Li_xAg herringbone phases. Mechanisms of Li_xAg alloy formation, lithiophilicity, stability of $Li/Li_xAg(111)$ interface, and the growth mode of Li islands are discussed. We further explore electric-field driven Li transport, using the STM tip for both introducing a localized field and subsequent characterization tool. Together, these results bridge atomic-scale surface

science and device-level interface engineering, offering mechanistic insights for next-generation Li-metal batteries.

9:30am **SS-FrM-6 Tracking Conducting Oxygen Ions in Solid Oxide Fuel CellElectrolytes by NAP-XPS**, *Po-Chiao Li,* National Synchrotron Radiation Research Center, Taiwan*;* ***Bo-Hong Liu,*** National Sun Yat-sen University, Taiwan

Solid oxide fuel cells (SOFCs) are an important energy technology for stationary power generation, distributed energy systems, and integration into future hydrogen economies.[1] Yttria-stabilized zirconia (YSZ), which conducts oxygen ions O^{2-}, is the most common solid electrolyte. The high operating temperatures of 600–1000 °C is considered a drawback, as it results in heat lost, thermal stress, and materials degradation.[2] Fundamental understanding to the behavior of the conducting ion of the electrolyte is a key for the design and improvement of novel solid electrolytes. In this talk, I will present the study of YSZ-based SOFC model systems using Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). On a YSZ single crystal, we confirmed the presence of the thermal activated oxygen ion. The oxygen ion induces chemical shift in the Y 3d binding energy while marginal change is shown in the Zr 3p spectra. This evidences the local electronic environment modulation of yttrium during the oxygen ion conducting. We further elucidate the influence of gas environments, temperature, and the presence of electrode materials on the oxygen ion. The result provides basic understanding for designing advanced electrolytes with improved performance, durability, and lower-temperature operation.

Keywords:

Solid Oxide Fuel Cell (SOFC) Yttria-Stabilized Zirconia (YSZ)Oxygen Ion ConductivityNear-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS)(1) Shi, H.; Su, C.; Ran, R.; Cao, J.; Shao, Z. Electrolyte materials for intermediate-temperature solid oxide fuel cells. Progress in Natural Science: Materials International 2020, 30 (6), 764–774.(2) Kim, S. K.; Lee, H. J.; Moon, J. Y.; Jo, Y.-R.; Lee, J.; Park, J.-H.; Kim, S.-D.; Joo, J. H. Understanding the phase stability of yttria stabilized zirconia electrolyte under solid oxide electrolysis cell operation conditions. Journal of Materials Chemistry A 2024, 12 (14), 8319–8330.

9:45am **SS-FrM-7 Enhancing Hydrogen Evolution via Cation-Regulated Interfacial Proton Transfer on Single-Atom Catalysts**, ***Zhen Meng***, *Xiaofeng Feng,* University of Central Florida

Hydrogen evolution reaction (HER) in neutral electrolytes is typically limited by sluggish proton transfer at the electrode–electrolyte interface. Although electrolyte cations are recognized as key components of the electrochemical interface, how they regulate interfacial proton-transfer kinetics on single-atom catalysts remains unclear. Here, we investigate neutral HER on Fe-N-C and Co-N-C single-atom catalysts in Na^+- and NH_4^+-containing electrolytes to reveal how cations modulate proton-transfer processes. Compared with Na^+, NH_4^+ substantially enhances HER activity on both catalysts and increases the exchange current density by more than 20-fold,indicating accelerated intrinsic HER kinetics. The Tafel slopes in Na^+ and NH_4^+ electrolytes are comparable, suggesting that NH_4^+ increases the reaction rate without altering the apparent HER pathway. Rotating ring-disk electrode (RRDE) control experiments indicate that the activity enhancement cannot be explained by bulk buffering effects or suppression of local pH variation. Instead, computational studies and in situ spectroscopic characterization reveal that NH_4^+ accumulation within the electric double layer reorganizes interfacial water, enables a more continuous hydrogen-bond network, and lowers the barrier for interfacial proton transfer. These interfacial modifications facilitate more efficient proton delivery from bulk electrolyte to the catalytic active sites. This work identifies ammonium cations as active regulators of interfacial proton-transfer kinetics in neutral HER and establishes cation-controlled interface engineering as an effective strategy for tuning electrocatalytic activity on single-atom catalysts.

