Surface Science
Room Central Hall - Session SS-ThP

Surface Science Poster Session

SS-ThP-2 Near Ambient Pressure XPS Indicates that the Relevant State of Silver under Ethylene Epoxidation Conditions is Mostly Metallic, *Elizabeth E. Happel,* Tufts University*; P. Christopher,* University of California at Santa Barbara*; M. Montemore,* Tulane University*; E. Sykes,* Tufts University

Epoxidation reactions are some of the highest value processes in the chemical industry; however, despite decades of research, the mechanism of ethylene epoxidation is still under debate. A central question in the field is the state of the industrial Ag catalyst under reaction conditions. Controversy remains about whether the active site for selective oxidation is metallic or oxidized and several in situ studies have reported the presence of both phases. We utilize near ambient pressure XPS under both purely oxidizing conditions and ethylene: oxygen ratios at a temperature that yields the same reactant chemical potentials as a typical flow reactor. Our XPS results reveal that electrophilic and nucleophilic oxygen formed on Ag(111) after exposure to pure oxygen at 433 K, with a O : surface Ag ratio of 0.11. However, when ethylene is introduced to the oxygen atmosphere at an industrially relevant 5:2 ratio, the nucleophilic oxygen is reacted away immediately, and the electrophilic oxygen coverage slightly increases which we attribute to the formation of carbonate which has the same binding energy as electrophilic oxygen. Most significantly, the O : surface Ag ratio decreases to 0.05, almost half of which is carbonate. These results indicate that the Ag(111) surface is mostly metallic under simulated reactor conditions meaning that Ag/oxide interfaces, at which the proposed oxametallacycle (OMC) intermediate is formed, must be considered in mechanistic epoxidation models.

SS-ThP-3 Surface Chemistry of Zirconium Borohydride on Zirconium Diboride (0001), *M. Trenary, Ayoyele Ologun,* University of Illinois - Chicago

Transition metal diborides are known to either have a metal-terminated or boron-terminated surface. While group-V MB_2 has boron-terminated surfaces, group-IV MB_2 has metal-terminated surfaces. ZrB_2, a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C and can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride $Zr-(BH_4)_4$ as a precursor. Using reflection absorption infrared spectroscopy (RAIRS), we investigated the surface chemistry of ZrB_2 growth from $Zr-(BH_4)_4$ on a $ZrB_2(0001)$ surface. Using low-energy electron diffraction and X-ray photoelectron spectroscopy (XPS), we demonstrate that ZrB_2 can have a boron-terminated surface in boron-rich conditions. The RAIR spectrum obtained after exposing the surface at 90 K to $Zr-(BH_4)_4(g)$ matched that of the pure compound, indicating adsorption without decomposition. However, new surface intermediates were formed upon heating to 280 K, as shown by the presence of vB-Ht stretch (2569 cm^{-1}) and δH-B-H (1228 & 1057 cm^{-1}) peaks in the RAIR spectra. Decomposition of $Zr(BH_4)_4$ on $ZrB_2(0001)$ surface at 1173 K revealed a $\sqrt{3}\times\sqrt{3}$ boron terminated surface, with a stoichiometry of $ZrB_{2.60}$. In contrast to the zirconium-terminated surface, the boron-terminated surface is resistant to oxidation.

SS-ThP-4 Selective Hydrogenation of 1,3-butadiene on a Pd/Cu (111) Single-Atom-Alloy, *Mohammad Rahat Hossain, M. Trenary,* University of Illinois at Chicago

Selective hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) is critical in refining alkene streams for high-quality polymer production. Typically, Pd and Pt are employed in hydrogenation reactions due to their nearly negligible barrier for H_2 activation. However, these catalysts are prone to coking and their high activity often reduces selectivity. Single-atom alloy (SAAs) catalysts are being developed to achieve high selectivity while retaining high activity. In an SAA, small amounts of an active metal, such as Pd or Pt, are doped into a less active host metal such as Cu. Previous work has shown that a Pd(111) surface exhibits superior selectivity for BD hydrogenation to 1-B compared to Pt(111),[1-4] suggesting that Pd/Cu(111) could be a suitable SAA model catalyst for this reaction. In this study, we investigated the adsorption and hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) over a Pd/Cu (111) SAA under ultrahigh vacuum (UHV) and ambient pressure conditions using reflection absorption infrared spectroscopy (RAIRS). Temperature programmed reaction spectroscopy (TPRS) in UHV showed that monolayer BD desorbs at 217 K, while 2nd-layer and multilayer BD desorb between 112 to 180 K. RAIRS detected gas-phase 1-B formation and BD consumption. In ambient pressure conditions, this reaction was found to be first-order (1.12±0.03) in H_2 and zero-order (-0.12±0.01) in BD, correlating to a turnover frequency of 36 s^{-1} at 380 K. The activation energy was calculated to be 63.2 ± 2.8 kJ/mol from an Arrhenius plot of the temperature dependence of the rate constant. Complete conversion of BD was found with 84% selectivity towards 1-B, without butane production. No surface species were detected during the reaction. Post-reaction analysis using Auger electron spectroscopy (AES) revealed carbon deposition, indicating some dissociation during hydrogenation.

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SS-ThP-5 The Influence of Substrate Roughness and Long-Range Molecular Order on 3-Mercaptopropionic Acid Displacement by 1-Decanethiol, *Lindsey Penland,* H. Hetti Arachchige, N. Dissanayake, R. Farber, University of Kansas

Thiolate self-assembled monolayers (SAMs) are widely used for their ability to tune the interfacial properties of Au surfaces for applications such as nano-fabrication and bio-functionalization. This molecular control over interfacial properties can be further enhanced by introducing a second molecular species, resulting in a binary SAM. Binary SAMs offer an appealing route to control the molecular scale density of specific functional groups. One approach to forming binary SAMs is through the displacement of one molecule with another through solution phase deposition. The fabrication of molecularly precise binary SAMs requires precise control of the molecular interactions and substrate properties, such as surface roughness.

In this work, using ultra-high vacuum scanning tunneling microscopy (UHV-STM) and solution-phase preparation methods, the relationship between chain length, functional group, and substrate roughness on the displacement of 3-Mercaptoproprionic Acid (MPA) by 1-Decanethiol (DT) was investigated. First, three categories of MPA substrates were prepared: **MPA-1)** well-ordered smooth surface formed during a 3 hr MPA incubation at 35 °C, **MPA-2)** disordered smooth surface formed during a 3 hr MPA incubation at 25 °C, and **MPA-3)** well-ordered rough surface formed during a 24 hr MPA incubation at 25 °C. Then, following the formation of **MPA-1, -2**, and **-3**, the substrates were sequentially placed in a 2 µM DT solution for 20 min, 60, min, 3 hr, and 24 hr. UHV-STM analysis of the MPA substrates showed that **MPA-1** and **MPA-2** had faster rates of displacement than **MPA-3** and resulted in a uniform high-density DT film across the surface. **MPA-3**, which started with a uniform MPA SAM and nanoscale roughness due to the formation of Au nano-islands across the substrate related to the longer MPA incubation time, had the slowest rate of displacement. Interestingly, the DT SAM that formed following displacement of the **MPA**-3 sample was comprised of the low-coverage, lying down phase (β) and 2-D gas phase (α) of DT. Ongoing work is focused on understanding the relationship between substrate roughness and MPA ordering on the slower displacement rate and low-density DT phases observed for **MPA-3**.

