Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room On Demand - Session HC-Contributed On Demand

Fundamental Discoveries in Heterogenous Catalysis Contributed On Demand Session

HC-Contributed On Demand-1 Operando Structural Characterization of Co-Promoted MoS$_2$ Nanoparticles Under Hydrodesulfurization Reaction Conditions Using the Reactor STM*, Mahesh Krishna Prabhu,* Leiden University, The Netherlands*; I. Groot,* Leiden University, Netherlands

Hydroprocessing plays a key role in reducing global SOx and NOx emissions in order to abate the global warming and the associated climate change. Understanding and improving the widely used Co-promoted MoS$_2$ catalysts for hydrodesulfurization (HDS) is an important step in this direction. In this presentation, operando structural characterization of Co-promoted MoS$_2$ nanoparticles at semi-industrial reaction conditions will be presented. ReactorSTM[1,2] has been used to obtain atom-resolved images of Co-promoted MoS$_2$ and closely associated phases such as CoS$_2$ under a gas mixture of hydrogen and methanethiol at industrially relevant conditions. Ex-situ XPS characterization has been performed to investigate the chemical changes occurring on the catalyst surface. Additionally, candidate atomic models to explain the STM images have been proposed. The results of this study provide valuable insights into the HDS activity of Co-promoted MoS$_2$ nanoparticles.

[1] Review of Scientific Instruments 85, 083703 (2014);[2] Nature communications volume 10, 2546 (2019)

HC-Contributed On Demand-4 Understanding Ligand-Directed Heterogeneous Catalysis: When the Dynamically Changing Nature of the Ligand Layer Controls the Hydrogenation Selectivity*, Swetlana Schauermann,* *C. Schroeder, M. Schmidt,* Kiel University, Germany

Selectivity of multi-pathway surface reactions depends on subtle differences in the activation barriers of competing reactive processes, which is difficult to control. One of the most promising strategies to overcome this problem is to introduce a specific selective interaction between the reactant and the catalytically active site, directing the chemical transformations towards the desired route. This interaction can be imposed via functionalization of a solid catalyst with ligands, promoting the desired pathway via steric constrain and/or electronic effects. The microscopic-level understanding of the underlying surface processes is an important prerequisite for rational design of this new class of ligand-functionalized catalytic materials.

In this contribution, we present a mechanistic study on formation and dynamic changes of a ligand-based heterogeneous Pd catalyst for chemoselective hydrogenation of a,b-unsaturated aldehyde acrolein. Deposition of allyl cyanide as a precursor of a ligand layer renders Pd highly active and nearly 100 % selective toward propenol formation by promoting acrolein adsorption in a desired configuration via the C=O end. Employing a combination of real space microscopic (STM) and *in operando* spectroscopic (IRAS) surface sensitive techniques, we show that an ordered active ligand layer is formed under operational conditions, consisting of stable butylimin species. In a competing process, unstable amine species evolve on the surface, which desorb in the course of the reaction. Obtained atomistic-level insights into the formation and dynamic evolution of the active ligand layer under operational conditions provide important input required for controlling chemoselectivity by purposeful surface functionalization.

HC-Contributed On Demand-7 Derivatization Effect of Cobalt Phthalocyanine on the Catalytic Activity for Carbon Monoxide Reduction*, Yutaro Umejima,* *J. Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

The electrochemical conversion of carbon monoxide (CO) has attracted attention for its use in renewable energy sources. In general, noble metals have been commonly used as effective catalysts for the carbon monoxide reduction (COR) reactions. However, noble metals have many problems including high overpotential and high cost. Therefore, noble-metal-free catalysts with high COR reaction activity are required. Recently, cobalt phthalocyanine (CoPc) has been confirmed to exhibit a high activity in the COR reaction [1].On the other hand, it has been found that the catalytic activity of the iron phthalocyanine (FePc) molecule for oxygen reduction reaction (ORR) is significantly improved by its derivatization [2].

In this study, we elucidate the change in catalytic activity with derivatization of CoPc for the reduction process of CO using first-principles calculations. The catalytic activity for the COR reactions was evaluated using the computational hydrogen electrode model proposed by Nørskov *et al*. [3] For derivative molecules of CoPc, we considered CoAzPc-4N and CoAzPc-8N. It has been confirmed that such an introduction of N to Pc results in the catalytic activity improvement for ORR [2]. The CoAzPc-4N and CoAzPc-8N molecules have four pyridine and pyrimidine rings, respectively, instead of the four benzene rings of CoPc. In order to evaluate catalytic activities of CoPc and its derivatives for COR reaction, we calculated free energies for various intermediates. Methane and methanol were assumed as final products.