10:00am **SS-FrM-8 Translating Interfacial Ion Activity to Electrochemical Reactivity**, ***Samuel Johnstone***, *Seth Anderson, Evan Grothen, Matthew Gebbie,* University of Wisconsin - Madison

Electrochemical reactivity hinges on the local environment at electrode-electrolyte interfaces, where interactions between the charged electrode, reactive species, and electrolyte ions combine to dictate charge transfer. Of significant interest is how interfacial ion assembly can be leveraged to control reactivity, and many recent studies have worked to identify how particular ions can influence the rate and selectivity of reactions such as hydrogen/oxygen evolution and CO_2 reduction. Electrostatically, ions with the opposite charge as the electrode (counterions) are expected to have a large presence at the interface, while ions with the same charge (co-ions) are expected to have a minor presence. However, many reaction systems utilize large polarizations and highly concentrated electrolytes, leading to correlated, charge-dense interfaces containing both counterions and co-ions. Therefore, it is important to consider the influence of both the counterion and the co-ion on reactivity and determine whether the combined effect of correlated ions differs from what would be expected from each ion individually. Here, we study the hydrogen evolution reaction in mixed salt electrolytes and show that counterions and co-ions act in tandem to significantly alter the interfacial water structure and influence the rate of reaction. We use a combination of interfacial techniques, including X-ray absorption spectroscopy and atomic force microscopy, to connect reactivity to changes in the structural and chemical makeup of the interface and again show that both ionic species together determine interfacial properties. Overall, our work provides fundamental insight into how correlated interfaces play a key role in modulating electrocatalytic reactions.

10:30am **SS-FrM-10 Caught in the Act: Correlating Chemical Transformations and Structural Evolution Under Reaction Conditions**, ***Slavomir Nemsak,*** Lawrence Berkeley National Laboratory **INVITED**

Understanding how catalysts behave under operating conditions remains a central challenge in surface science. This talk presents a multimodal platform combining ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and grazing incidence X-ray scattering (AP-GIXS) at the APPEXS endstation of the Advanced Light Source, enabling simultaneous chemical and structural characterization at the same sample spot under identical conditions. Case studies include Ni nanoparticle exsolution from perovskite hosts, Ag-Cu bimetallic nanoparticles restructuring during photocatalytic CO_2 reduction, hydrogen storage in Pd-Ni nanoparticles, ligand oxidation on $NaYF_4$ nanoparticles, and nanopatterned ceria under H_2 and CO_2 atmospheres. Through this examples, we demonstrate how coupled chemical and morphological dynamics are revealed only through simultaneous measurement. Neither technique alone captures the full picture, but together they establish mechanistic links between surface chemistry and structural evolution that are directly relevant to catalyst design.

11:00am **SS-FrM-12 The Importance of Interfacial Water for Achieving Long-Range Ordered Assemblies**, ***Kevin Rosso***, *Xiaoxu Li,* Pacific Northwest National Laboratory*; Tuan Ho,* Sandia National Laboratories, USA*; Duo Song, Sebastian Mergelsberg, Jianbin Zhou, Yining Wang, Narendra Adhikari, Nabajit Lahiri, Yatong Zhao,* Pacific Northwest National Laboratory*; Honghu Zhang,* Brookhaven National Laboratory*; Lili Liu,* Pacific Northwest National Laboratory*; Ruipeng Li,* Brookhaven National Laboratory*; Ping Chen, Mark Bowden, James De Yoreo, Zheming Wang, Carolyn Pearce, Xin Zhang,* Pacific Northwest National Laboratory

Self-assembly of nanocrystals by oriented attachment (OA) is a basis for growing larger crystals with defects organized along relict particle boundaries. A critical stage during OA events is the solvent separated state, in which the Angstrom-scale intervening water layers coating the particles provide the time in close proximity needed for interparticle torque acting across the gap to co-align particles.

This talk will feature new experimental and computational insights into how water structure on particle surfaces impacts particle interactions, using two illustrative systems.First, we examine the dispersion/aggregation of three morphologies of hematite nanocrystals in varied aqueous solutions using ex situ electron microscopy and in situ small-angle x-ray scattering. We demonstrate a unique tendency of (104) hematite nanoparticles to maintain a monodisperse state across a wide range of solution conditions not observed with (001)-and (116)-dominated particles, which instead form disordered aggregates. Density functional theory calculations reveal an inert, densely hydrogen-bonded first water layer on the (104) facet that favors interparticle dispersion.The finding clearly shows that facet-engineering is a route to controlling the hydration forces that influence the lifetime of the solvent-separated state.

Second, we demonstrate how macroscopic gibbsite mesocrystals emerge from nanoplates guided into staggered positions by directional sliding determined by intervening water layers. Electron microscopy and X-ray scattering reveal the monoclinic superlattice structure, based on nanoplate stacking with a uniform ≈50° stagger along the gibbsite [010] direction. In situ liquid-cell transmission electron microscopy captures preferential sliding along the gibbsite [010] direction, decelerating with increasing particle overlap. Molecular dynamics simulations reveal that this staggered

arrangement corresponds to a global free-energy minimum, rather than full alignment. The simulations also confirm that with 1-2 intervening water layers, particle sliding along the [010] direction is energetically favored.The finding clearly shows the critical role of interfacial water for achieving long-range ordered assemblies.