SS-ThP-6 Visualizing on-surface Intramolecular C-C Coupling Reaction Using Scanning Tunneling Microscopy and Tip-Enhanced Raman Spectroscopy, *Soumyajit Rajak,* N. Jiang, University of Illinois, Chicago

Metal surface-supported physicochemical transformations provide additional degrees of freedom to tune the structural and electronic properties of molecular functional materials. To obtain a higher degree of control over the reaction outcome, submolecular scale characterization of the chemical intermediates and their local environment is required. Determining the real-space surface adsorbed configurations of molecules is challenging using ensemble-averaged surface science techniques. Again, probing the effect of the local environment of chemical species is challenging because the spatial resolution of conventional optical spectroscopic techniques is limited by the diffraction limit of light. Coupling light with plasmonic nano-objects creates highly localized surface plasmons (LSPs), which allows us to break the diffraction limit. Herein we present a combined topographical and chemical analysis of different surface-adsorbed configurations and surface-sensitive arrangements of a tetrabenzoporphyrin molecule and their chemical reactivity on a metal surface using angstrom-scale resolution scanning tunneling microscopy (STM) and ultra-high vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Low temperature (77K) scanning tunneling microscopic images and localized surface plasmon resonance enhanced Raman signals reveal different adsorbate configurations of single molecule entities and their thermal reaction products with a fundamental view of adsorbate-substrate

binding interactions. TERS uses the apex of the STM tip made of a plasmonic metal as a nano object to couple light to the near field. The Raman modes of the nanostructure underneath this tip are enhanced by the nano-confined surface plasmons which allows us to obtain chemical information with Angstrom scale spatial resolution. The atomic scale insights obtained into the local environment enable precise control over the fabrication of molecules with tailored optoelectronic properties.

SS-ThP-7 Click Chemistry on Functionalized Silicon Surfaces: UHV- and Solution-Based Strategies, *T. Glaser,* Justus Liebig University Giessen, Germany; *J. Meinecke,* Philipps University Marburg, Germany; *C. Länger, L. Freund,* Justus Liebig University Giessen, Germany; *U. Koert,* Philipps University Marburg, Germany; **Michael Dürr,** Justus Liebig University Giessen, Germany

Click chemistry is a well-known and established reaction scheme in organic chemistry for the synthesis of well-defined organic molecular structures. The direct application of click chemistry reactions to selectively functionalized silicon surfaces could thus open the route to synthesizing new organic molecular architectures on these substrates, e.g., with tailored optical or physicochemical properties ("more than Moore"). However, click reactions such as the most prominent alkyne-azide coupling are performed in the presence of a catalyst dissolved in an adequate solvent. On the other hand, highly reactive surfaces such as the technologically most important Si(001) surface, are typically prepared and stored under UHV conditions in order to guarantee a high level of cleanliness and structural perfection. The direct application of solution-based click chemistry schemes to such vacuum processed surfaces thus seems as an experimental contradiction.

Here we show two different approaches to solve this problem: First, we demonstrate how to combine surface functionalization performed under UHV conditions with a solution-based alkyne-azide click reaction in order to build organic molecular architectures on functionalized semiconductor surfaces. The UHV-based functionalization of the Si(001) surface was realized via chemoselective adsorption of ethinyl cyclopropyl cyclooctyne (ECCO) from the gas phase [1]. The samples were directly transferred from UHV into the azide solution without contact to ambient conditions. The second organic layer was then coupled in acetonitrile solution via the copper-catalyzed alkyne-azide click reaction. Each reaction step was monitored by means of X-ray photoelectron spectroscopy in UHV; the N 1s spectra clearly indicated the click reaction of the azide group of the two test molecules employed, i.e., methyl-substituted benzylazide and azide substituted pyrene. Using optimized copper (I) catalysts, effective reaction yields of up to 75 % were obtained [2].

Second, a carefully tuned enolether/tetrazine cycloaddition was shown to be applicable even under UHV conditions and without catalyst [3]. We employed this reaction for coupling a tetrazine molecule to an enol ether group which was covalently attached on a Si(001) surface via cyclooctyne as a linker.

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SS-ThP-8 Adsorption of Fluorinated β-Diketones on a Surface of Zno Nanopowder: Dependence of Adsorbates on the Chemical Structure, *Sanuthmi Dunuwila, A. Teplyakov,* University of Delaware

This study investigates the surface modification of ZnO nanopowder using gas-phase fluorinated β-diketones, namely hexafluoro acetylacetone (hfacH) and trifluoro acetylacetone (tfacH), to elucidate their attachment chemistry.

Surface modification was investigated through i*n-situ* infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and solid-state NMR analysis (ssNMR) to determine the dominant adsorbate on nanopowder surfaces. To supplement the experimental findings, density functional theory was employed to identify stable surface species of ZnO nanopowder.

This study examines how the binding behavior of β-diketones on the ZnO surface varies depending on the specific nature of the β-diketone molecule. The gas phase for both diketones investigated consisted of the mixture of enol and ketone forms, with enol being most dominant for hfacH. Despite this observation, surface adsorption is dominated by the tetra-σ-bonded diketonate, which is very different from the commonly accepted adsorption model for β-diketones on oxide surfaces. In the case of tfacH, the adsorption is indeed dominated by the dissociated enolate form. These differences are apparently governed by the amphoteric nature of ZnO. When a more basic oxide material, MgO, is used, hfacH does form enolate as a dominant adsorbate, as confirmed by ssNMR.

This work expands our understanding of the β-diketone adsorption on oxide materials that is used in a variety of applications, from surface sensitization to heterogeneous catalysis, and from material growth to etching.

SS-ThP-9 In-situ X-Ray Absorption Spectroscopy (XAS) study of CeO2-based Catalysts for CO$_2$ Hydrogenation, *Irene Barba-Nieto,* Brookhaven National Laboratory, Spain; *J. Rodriguez,* Brookhaven National Laboratory

Carbon dioxide (CO$_2$) is the main gas responsible for the greenhouse effect in Earth's atmosphere, leading to higher global temperatures and climate change. To limit global warming to 1.5ºC and reach net zero carbon dioxide emissions by 2050, it is necessary to advance in industrial processes that facilitate the generation of clean fuels from CO$_2$. One of the most promising strategies in this regard is the utilization of CO$_2$ and its transformation into valuable chemicals.

This study examines the effectiveness of two catalyst types, RuCeO$_2$ and RuCeO$_2$-TiO$_2$ systems, for converting CO$_2$ into methane. Results demonstrate that despite lower Ru content, TiO$_2$-containing systems exhibit significantly enhanced catalytic activity for CO$_2$ conversion to methane. To understand this fact, in situ X-ray absorption measurements have been carried out on the Ru K-edge and Ce L$_3$-edge analyzing their behavior under H$_2$, CO$_2$ and H$_2$+CO$_2$ between 30ºC to 250ºC. The Ru K-edge results indicate that the RuCeO$_2$ systems display a remarkable oxidation-reduction capacity, as evidenced by the reduction of the metal center in the presence of both H$_2$ and CO$_2$/H$_2$, along with its oxidation in CO$_2$ atmosphere. However, this behavior undergoes a drastic change in the TiO$_2$-containing catalyst, as a consequence of strong CeO$_2$-TiO$_2$ interactions, where the presence of hydrogen at 250ºC leads to irreversible reduction of Ru.

The analysis of the Ce L$_3$-edge revealed that the RuCeO$_2$ systems predominantly exhibit Ce^{4+}, which was observed to undergo partial reduction under both H$_2$ and H$_2$/CO$_2$ atmospheres, followed by its re-oxidation under CO$_2$. However, the RuCeO$_2$-TiO$_2$ catalysts demonstrate a substantially higher concentration of Ce^{3+} compared to the RuCeO$_2$ sample under all conditions (H$_2$, CO$_2$, H$_2$/CO$_2$), with the amount of Ce^{3+} further increasing under atmospheres with H$_2$ and H$_2$/CO$_2$.

Therefore, the XAS findings indicate that the presence of TiO$_2$ in the catalysts stabilizes the metallic state of Ru, which remains in this state during the methanation reaction. Moreover, TiO$_2$ promotes the formation of Ce^{3+}, enhancing the catalysts' reactivity. This effect is attributed to TiO$_2$ facilitating an electronic transfer at the interface and perturbing the regular fluorite geometry of ceria, thus promoting the presence of Ce^{3+}. A trend that is in agreement with previous studies for CeO$_2$/TiO$_2$(110) model systems. The presence of Ce^{3+} significantly impacts the catalytic properties of the sample, aiding in the oxidation-reduction of Ce and stabilizing Ru. Consequently, the presence of reduced cerium plays a crucial role in determining the surface chemistry of the catalyst, crucial for efficiently converting CO$_2$ into methane.