It has been confirmed that (1) the reaction proceeds as CO→*CO→*CHO→*CHOH→*CH$_2$OH→CH$_3$OH, (2) methanol is the most stable final product, and (3) the reaction determining step is *CHO→*CHOH for CoPc and its derivatives. The overpotentials of CoPc, CoAzPc-4N, and CoAzPc-8N at the reaction determining step are estimated to be 1.21 V, 1.18 V, and 1.14 V, respectively; such derivatization of CoPc improves the catalytic activity of the COR reaction as well as the ORR of FePc. It has been concluded that the substitution by the electron-withdrawing species leads to the higher catalytic activity of CoPc for the COR reaction.

References

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[2] H. Abe, Y. Hirai, S. Ikeda, Y. Matsuo, H. Matsuyama, J. Nakamura, T. Matsue, H. Yabu, NPG Asia Materials **11**, 57 (2019)

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HC-Contributed On Demand-10 Surface Characterization and Methane Activation of SnO$_x$/Cu$_2$O/Cu(111) Inverse Model Catalysts*, Jindong Kang,* Stony Brook University*; J. Rodriguez ,* Brookhaven National Laboratory

Many efforts have been devoted to efficiently utilize methane, the primary component of abundant low-cost natural gas and a major contributor to global warming. Therefore, the conversion of methane to other value-added chemicals has been one of the intensive studies in catalysis in the past several decades. The key to converting methane to such chemicals is to activate highly stable C-H bonds in methane and control the first C-H bond dissociation known as the rate limiting step in the direct methane conversion process. The aim of this project is to develop an efficient catalyst which can reduce the energy barrier for the first C-H bond dissociation and activate methane at low temperatures. Herein, we introduce a novel SnO$_x$/Cu$_2$O/Cu(111) inverse model catalyst. The surface structure and the chemical state of SnO$_x$ nanoclusters on Cu$_2$O/Cu(111) were investigated by Scanning Tunneling Microscopy (STM) and Ambient Pressure X-ray Photoemission Spectroscopy (AP-XPS). Our results show that this novel catalyst activates methane at low temperature and will provide new guidance to design new efficient catalysts for the methane conversion.

HC-Contributed On Demand-13 Crystal Plane Effect of Cu$_2$O Clusters on the Catalytic Performance of Pt/Cu$_2$O under CO Oxidation*, Seunghwa Hong,* *H. Choi, D. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Metal nanoparticle supported on metal oxide is the most widely used heterogeneous catalyst. In supported metal catalyst, the interface between metal and support modify their coordination and electronic structure due to strong metal-support interaction (SMSI) which result in altering catalytic performance. Thus, controlling the interface of metal and support is a key strategy for enhancing catalytic activity. However, a fundamental understanding of SMSI is not fully unveiled due to difficulties in characterization in actual catalytic reaction conditions. Herein, using Cu$_2$O nanocubes and octahedral clusters as model catalysts, we investigated the catalytic performances of Pt/Cu$_2$O by using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and diffuse reflectance FT-IR spectroscopy (DRIFT) as in-situ characterization technique. The catalytic measurement as well as in-situ surface characterization results indicates that the facet-dependent interfacial site affects the catalytic activity of CO oxidation significantly, implying the tunability of the catalytic activity by controlling the crystal plane of Cu$_2$O.

HC-Contributed On Demand-16 Catalytic Synergy on PtNi Bimetal Catalysts Driven by Interfacial Intermediate Structure*, **Taek-Seung Kim,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)*; J. Kim,* Institute for Basic Science (IBS), Korea (Republic of)*; H. Song, D. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Korea (Republic of)

