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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2. Aizawa, T.; Hayami, W.; Otani, S. Adsorption of H_2, $^2H_2$, O_2, and CO on ZrB_2(0001). *The Journal of Chemical Physics* **2002**, *117* (24), 11310–11314.

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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2. Mize, C. J., Crosby, L. D., Lander, E. K., Roy, S. “Modeling the Subsurface Adsorption of Atomic Oxygen in Silver from High Vacuum to High Pressure”, *Phys. Chem. Chem. Phys. 27*, 7816-7825 (2025).

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.

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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.

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Author Index

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