SS-ThP-10 Insights from the Atomic Scale: Cobalt Sulfide Sheets on Au(111) and Initial Oxidation of Pt(111), *D. Boden, M. Prabhu, M. Rost, I. Groot,* **Jörg Meyer,** Leiden University, Netherlands

This poster highlights two recently published articles from a successful experiment-theory collaboration within the Leiden Institute of Chemistry:

1. Cobalt Sulfide Sheets on Au(111) [1] Transition metal dichalcogenides (TMDCs) are a type of two-dimensional (2D) material that has been widely investigated by both experimentalists and theoreticians because of their unique properties. In the case of cobalt sulfide, density functional theory (DFT) calculations on free-standing S−Co−S sheets suggest there are no stable 2D cobalt sulfide polymorphs, whereas experimental observations clearly show TMDC-like structures on Au(111). In this study, we resolve this disagreement by using a combination of experimental techniques and DFT calculations, considering the substrate explicitly. We find a 2D CoS(0001)-like sheet on Au(111) that delivers excellent agreement between theory and experiment. Uniquely this sheet exhibits a metallic character, contrary to

most TMDCs, and exists due to the stabilizing interactions with the Au(111) substrate.

2. Initial Oxidation of Pt(111) [2]
In situ scanning tunneling microscopy experiments on the initial oxidation of Pt(111) found complex intermediary platinum surface oxides, consisting of spoke wheel and stripe structures [3]. The structure of the spoke wheels is poorly understood because of their size and complexity. Here we employ atomistic thermodynamics based on an established reactive force field to investigate the structure and stability of spoke wheels at the elevated temperature (>530 K) and pressure (1–4 bar) conditions of the in situ experiments. At those conditions, the thermodynamic stability of the structural model for the spoke wheel is similar to that of the stripes, while the degree of surface oxidation is much lower. The spoke wheel is found to be much more stable than partially formed stripes with a similar degree of oxidation. These results are consistent with experimental findings, where the spoke wheel is observed first, at slightly lower oxygen pressures. They thus provide a better understanding of the oxidation pathway for Pt(111)-based catalysts in the context of oxidative catalysis.

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SS-ThP-11 Hard X-Ray Photoelectron Spectroscopy Reveals Fe Segregation in NiFe Electrodes During Oxygen Evolution Reaction, *Filippo Longo,* Chemical Energy Carriers and Vehicle Systems Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; P. Lloreda Jurado, J. Gil-Rostra, A. González-Elipe, F. Yubero,* Nanotechnology on Surfaces and Plasma, Institute of Materials Science of Seville (CSIC-US), Seville, Spain*; A. Borgschulte,* Chemical Energy Carriers and Vehicle Systems Laboratory, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Alkaline water electrolysis represents one of the simplest methods employed to perform water splitting reaction [1]. This process is one of the most efficient ways of producing H_2 and O_2 at low cost and high purity [2]. The bottleneck of this reaction stems from the sluggish kinetics of the anodic reaction, i.e., the oxygen evolution reaction (OER), which consists of a four-electron transfer process [3]. The extraordinary performance of NiFe as electrocatalysts for the OER [4] is still a subject of debate. The changes that occur on the electrode surface during electrochemical reactions add another dimension of complexity, which hinders the rational design of electrodes for water splitting. Particularly for binary alloy electrodes, there are various phenomena ranging from the formation of oxides, (oxy)hydroxides and the associated segregation of metal atoms. In this work, we study various NiFe electrodes as model systems for the OER. We have developed the procedure for the quantification of chemical depth-profiling by XPS/HAXPES measurement, showing a marked Fe segregation and dissolution. The results explain the electrochemical performance of NiFe electrodes for OER. All the electrodes studied suffer from segregation of iron and subsequent formation of FeO_x on the surface, with only minor influence from morphology, porosity and total Fe content.

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SS-ThP-12 Surface Modification of Titanium Dioxide Nanomaterials via Functionalization with Triol Compounds, *Asishana Onivefu, A. Teplyakov,* University of Delaware

Surface modification of titanium dioxide (TiO2) nanoparticles with trimethylolpropane (TMP) and dimethylolpropionic acid (DMPA) holds significant promise for advancing various technological applications. This research explores the functionalization of TiO2 nanomaterials and compares with pigmentary TiO2 surface coatings technologies used at industrial scale. Through a combination of experimental techniques including FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations, the interactions between surface modifiers and TiO2 are elucidated, revealing the formation of specific surface adsorbates. The results obtained from these studies demonstrated the displacement of surface impurities by adsorption of

functionalized small molecules and evaluated the displacement processes among these surface modifiers. Hexafluoroacetylacetone (Hfac) was used as a test compound in displacement investigations utilizing fluorine as a spectroscopic label to precisely trace the displacement chemistry with XPS. This work provides fundamental understanding and offers novel strategies and valuable insights for enhancing the performance of TiO2-based materials.

SS-ThP-13 Model Studies of Single-Atom Alloy (SAA) Catalysts, *F. Zaera, Ravi Ranjan,* University of California - Riverside

Single-atom alloy (SAA) catalysts have become a prominent way to enhance selectivity in a number of catalytic processes.The mechanism by which these alloys attain their improved performance is still being debated, however, especially when considering the effect of the reaction environment on their structure and chemical composition.We have embarked on a project to emulate those catalysts using model systems where the metals are dispersed as nanoparticles (NPs) onto a flat oxide surface under controlled ultra-high vacuum (UHV) conditions, characterized using a combination of surface-sensitive techniques, and tested for their catalytic behavior using a so-called high-pressure cell. This work focuses on the characterization of the nature of surfaces of SAA catalysts made out of Pt (minority) and Cu (majority) metals and their performance for the promotion of the hydrogenation of unsaturated aldehydes. $Cu/Ta_xO_y/Ta$ surfaces have been prepared via the oxidation of a Ta crystal followed by the vapor deposition of controlled amounts of Cu and characterized using reflection-absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) together with carbon monoxide (CO) as a probe molecule. A series of changes in the RAIRS data has been observed as a function of the Cu deposition time, an indication of the development of the Cu NPs from small clusters of atoms with multiple low-coordination sites to larger NPs with more basal planes exposed. These Cu NPs were found to form stable in the temperature range from 300 K to 600 K, but to change beyond 600 K. Like Cu, Pt and Cu-Pt NPs can be grown and characterized via CO titrations using RAIRS and TPD, following a similar approach. Kinetic measurements under catalytic conditions can then be performed to test the efficacy of the Cu, Pt, or Cu-Pt NPs catalysts supported on the tantalum oxide surface and to identify the appropriate structure-reactivity correlations.