Platinum–based bimetallic catalysts exhibit surface atomic rearrangement at various adsorbate environments, which significantly impacts catalysis. A molecular-level understanding of intermediate structures on model catalysts including single crystal and nanoparticle surfaces under reaction conditions is essential for developing novel, high-performance bimetal catalysts. By using *operando* surface techniques on PtNi single crystal and nanoparticles, we address the issue of bridging pressure/materials gap in the molecular mechanism of bimetallic synergy effect. We show that intermediate Pt-NiO_{1-x} interfacial structures drive the catalytic synergistic effect observed on both single crystal Pt_3Ni (111) surface and Pt_3Ni nanocrystals. *Operando* surface techniques, including ambient pressure scanning tunneling microscopy and X-ray photoelectron spectroscopy (AP-XPS), were used to probe the Pt-NiO_{1-x} interfacial structures on Pt_3Ni (111). The DFT calculation confirms the role of intermediate structure which boosts the catalytic activity of CO oxidation. For further understanding of the bimetallic synergy in the Pt_3Ni nanocrystal, we utilized environmental transmission electron microscopy, and operando spectroscopies including AP-XPS and diffuse reflectance infrared Fourier-transform spectroscopy. Real-time microscopic observation at ambient pressure shows the formation of oxygen-driven Ni oxides clusters on the surface and direct evidence of Pt-NiO_{1-x} interfacial structure formation. Spectroscopic analysis and catalytic measurements elucidate the role of Pt-NiO_{1-x} interfacial structures and the catalytic reaction mechanism for CO oxidation. Our results indicate that oxide-metal interfacial intermediate structures is directly related to the enhancement of the catalytic activity, and strong metal-support interaction effect observed in mixed catalysts.

HC-Contributed On Demand-19 Reactivity of Butanol on TiO_2/Au(111) Inverse Model Catalysts*, **Lyssa Garber**, A. Galgano, C. Rogers, A. Baber,* James Madison University

Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon neutral cycle. Biobutanol has low volatility and multiple transportation options making it an attractive alternative fuel. To better understand how butanol breaks down in heterogeneous catalytic processes, temperature programmed desorption (TPD) is used to investigate its reaction on TiO_2/Au(111). Inverse model catalysts of interest were formed by depositing TiO_2 nanoparticles onto Au(111) using physical vapor deposition. Low temperature desorption features help to understand how the molecule adorbs to the surface while the high temperature peaks are used to understand chemical reactivity and selectivity. Low temperature peaks indicate different molecular packing of 1- and 2-butanol. The major high temperature products from the reaction of 2-butanol on TiO_2/Au(111) are 2-butanone and butene, observed at ~500 K. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. Preliminary studies of the reaction of 1-butanol indicate that both reduced and oxidized products are formed, but need to be further studied to identify the species and stability. Atomic force microscopy (AFM) images show that the inverse model catalyst has ~0.16 ML of TiO_2 dispersed across the Au(111) surface in predominantly 1D nanoparticles. Early studies of butanol on TiO_2/Au(111) suggest that the structure affects the reactivity and stability of butanol at high temperatures.

HC-Contributed On Demand-22 Surface-Dependent Selectivity of Ethanol With TiO_2 Modified Au(111) Model Catalysts*, **Clayton Rogers**, D. Boyle, M. DePonte, A. Baber,* James Madison University

The dehydrogenation of small primary alcohols is widely used to produce H_2 and aldehydes to be used as feedstock chemicals for further manufacturing processes. While wet dehydrogenation is used in industry, it is wasteful and complicates the separation process for the desired products. The use of reducible oxides provides an easily regenerated source of oxygen on Au(111) for the reaction of ethanol. Depending on the surface preparation conditions, Au(111) supported TiO_2 nanoparticles react with small alcohols to form either oxidization or elimination products. In this work, we investigate the role of surface modifications on the selective oxidation of ethanol to acetaldehyde over the elimination reaction to form ethylene and water. A systematic study of ethanol reactivity over several TiO_2/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO_2/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x (x<2) and coverage of TiO_2. Atomic force microscopy (AFM) was used to study the structure of the Au(111) supported TiO_2 nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) was used to monitor the selectivity of the reaction between ethanol and TiO_2/Au(111). Low coverages of fully oxidized TiO_2 nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde, and subsequent experiments indicate that selectivity is not affected, even without reoxidation treatments.