Our collective insights highlight the central role that interfacial water plays in determining the residence time and energy landscape for interparticle configurational searching during aggregation, in turn determining the extent of order achieved and the corresponding properties of the aggregates themselves.

11:15am **SS-FrM-13 Surface Hydration and Antifouling Activity of Zwitterionic Polymers*, Zhan Chen,*** University of Michigan

Zwitterionic materials are well known for their outstanding antifouling properties and have been widely explored in biomedical applications, drug delivery systems, and marine coatings. These properties are generally attributed to the strong surface hydration they maintain. However, probing this hydration in situ is challenging because it occurs at the solid–liquid interface. To address this, we have employed sum frequency generation (SFG) vibrational spectroscopy to study the interfacial hydration of several zwitterionic polymers, including poly(carboxybetaine), poly(sulfobetaine), and poly(trimethylamine N-oxide). As a second-order nonlinear optical technique, SFG provides intrinsic surface sensitivity at the sub-monolayer level due to its selection rules.

Our findings reveal that strongly hydrogen-bonded water molecules dominate the polymer–water interface, giving rise to the robust hydration layer characteristic of these materials. pH-dependent measurements further show that the surface hydration of poly(carboxybetaine) varies with pH, whereas poly(sulfobetaine) remains largely unaffected. These trends closely align with their respective antifouling performances, reinforcing the idea that surface hydration plays a central role in governing antifouling behavior.

Additional SFG studies demonstrate that protein adsorption does not significantly disrupt the hydration layer of zwitterionic polymers, in contrast to polyethylene oxide, whose surface hydration can be compromised by proteins. This highlights a key advantage of zwitterionic systems. Interestingly, mussels tend to avoid settling on zwitterionic surfaces; however, when physically constrained to remain in contact, they can still achieve strong adhesion. SFG results suggest that, unlike on conventional fouling surfaces where mussels first dehydrate the interface, they instead exploit interfacial water and adhesive proteins to bind to zwitterionic materials.

We also found that dissolved salts can weaken surface hydration through charge screening effects, potentially reducing antifouling performance. Nevertheless, when the spatial separation between charges within the zwitterionic structure is small, hydration remains strong even under high-salt conditions. Poly(trimethylamine N-oxide), with its closely spaced charges, is particularly effective at resisting salt-induced screening and maintaining a robust hydration layer.

11:30am **SS-FrM-14 Energetics of Water and Methanol Adsorption on CO-Precovered Pt (111) Surfaces: Solvent - Adsorbate Interactions*, Arjan Saha,*** Washington State University*; Valeria Chesnyak,* Oregon State University*; Marcus Sharp,* Pacific Northwest National Laboratory*; Nida Janulaitis,* University of Washington*; Zbynek Novotny,* Pacific Northwest National Laboratory*; Charles T. Campbell,* University of Washington*; Líney Árnadóttir,* Oregon State University*; Zdenek Dohnálek,* Pacific Northwest National Laboratory

Carbon monoxide (CO) is among the most widely studied molecules in surface science, serving as a probe for surface structure, a reactant in catalytic processes, and a model adsorbate for investigating adsorbate–adsorbate interactions. Here we employ single-crystal adsorption calorimetry (SCAC) and sticking coefficient measurements to understand the influence of preadsorbed CO on the interaction of Pt(111) with prototypical solvents, methanol and water (D2O). At 100 K, the initial sticking probability of D2O on CO/Pt(111) is high (~0.9) and increases asymptotically to unity with increasing D2O coverage. The corresponding D2O heat of adsorption remains constant over submonolayer coverages and is identical to that of water multilayers. This suggests that D2O binds more weakly on the CO/Pt(111) as compared with bare Pt(111). Therefore, the measured heat arises mainly from D2O–D2O hydrogen bonding, as CO blocks the Pt sites. As the temperature increases from 100 to 130 K, the initial sticking probability decreases from ~0.9 to ~0.2. This indicates that isolated water monomers become unstable and desorb with high probability before they can find other waters by diffusion and be stabilized via cluster formation. With increasing D2O coverage, the sticking probability again increases asymptotically to unity, but only at coverage well above 1 ML. This behavior indicates the formation of three-dimensional D2O clusters, demonstrating that the CO-covered Pt surface behaves as a non-wetting surface for water adsorption. Analogous studies for methanol on CO/Pt(111) reveal a similar trend in the heat of adsorption, indicating that methanol adsorption is also dominated by methanol–methanol hydrogen bonding rather than methanol–Pt interactions. These results show the impact of coadsorbed species on solvent binding and provide important insights into surface interactions relevant to electrodes and catalytic metal nanoparticles.

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