SS-ThP-14 Enhancing Gas-Evolving Electrocatalysis by Tuning the Wetting Properties of Catalyst Microenvironment, *Kaige Shi, X. Feng,* University of Central Florida

Electrocatalysis plays a critical role in the conversion between electricity and chemical fuels. In addition to the development of electrocatalysts, efforts are made to understand and control their local environment during operations, which may influence the mass transport and kinetics of the reactions. Particularly, when gas-phase reactants or products are involved, the wetting properties of the microenvironment around catalytic sites can determine the distribution and diffusion of gas and liquid near the catalyst, and thus impact the catalytic performance. Here we present a study of catalyst microenvironment by controlling the wetting properties of carbon black, which is widely used as a catalyst support in electrocatalysis. We chose the electro-oxidation of hydrazine (N2H4) on carbon-supported Pt nanocatalyst and tuned the wetting properties of carbon support by doping of fluorine (F) or oxygen (O). Interestingly, the electrode with F-doped carbon (more hydrophobic) exhibited a higher activity than that with pristine carbon black. This is attributed to the accelerated removal of N2 gas generated from the catalyst, which would otherwise block the catalyst surface from liquid reactant. Furthermore, the electrode with O-doped carbon (more hydrophilic) showed an even higher activity, benefiting from the increased exposure of catalytic sites to liquid reactant. Our work demonstrates that controlling the catalyst microenvironment by doping of carbon black as catalyst support can be a powerful approach to enhance gas-evolving electrocatalysis.This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

SS-ThP-15 Advanced Evaluation of Sub-nm Surface Roughness using Electron Diffraction, *Rivaldo Marsel Tumbelaka, K. Hattori,* Nara Institute of Science and Technology, Japan

Achieving precise control over surface roughness at the sub-nanometer scale is paramount for enhancing the physical properties of semiconductor materials, particularly their electrical transport characteristics. Current methodologies, predominantly scanning probe microscopy, facilitate quantitative roughness assessment but face challenges when applied to surfaces with intricate structures such as vertical and facet faces of three-dimensional (3D) structures, owing to steric hindrance. Our prior research

effectively utilized reflection high-energy electron diffraction (RHEED) to observe atomic ordering on various structure surfaces in different directions, overcoming the challenge of steric hindrance [1-3]. In this study, we explore the potential of RHEED as an alternative avenue for evaluating surface roughness. Kinematic diffraction theory introducing diffraction spots from atomic positions, we explore the correlation between RHEED spot profile and surface roughness. Our approach involves systematically analyzing RHEED intensity profiles alongside surface roughness measurements of Highly Ordered Pyrolytic Graphite (HOPG), serving as a prototype sample.

HOPG samples with varying degrees of surface roughness were prepared via Ar sputtering, and their roughness was assessed using atomic force microscopy (AFM). Figure 1(a) shows a typical RHEED pattern for the HOPG whose roughness was 0.163 nm. Through the analysis of RHEED spot profiles, we discerned distinct intensity components, and , corresponding to sharpened and broadened spot intensities, respectively (Fig 1(b)). Our findings reveal an excellent correlation between increased surface roughness and the ratio of broadened spot intensity to total intensity (Fig 1(c)), indicating RHEED's adaptability for quantitative evaluation of surface roughness. This study not only shows how effective RHEED can be in measuring surface roughness but also demonstrates its usefulness in analyzing complex 3D surfaces in small-scale research and making semiconductor devices. The details will be discussed in the presentation.

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SS-ThP-16 Post-Synthesis Characterization of PtNi Nanowires for Enhanced Durability and Efficiency, *Cesar Saucedo, J. Mann, S. Zaccarine,* Physical Electronics USA

Polymer electrolyte membrane fuel cells (PEMFCs) offer a promising avenue for sustainable electricity production with minimal environmental impact. However, their widespread adoption faces challenges due to durability concerns and the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. Consequently, to advance PEMFCs, there is a pressing need for the advancement of catalyst technologies to overcome these limitations. Previous works has looked at the synthesis of extended-surface platinum-nickel (PtNi) nanowires (NWs) via atomic layer deposition (ALD) and their durability. Here we show how the composition and chemical states of the nanowires evolve after a series of post-synthetic modifications designed to maximize the longevity of these nanowires as catalysts. By combining complimentary surface analytical techniques (X-ray photoelectron spectroscopy, hard X-ray photoelectron spectroscopy, and nanoscale Auger electron spectroscopy) we develop a more complete model of the complex chemical nature of these catalysts than any single technique could by itself, accelerating the development of more durable and efficient PEMFC catalysts.

SS-ThP-17 Temperature Dependence of Surface-Catalyzed Ullmann Coupling via Activation of Highly Labile C-I, *Chamath Siribaddana, N. Jiang,* University of Illinois Chicago

The surface-catalyzed Ullmann-coupling via activation of highly labile C-I was studied on Au(111) using metal β-diketonato molecules with scanning tunneling microscopy. Unexpectedly the C-I bonds do not dissociate upon deposition of the molecule on the Au(111) surface held at room temperature which is known to catalyze the C-I dissociation reaction under such conditions. Rather the molecules form self-assembled monolayers stabilized by halogen bonds on Au(111). Annealing this sample to 100° C or direct deposition of the molecules on a Au(111) substrate held at 100° C triggers C-I bond cleavage. However, at 100° C intact C-I bonds can be observed, as only a portion of the molecules undergo C-I dissociation. Annealing to 200° C results in complete dehalogenation of the molecules and forming two types of COFs with triangle and cross-shaped connections. The dissociated Iodine atoms are incorporated within the COF. The two kinds of COFs exhibit only short-range network order due to the irreversible nature of the C-C bond formation. This trend is observed up to annealing temperatures of 370° C and no preference is observed towards one type of COF throughout this temperature range. Annealing temperatures beyond 400° C results in the decomposition of the molecules into its ligands which form a COF different from the COFs formed by the molecule.

SS-ThP-18 Accurate SIMS Characterization of Indium Implant in Silicon, *Xuefeng Lin, S. York, N. Kaushik,* Micron Technology

Secondary ion mass spectrometry (SIMS) is an ideal technique to provide indium (In) implant depth profiles in Si. However, this approach faces a critical challenge for overcoming the Si molecular mass interferences (MIs). These MIs can create high backgrounds during profiling and create an ambiguous determination of true In depth distributions. This phenomenon is especially true for SIMS analysis of lower dosed In implants <1E15 (at/cm^2). The challenge is that the combination of three Si isotopes creates significant MIs with a high mass resolution (MR) > ~45370 needed for separation from In. This is far beyond the magnetic sector dynamic SIMS mass separation capability <10000MR. A special SIMS analysis method of energy filtering by applying an offset voltage has been often used to minimize or remove the Si MIs for In implant analysis. However, applying the different voltage offsets produces different In tailing profiles and background levels. Fig. 1 shows seven SIMS depth profiles acquired on In30KeV7.85E13 implanted in Si, acquired by applying seven voltage offsets from -10 to -30eV, which create different In background levels and tailing profile shapes below 1E18 (at/cm^3). Increasing the voltage offset values from -10 to -30eV reduces the In background levels and shrinks the tailing profiles (Fig. 2, as determined at 100nm depth scale). Some previous SIMS studies used the background subtraction rather than applied voltage offset to characterize and obtain the precise In implant profiles, but determination of the specific subtraction value might be an issue since different subtractions would also affect the measured In implant doses and shapes. Fig. 3 shows the same SIMS In implant depth profiles with no subtraction and no voltage offset in green, and light and heavy subtractions in red and blue. To obtain more accurate In implant profiles in Si to overcome random background subtraction issues, we have used SIMS analysis combined with TCAD simulation. This combined method uses an appropriate voltage offset to obtain the SIMS profiles and then it is compared with the TCAD simulation, as shown in Fig. 4. Although several different voltage offsets have to be used to obtain the SIMS depth profiles to match the TCAD simulations to determine the applied voltage offsets at the beginning, once the SIMS analysis protocol is established, the analysis recipes would be used for analyzing the similar In implants in Si. In addition, we present the first study of using secondary ion energy distribution to determine the voltage offsets for analyzing In implants (Fig. 5) and that data will be shown in a full paper.

SS-ThP-19 Monitoring the Dynamics of Carbon-Carbon Bond Formation in Solid-Gas Heterogeneous Photoinduced Reactions, *Aakash Gupta, K. Blackman, A. Rodriguez,* Department of Physics, University of Central Florida*; M. Vaida,* Department of Physics and Renewable Energy and Chemical Transformations Cluster, University of Central Florida

Carbon-carbon (C-C) bond formation is paramount for a large variety of man-made chemicals such as commodity chemicals, synthetic materials, and pharmaceuticals. Monitoring the dynamics of the C-C bond formation in real time at surfaces and how this is influenced by the surface properties could be a game changer in improving the efficiency of various heterogeneous reactions. To study the dynamics of C-C bond formation, an experimental technique is employed that combines time-of-flight mass spectrometry with pump-probe spectroscopy and fast surface preparation with molecules. CH$_3$I and CO are used as precursor molecules. These molecules are dosed on metal oxides such as titanium dioxide and cerium oxide, on which the reactions are monitored.

The reaction is triggered by the pump laser pulse at a central wavelength of 266 nm which excites CH$_3$I into the dissociative A-band, which leads to the formation of CH$_3$ and I fragments. Subsequently, the probe laser pulse in ultraviolet spectral domain will ionize the reaction intermediates and final products, which are immediately removed from the surface by a static electric field and detected by the time-of-flight mass spectrometer. By varying the pump-probe time delay, the formation dynamics of CH$_3$ intermediate, as well as the reaction of CH$_3$ with CO, which leads to the formation CH$_3$CO (acetyl) and finally to CH$_3$COCH$_3$ (acetone) will be monitored. Details on CO and CH$_3$I partial pressure dependence as well as the influence of the surface composition and temperature will be presented.

SS-ThP-20 Transient Kinetics Study of CO Adsorption and Dissociation on a Ru (001) Surface Crystal, *Eliseo Perez Gomez,* Stony Brook University*; A. Boscoboinik,* Center for Functional Nanomaterials, BNL*; S. Sikder,* Stony Brook University

The adsorption and dissociation of carbon monoxide (CO) on metal surfaces is a fundamental reaction with many applications in the field of surface

chemistry. Particularly, this research studied the reaction between CO and a Ru (0001) single crystal. The adsorption and dissociation of the gas were investigated through the use of techniques such as infrared spectroscopy (IR) and mass spectroscopy (MS). We also employed a pulsing valve system, where controlled pulses of CO (and other reactant gases) influence the surface reaction. The effects of temperature and pressure on the adsorption kinetics and subsequent dissociation were explored in detail, to reach a broad understanding in the transient kinetics of the reaction. By modifying various parameters, the intention is to optimize the dynamic reaction conditions. Through this comprehensive approach, we sought to contribute valuable insights into the mechanisms driving CO adsorption and dissociation, with implications for catalysis and surface science applications.

SS-ThP-21 Bimetallic Pt-Sn and Ni-Cu Catalysts for Dehydrogenation Reactions Designed for Hydrogen Storage and Transportation, *Mengxiong Qiao, F. Li,* University of South Carolina*; A. Ahsen,* Gebze Technical University, Turkey*; D. Chen,* University of South Carolina

The use of liquid organic hydrogen carriers (LOHC) for the safe transport and storage of hydrogen requires the development of more selective catalysts for the dehydrogenation step. For example, the methylcyclohexane (MCH)-toluene pair is an attractive choice for a LOHC system, but a more selective dehydrogenation catalyst that is less prone to deactivation by fouling is needed. The bimetallic Pt-Sn and Cu-Ni systems are promising candidates for selective dehydrogenation catalysts; the addition of Sn to Pt catalysts is known to improve stability and decrease deactivation, and the addition of Cu to Ni catalysts may serve to break up the Ni ensembles that are responsible for nonselective decomposition. Model catalyst surfaces are prepared in ultrahigh vacuum (UHV) by deposition of thin films of Sn and Cu on Pt(111) and Ni(111) respectively, as well as by sequential vapor deposition of the two metals on a rutile $TiO_2(110)$ support. The surface compositions and bimetallic cluster sizes are investigated by low energy ion scattering, temperature programmed desorption with CO as a probe molecule, X-ray photoelectron spectroscopy, and scanning tunneling microscopy. Our studies have shown that Sn on Pt clusters tend to be rich in Sn due to the higher surface free energy of Pt compared to Sn, but cluster surfaces with a low concentration of Sn can also be prepared by deposition of small coverages of Sn on existing Pt clusters. In contrast, Cu on Ni clusters exhibit low Cu concentrations due to the diffusion of Cu into Ni, which is consistent with the facile alloying of Ni and Cu. A high-sensitivity recirculating loop microreactor system has been constructed for investigating the activity for MCH dehydrogenation on the bimetallic model surfaces under catalytically relevant atmospheric pressures; the microreactor is coupled directly to the UHV chamber so that the model catalysts can be transferred between the microreactor and UHV chamber without exposure to air.

SS-ThP-22 Coverage-Dependent Adsorption and Reactivity of Formic Acid on $Fe_3O_4(001)$, *Jose Ortiz-Garcia,* Pacific Northwest National Laboratory*; M. Sharp,* Washington State University*; Z. Novotny, B. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory

Formic acid (FA) is a crucial intermediate in important catalytic reactions such as Fischer-Tropsch synthesis and water-gas shift. On oxide surfaces, FA generally undergoes decomposition to CO or CO_2 through decarbonylation or decarboxylation mechanisms. We study the adsorption of FA on the reconstructed $Fe_3O_4(001)$ surface, followed by stepwise annealing using a combination of scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy, low-energy electron diffraction, and temperature programmed desorption (TPD). Dissociative adsorption of formic acid leads to the adsorbed formate and hydroxyl species on the surface. At low coverages, isolated formates and hydroxyls are observed. At intermediate coverages, local clustering of formate is observed, giving rise to both (1×1) and (2×1) surface periodicities. A fully saturated surface shows formates arranging predominantly in the (1×1) periodicity but retains some formates in the (2×1) periodicity in agreement with prior studies.[1] Annealing the surface to 450 K induces the formation of a well-ordered surface with a (1×1) periodicity, which results in the lifting of the surface reconstruction. Stepwise annealing enables monitoring of formate reactivity and surface structure changes. Two major peaks are observed via TPD at 525 and 565 K, indicating that the formate undergoes decarbonylation to CO and H_2O, with decarboxylation to CO_2 as a minor reaction pathway. STM reveals that annealing to 550 K leads to a partial recovery of the surface reconstruction and a possible formation of single oxygen vacancy defects. Further annealing to 650 K, which leads to the conversion of all formate species, reveals the formation of pits extended along the Fe rows. This is consistent with the non-stoichiometric formic acid decarboxylation accompanied by water formation proceeding via the Mars van Krevelen mechanism. We are currently focusing on understanding the initial stages of pit formation and the role of hydroxyls in reaction mechanisms. This work underscores the significance of fundamental studies to unravel the effect of structural changes on reaction mechanisms and dynamics.

SS-ThP-23 Using Single-Layered COFs to Stabilize Single-Atom Catalysts on Model Surfaces, *Yufei Bai, D. Wisman, S. Tait,* Indiana University Bloomington

Single-atom catalysts (SACs) combine the advantages of homogeneous and heterogeneous catalysts by limiting the reaction sites to isolated single metal atoms with well-defined chemical properties. A metal-ligand coordination method to stabilize SACs has been developed by the Tait group, in which 1,10-phenanthroline-5,6-dione (PDO) was used as ligand to coordinate with metal such as Pt, Fe, and Cr. To further improve the stability of SACs and increase the metal loading, we have synthesized single-layered covalent organic frameworks (sCOFs) on model surfaces under ultra-high vacuum (UHV) conditions or under ambient conditions. These networks with high porosity and stability were used to confine single Pt atoms coordinated with ligands into sCOF pores. Under UHV conditions, the successful formation of sCOF with regular hexagonal pores on the Au(111) surface was achieved by surface-mediated Ullmann radical coupling of 1,3,5-tris-(4-bromophenyl)benzene (TBB). Further sequential deposition of PDO ligand and Pt on the TBB-sCOF surface allowed the formation of single-site Pt catalysts by coordination interaction. The scanning tunneling microscopy (STM) images show the confinement of PDO in the sCOF pores, while X-ray photoelectron spectroscopy (XPS) has proven the existence of oxidation state of Pt, which is an indication of the single atom character. Under ambient conditions, an imine-linked sCOF was formed on the highly oriented pyrolytic graphite (HOPG) surface by a solid-vapor interface mechanism which allows for a high quality sCOF with long-range order. STM characterization has shown that regular sCOF networks with few defects were formed on the HOPG surface. This sCOF is facile to prepare and can be stored stably under ambient conditions for several weeks. These systems which combine the COF and metal-ligand coordination strategy to stabilize SACs offer the possibility to achieve higher stability and greater loading in SACs.

SS-ThP-24 N-doped Graphene Synthesis through N2+ Irradiation, *Buddhika Alupothe Gedara, P. Evans, Z. Dohnalek, Z. Novotny,* Pacific Northwest National Laboratory

Hydrogen (H_2) is one of the most promising clean and renewable energy sources. Nevertheless, the storage of hydrogen shows poor performance due to the low gravimetric and volumetric densities. Nitrogen-doped graphene (Gr) has been identified as a potential material for H_2 storage. Here, we study the growth of Gr on a Ru(0001) surface by chemical vapor deposition (CVD) of pyridine and N-doping through N_2^+ beam irradiation using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). A high-quality Gr film with low N densities was obtained by pyridine CVD on Ru(0001) at 1063 K. Higher concentrations of N-dopants were introduced on the Gr/Ru(0001) through low-energy N_2^+ irradiation at 100 eV.Nitrogen can be embedded in the Gr lattice preferentially in two configurations, namely graphitic N (N substituted in the C lattice) and pyridinic N (substitutional N next to a C vacancy). Atomically resolved STM images of graphitic and pyridinic-N defects demonstrate their preferential locations within the Gr Moiré. XPS shows that coverage of up to 3.9% of pyridinic-N and 2.3% of graphitic N can be embedded into the high-quality Gr film using N_2^+irradiation at room temperature, indicating a preferential formation of pyridinic N over graphitic N. Only graphitic N was observed upon annealing the ion-irradiated Gr/Ru(0001) to 1063 K, revealing higher thermal stability of graphitic N over pyridinic N. Our current efforts center on the adsorption studies of atomic hydrogen, its interactions with N dopants, and thermally induced diffusion.

SS-ThP-25 Coverage Dependent Interaction of N-Methylaniline with Pt (111) Surface, *Bushra Ashraf, D. Austin,* University of Central Florida*; N. Brinkmann, K. Al Shamery,* Carl von Ossietzky University Oldenburg, Germany*; T. Rahman,* University of Central Florida

The study of N-methylaniline (NMA) coverage dependent adsorption and reaction on the Pt(111) surface has gained attention because of the alkyl and aromatic amine interaction with transition metal surface.In this work, we use Density functional theory (DFT)simulations and experiment to study the structural and electronic properties of coverage dependent adsorption of NMA on Pt(111) surface. Firstly, we found that the molecule adheres to the surface by forming bonds with both the phenyl ring and the nitrogen (N) atom at the lower coverage. However, as coverage increases, a

fascinating phenomenon unfolds: the phenyl ring undergoes a distinctive tilting motion away from the surface. This tilting is accompanied by a change in the incline angle, transitioning from a mere 2° at low coverage (approximately 0.02 ML) to a substantial 33° at higher coverage (around 0.17 ML). This structural transformation also brings about a variation in the adsorption energy, shifting from -2.9 eV at low coverage to -1.5 eV at high coverage. Secondly, Bader charge analysis provided further insights into these interactions. At low coverage, the charge is sharing between the N atom and the surface Pt atom and from the surface to the carbon (C) atoms with in the phenyl ring. In contrast, at higher coverage, charge sharing primarily takes place through the N atom to the surface. This shift towards a more robust and bi-centered bonding with the surface at lower coverage indicates an increased propensity for molecular dissociation under these conditions. Finally, the analysis of the projected density of states shed more light on revealing the hybridization of the N p_z orbital with the Pt d_{z2} orbital at higher coverage. Conversely, at low coverage,hybridization of the carbon p_z orbital with the Pt d_{z2} orbital was observed, alongside Pt-N hybridization. These observations regarding molecular adsorption at different coverages indicated that, at high coverage, the molecule easily lifts off intact from the surface, while at low coverage, it tends to break into smaller fragments, consistent with experimental findings.

SS-ThP-26 Effect of an Electric Field on the Co Adsorption on Pt, *Steven Arias, D. Stacchiola, J. Boscoboinik,* Brookhaven National Laboratory
The adsorption of carbon monoxide (CO) on platinum (Pt) has been widely studied in the literature. Pt is one of the most frequently used active metals in catalysis, with CO playing an important role in many reactions, including hydrogenation, oxidation, and car emission controls. Here, we present our preliminary progress on the study of the effect of an electric field on CO adsorption on Pt. To do this, we designed a device that can apply a direct electric field to the surface of our Pt catalyst. A layer of porous alumina was synthesized on a Pt film, to allow CO molecules to diffuse through, making the underlying Pt accessible. A layer of graphene is added on top of the porous layer to complete the device. The bottom Pt and the top layer of graphene are biased to apply an electric field that directly interacts with the Pt surface where the CO is being adsorbed. Using infrared reflective adsorption spectroscopy (IRRAS) we study the effect of such fields on CO adsorption.

SS-ThP-27 Generating Defects in Semiconductor Monolayers on Metal Surface, *Sayantan Mahapatra, J. Guest,* Argonne National Laboratory, USA
Nanoscale observation and deliberate engineering of atomic defects within semiconductor transition metal dichalcogenides (TMDs) hold significant importance for their utilization in cutting-edge quantum optics and nano-electronic devices. Here, we demonstrate a versatile approach in generating single defects on TMDs monolayers using a photon source. The newly generated defects were visualized via scanning tunneling microscopy (STM) at room temperature at the atomic level. These defects can act as single-photon emitters (SPE) and their performance remains excellent in high vacuum conditions. Furthermore, our simulations provide insights into the defect formation energies on metal surfaces compared to an insulating surface. The charge transfer between the metal and monolayer TMDs plays a significant role in generating the defects. Furthermore, simulation also sheds light on the mono- or di-chalcogen vacancies as the potential candidates for these defects, thereby providing a direct match between theory and experiment.

SS-ThP-28 Characterization of Oxygen on Rh-Based Model Catalysts, *Maxwell Gillum, A. Gonzalez, E. Serna-Sanchez, A. Kerr, S. Danahey, D. Killelea,* Loyola University Chicago
The studies presented investigate the influence that surface and defect geometry have on the kinetics and reactivity of oxygen on various Rh-based model catalysts. The experiments focus on gaining structural information about the oxygen species present on the surface under various oxidative conditions utilizing scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). These techniques are used in unison with temperature programmed desorption (TPD) and Meitner-auger electron spectroscopy (MAES) to identify optimal conditions for further study

SS-ThP-32 Weakly and Strongly Adsorbed H₂O Layers on Hydroxylated SiO₂ Surfaces: Dependence on H₂O Pressure at Various Temperatures, *Samantha Rau, R. Hirsch, M. Junige,* University of Colorado Boulder; *A. Rotondaro, H. Paddubrouskaya, K. Abel,* Tokyo Electron America, Inc.; *S. George,* University of Colorado Boulder
Although H_2O adsorption on SiO_2 surfaces has been studied extensively, there are still many questions about the nature of the H_2O adsorbed layer. In this work, the H_2O layer thickness on flat hydroxylated SiO_2 surfaces was examined in a vacuum environment using in situ spectroscopic ellipsometry (SE). The H_2O water layer thickness was measured versus H_2O pressure at various temperatures. Complementary Fourier transform infrared (FTIR) analysis was also performed on SiO_2 powders.

Flat SiO_2 surfaces were hydroxylated using H_2O_2 plasma exposure to produce a hydrophilic surface with a water contact angle of < 10°. The in situ SE measurements were then conducted in a warm-wall vacuum chamber designed with a temperature-controlled sample stage. The H_2O layer thickness was measured versus pressure at various temperatures (Figure 1). The H_2O pressures were varied up to the saturation H_2O vapor pressure corresponding to the sample temperature. The H_2O layer thickness versus relative humidity was consistent with general expectations from the BET adsorption isotherm model.

The SE measurements showed that there were two distinct types of H_2O layers: a weakly adsorbed layer and a strongly adsorbed layer (Figure 2). The weakly adsorbed layer could be added or subtracted by increasing or removing the H_2O pressure. The strongly adsorbed layer was not lost by removing the H_2O pressure. However, the strongly adsorbed layer could be desorbed by heating the sample stage to 120°C. The SE measurements characterized the layer thicknesses for the weakly and strongly adsorbed layers versus H_2O pressure at various sample temperatures.

Using repeating H_2O exposures, the strongly adsorbed layer reached an approximate plateau at ~1 Å at various temperatures. In contrast, the weakly adsorbed layer obtained higher thicknesses at larger H_2O pressures. For example, the weakly adsorbed layer thickness was 7 Å at 92% relative humidity at 30.4°C (30 Torr). The FTIR investigations on SiO_2 powders were in qualitative agreement with the SE studies. These studies confirm the existence of a strongly adsorbed vicinal layer and a weakly adsorbed layer explained by the BET model on hydroxylated SiO_2.

SS-ThP-34 Insight into the Synergistic Effect of the Oxide–Metal Interface on Hot Electron Excitation, *Si Woo Lee,* Inha University, Republic of Korea
Understanding the role of electron transfer by energy dissipation during chemical reactions on metal catalyst surfaces is significant for elucidating the fundamental phenomena at solid−gas and solid-liquid interfaces [1]. Electronic excitation by molecular interactions between reactants and catalyst surfaces generates a flow of excited electrons with an energy of 1−3 eV; these are called hot electrons [2]. To reveal the chemically induced electronic excitations on metal catalyst surfaces, metal-semiconductor catalytic nanodiodes can be used for real-time hot electron detector [3]. In addition, recently, it was found that when the metal-oxide interface is formed, the excitation of hot electrons can be amplified [4].In this work, by employing our catalytic nanodiodes with well-defined oxide–metal interfaces [CeO₂ nanocubes (NCs)/Pt/TiO₂ Schottky nanodevices], which is the first platform for the quantitative analysis of electron transfer at interfacial sites, we observed electronic excitation under H2 oxidation at the CeO₂/Pt interface in real time. Direct measurement of the electron transfer as a function of the concentration of interfacial sites (by controlling the coverages of deposited CeO₂ on Pt) allowed us to investigate the effect of the oxide–metal interface on nonadiabatic electronic excitation during catalytic H_2 oxidation. Surprisingly, we observed that the efficiency of hot electron excitation was the highest at a specific concentration of CeO₂/Pt interfacial sites, confirming that the interface enhances hot electron excitation under exothermic catalytic reactions. Our operando techniques using Schottky nanodiodes with well-controlled oxide–metal interfaces enabled us to uncover the quantitative relationship between the nanoscale interface and hot electron excitation, thereby optimizing the catalytic performance, contributing to the rational design of future hot electron-based catalysts [5].References[1] Si Woo Lee *et al., Nano Letters,* **2023,** *23 (11),* 5373[2] Si Woo Lee *et al., Surface Science Reports,* **2021,** *76 (3),* 100532[3] Si Woo Lee *et al., ACS Catalysis,* **2019,** *9 (9),* 8424[4] Si Woo Lee *et al., Nature Communications,* **2021,** *12 (40),* 1[5] Eunji Lee *et al., ACS Catalysis,* **2024,** *14 (8),* 552

SS-ThP-35 Ab Initio Studies on Solid-Liquid Interfaces via Machine-Learned Force Fields, *A. Kretschmer, Markus Valtiner,* Christian Doppler Laboratory for Surface and Interface Engineering, Austria

In order to unravel the aqueous behavior at the solid liquid interface, we employ ab initio molecular dynamics simulations. To minimize finite-size artifacts of the simulation cell, but retain the chemical accuracy of ab initio simulations, we use on-the-fly machine-learned force fields as employed by the Vienna Ab Initio Simulation Package. We investigate two model systems, first we study the hydrophobic gap on graphene stacks with up to 4 layers, and second the dissolution behavior of different ionic salts. The salts are NaI, AgF, and NaCl, which all crystallize in the same NaCl structure, but have decreasing molar solubilities in water in the listed order. We first use static density functional theory calculations to relax the individual phases separately, which is then followed by training the force fields. We compare different functionals, PBE and RPBE, both with and without Grimme D3 corrections, R2SCAN+rVV10, and vdW-DF-cx, to find the optimal compromise in the description of the two phases. The lattice parameters of graphite are best reproduced by the PBE-D3 functional, while the other functionals with dispersion treatment perform reasonably well. The PBE and RPBE functionals without Grimme corrections on the other hand lead to dramatically overestimated c axes. The lattice parameter of the ionic salts is almost exactly reproduced by the vdW-DF-cx functional, but at more than 150-fold the computational expense compared to the other functionals, while the PBE and RPBE functionals overestimate the lattice parameter slightly. The PBE-D3, RPBE-D3 and R2SCAN+rVV10 functionals on the other hand slightly underestimate the lattice parameter. In bulk water, the bond lengths and angles are overestimated by roughly 3% consistently across all functionals, only the R2SCAN+rVV10 functional performs slightly better at 2% overestimation. Each phase is first trained separately by ab-initio simulations, until the Bayesian error threshold of the forces is undercut consistently. Thus, the interactions within the phase are learned in a smaller simulation cell, saving computation time. After training the individual phases, the solid phase is joined with the liquid phase and trained together to include the interface interactions into the force field. This training regime allows efficient training of the force field that can then be applied to much larger simulation cells than the training data.

SS-ThP-36 A Highly Integrated Correlative Microscopy Platform for In-Situ AFM-SEM-EDS, *Kerim T. Arat, W. Neils,* Quantum Design Inc.*; S. Spagna,* Quantum Design International

The integration of AFM and SEM techniques within a single platform implemented in a highly integrated tool offers the advantage of utilizing the complementary strengths of two different imaging modalities without the inherent complications of sample transfer. This is not only a significant improvement in time to results but also ensures high confidence in correlation accuracy and eliminates the risk of sample contamination.

In previous work, we developed a correlative microscopy platform that combines AFM and SEM [1]. These techniques can map the surface in high resolution. The trunnion stage, with up to 80° tilt capability, allows monitoring of process quality such as tip measurement or monitoring tip-sample interaction [2]. In addition to topography, the platform is able to extract electrostatic and magnetic information from the sample with electrostatic force microscopy (EFM) and magnetic force microscopy (MFM) modes. However, none of these provide the ability to determine the sample's elemental composition.

We have extended the capabilities of the correlative platform with an energy-dispersive X-ray spectrometer (EDS) to extract elemental information from the sample. The spectrometer is based on the silicon drift detector (SDD), which provides high energy resolution (< 133 eV, Mn-Kα).Its graphene-based window offers detection of elements down to carbon. The EDS elemental identification algorithm uses a background subtraction method and compares the resulting spectra to reference datasets based on the NIST database [3]. Both hardware and software integration allow correlation of elemental information with the other imaging modalities that the tool can provide where one can superimpose topography and elemental information.

Integration of EDS adds a significant analysis capability to AFM-SEM techniques applicable to a diverse range of materials such as metals, alloys, ceramics, and polymers. With this addition, researchers can obtain in-situ correlation of high-resolution, localized elemental information with high-resolution lateral and vertical topographical information, without the complications of sample transfer.

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SS-ThP-37 In-Situ Characterization of Au Capping on Superconducting Nb(100), *Van Do, H. Lew-kiedrowska,* University of Chicago*; C. Kelly,* National Cheng Kung University (NCKU), Taiwan*; S. Willson, S. Sibener,* University of Chicago

Nb is the highest temperature elemental superconductor, however, its application in particle accelerators and quantum computers are limited by growth of surface native Nb oxides. Au capping layers have been shown to prevent deleterious Nb oxidation, however, Au adsorption, growth, and morphology on Nb has not been fully investigated. This work characterizes physical deposition and subsequent anneals of sub-monolayer to monolayer converges of Au on Nb(100) using Scanning Tunneling Microscopy, X-ray and UV Photoelectron Spectroscopy, and Auger Electron Spectroscopy. Our preliminary results show Au island formation at annealing temperatures as low as 350 ℃. Additionally, Au continued to sinter, forming larger islands with increasing temperature until desorption at 900 ℃.

SS-ThP-38 Characterization of Oxidized Rhodium Surface Structures, *Elizabeth Serna-Sanchez, D. Killelea,* Loyola University Chicago

Heterogeneously catalyzed oxidation reactions, such as the catalytic process of converting CO to CO_2, are extensively utilized for the production of modern commodities. However, there remain key questions about the atomic level details of these catalytic processes. In order to further our understanding of the process, the investigation herein will focus on characterization of the structures formed and quantification of the amount of oxygen in and on stepped Rh surfaces.A curved Rh(111) crystal will be employed, where the step with varies monotonically across the face from the (111) apex. Scanning tunneling microscopy (STM) images will help to illustrate how the behavior of oxygen will be affected by features such as surface defects and step width. Alongside the STM, other techniques such as Meitner-Auger electron spectroscopy (MAES), temperature programmed desorption (TPD), and low energy electron diffraction (LEED) will be used to identify the various species of oxygen and the structures they form on the surface.

SS-ThP-39 Investigation of Carbon Monoxide (CO) Oxidation on Rh(111) with Reflectance Absorbance Infrared Spectroscopy (RAIRS) and Temperature Program Desorption (TPD), *Alexis Gonzalez, D. Killelea,* Loyola University Chicago

To create accurate models of catalysis, the speciation and kinetics of catalytic systems must first be experimentally determined. In previous studies, we have shown that Rh-based catalysts provided a robust model system to study oxidation reactions due to the reliability with which we can produce a limited number of oxygen species on the surface. This allowed for better control of the oxygenaceous species present in the system. By probing the reactivity of these various surface species, such as adsorbed surface oxygen and subsurface oxygen, using the CO oxidation reaction we were able to determine the influence of various oxygen species on kinetics of oxidation. Herein, we present preliminary data on how the integration of reflectance absorbance infrared spectroscopy(RAIRS) into our ultra-high vacuum (UHV) setup. IR and TPD spectra indicated that there was more carbon dioxide production on the Rh(111) surface prepared with molecular oxygen than the surface prepared with atomic oxygen. This seemingly contradicted what was expected due to the higher oxygen coverage on the surface prepared with atomic oxygen. IR spectroscopy was used concurrently with temperature programmed desorption (TPD) experiments to collect real time information about the surface composition of the crystal as the CO oxidation reaction was occurring.

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George, Steve: SS-ThP-32, 6
Gillum, Maxwell: SS-ThP-28, **6**
Gil-Rostra, Jorge: SS-ThP-11, 3
Glaser, Timo: SS-ThP-7, 2
Gonzalez, Alexis: SS-ThP-28, 6; SS-ThP-39, **7**
González-Elipe, Agustin R.: SS-ThP-11, 3
Groot, Irene: SS-ThP-10, 2
Guest, Jeffrey: SS-ThP-27, 6

Gupta, Aakash: SS-ThP-19, **4**
— H —
Happel, Elizabeth E.: SS-ThP-2, **1**
Hattori, Ken: SS-ThP-15, 3
Hetti Arachchige, Hirushan: SS-ThP-5, 1
Hirsch, Rebecca: SS-ThP-32, 6
Hossain, Mohammad Rahat: SS-ThP-4, **1**
— J —
Jiang, Nan: SS-ThP-17, 4; SS-ThP-6, 1
Junige, Marcel: SS-ThP-32, 6
— K —
Kaushik, Naveen: SS-ThP-18, 4
Kay, Bruce: SS-ThP-22, 5
Kelly, Chi: SS-ThP-37, 7
Kerr, Allison: SS-ThP-28, 6
Killelea, Dan: SS-ThP-28, 6; SS-ThP-38, 7; SS-ThP-39, 7
Koert, Ulrich: SS-ThP-7, 2
Länger, Christian: SS-ThP-7, 2
Kretschmer, Andreas: SS-ThP-35, 7
— L —
Länger, Christian: SS-ThP-7, 2
Lee, Si Woo: SS-ThP-34, **6**
Lew-kiedrowska, Helena: SS-ThP-37, 7
Li, Fangliang: SS-ThP-21, 5
Lin, Xuefeng: SS-ThP-18, **4**
Lloreda Jurado, Pedro Javier: SS-ThP-11, 3
Longo, Filippo: SS-ThP-11, **3**
— M —
Mahapatra, Sayantan: SS-ThP-27, **6**
Mann, Jenny: SS-ThP-16, 4
Meinecke, Jannick: SS-ThP-7, 2
Meyer, Jörg: SS-ThP-10, **2**
Montemore, Matthew M.: SS-ThP-2, 1
— N —
Neils, William K.: SS-ThP-36, 7
Novotny, Zbynek: SS-ThP-22, 5; SS-ThP-24, 5
— O —
Ologun, Ayoyele: SS-ThP-3, **1**
Onivefu, Asishana: SS-ThP-12, **3**
Ortiz-Garcia, Jose: SS-ThP-22, **5**
— P —
Paddubrouskaya, Hanna: SS-ThP-32, 6
Penland, Lindsey: SS-ThP-5, **1**
Perez Gomez, Eliseo: SS-ThP-20, **4**

Prabhu, Mahesh: SS-ThP-10, 2
— Q —
Qiao, Mengxiong: SS-ThP-21, **5**
— R —
Rahman, Talat: SS-ThP-25, 5
Rajak, Soumyajit: SS-ThP-6, **1**
Ranjan, Ravi: SS-ThP-13, **3**
Rau, Samantha: SS-ThP-32, **6**
Rodriguez, Alejandro: SS-ThP-19, 4
Rodriguez, Jose: SS-ThP-9, 2
Rost, Marcel: SS-ThP-10, 2
Rotondaro, Antonio: SS-ThP-32, 6
— S —
Saucedo, Cesar: SS-ThP-16, **4**
Serna-Sanchez, Elizabeth: SS-ThP-28, 6; SS-ThP-38, **7**
Sharp, Marcus: SS-ThP-22, 5
Shi, Kaige: SS-ThP-14, **3**
Sibener, Steven: SS-ThP-37, 7
Sikder, Sayantani: SS-ThP-20, 4
Siribaddana, Chamath: SS-ThP-17, **4**
Spagna, Stefano: SS-ThP-36, 7
Stacchiola, Dario: SS-ThP-26, 6
Sykes, E. Charles H.: SS-ThP-2, 1
— T —
Tait, Steven: SS-ThP-23, 5
Teplyakov, Andrew: SS-ThP-12, 3
Teplyakov, Andrew V.: SS-ThP-8, 2
Trenary, Michael: SS-ThP-3, 1; SS-ThP-4, 1
Tumbelaka, Rivaldo Marsel: SS-ThP-15, **3**
— V —
Vaida, Mihai: SS-ThP-19, 4
Valtiner, Markus: SS-ThP-35, **7**
— W —
Willson, Sarah: SS-ThP-37, 7
Wisman, David: SS-ThP-23, 5
— Y —
York, Scott: SS-ThP-18, 4
Yubero, Francisco: SS-ThP-11, 3
— Z —
Zaccarine, Sarah: SS-ThP-16, 4
Zaera, Francisco: SS-ThP-13, 3