HC-Contributed On Demand-25 Active Sites and Structural Transformation of $NiFeO_x$ Catalysts during Electrocatalytic Oxygen Evolution Reaction: Effects of Catalyst Loading and Support*, **Xingyi Deng**, D. Kauffman, D. Sorescu,* National Energy Technology Laboratory

Particle size, catalyst support, and in situ structural transformation can all impact the electrocatalytic activity of metal and oxide catalysts. Here we used a combination of ultrahigh vacuum catalyst synthesis, surface science characterizations including scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), electrochemical measurements, and density functional theory (DFT) modeling to study the electrocatalytic oxygen evolution reaction (OER) at $NiFeO_x$ catalysts deposited on Au(111) and highly oriented pyrolytic graphite (HOPG) electrodes. The formation of well-defined catalysts with precise loadings and atomic compositions allowed us to accurately track their composition and loading dependent electrocatalytic activity, monitor structural transformations that occurred during OER, and create realistic computational models. DFT calculations predicted Fe atoms residing at the edges of $NiFeO_x$ catalysts to be the most favorable OER reaction site, and soft X-ray absorption spectroscopy data suggested a higher population of undercoordinated Fe sites in small, as-synthesized $NiFeO_x$ catalyst particles. However, Au(111) substrates with low catalyst loadings experienced severe surface restructuring during OER that inhibited the activity of very small $NiFeO_x$ particles. At sufficiently high catalyst coverage the Au surface restructuring was suppressed and the $NiFeO_x$ catalysts transformed from their initial structure into an aggregated collection of smaller nanoparticles. The dual effects of Au surface restructuring and catalysts transformation created an unexpected loading-dependent activity trend for Au-supported catalysts. The detrimental impacts of surface restructuring were not found with HOPG substrates, and HOPG-supported $NiFeO_x$ catalysts demonstrated a more expected loading-dependent activity trend. Our study reveals some key fundamental insights into the $NiFeO_x$ catalyst system and points to the importance of catalyst transformations and substrate choice for understanding and optimizing OER performance.

HC-Contributed On Demand-28 Activation of O_2 on CeO_2 Nanoparticle Surfaces by Electron Transfer*, M. Brites Helú,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina*; A. Norton,* Department of Chemical Engineering, University of Delaware*; S. Collins,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina*; D. Stacchiola, J. Boscoboinik,* Center for Functional Nanomaterials, Brookhaven National Laboratory*; **Florencia Calaza**,* Instituto para el Desarrollo Tecnológico de la Industria Química INTEC (CONICET-UNL), Argentina

It is well known that VOCs being recognized as major responsible for the increase in global air pollution. Catalytic combustion is an efficient technology for the abatement of VOC, which are oxidized over a catalyst at temperatures much lower than those of the thermal process. Specifically, gold supported catalysts on CeO have shown a great performance in the oxidation of CO, methanol, toluene, etc. Besides, it is important to clarify the role of the support in such reaction. Ceria has the key property of high oxygen storage capacity which originates in its ability to rapidly switch from Ce^{+3} to Ce^{+4} oxidation states as the environment changes from reducing to oxidizing and vice versa. Its redox behaviour is influenced by the substituent lattice groups that could be incorporated during different catalyst pretreatments and could affect the oxidation of VOC. This could be understood as the influence of oxygen vacancies and/or **absorbed** or coadsorbed H on the activation of oxygen molecules. The latter leads to the formation of superoxide and peroxide molecules on the surface, which could in principle be highly reactive towards oxidation of organic molecules.

In this context, we study, by IR spectroscopy (DRIFTS) and mass spectrometry (MS), the interaction of O_2 with the modified CeO_2 based material, by creating vacancies following different treatments in reducing environments. The possible role of the vacancies and/or presence of H atoms in the electron transfer from the surface to the oxygen molecule is discussed. Using AP-XPS we are able to prove that the surface/near surface of CeOx presents a charging effect which could be due to accumulated charge/electrons which then transfer to O_2. Preliminary results showing reactivity of these activated molecular oxygen species (super- and peroxides) are presented regarding the catalytic oxidation of CO.

HC-Contributed On Demand-31 Comparison of Single Rh Adatoms on A-Fe_2O_3(1-102) and TiO_2(110) Stabilized by Adsorbed Water*, **Lena Haager**, F. Kraushofer,* TU Wien, Austria*; M. Eder,* TU München, Germany*; A. Rafsanjani-Abbasi, G. Franceschi, M. Riva, P. Sombut, M. Atzmueller, M. Schmid,* TU Wien, Austria*; C. Franchini,* Universitá di Bologna, Italy*; U. Diebold, G. Parkinson,* TU Wien, Austria

Despite its high cost, rhodium is a widely applied catalyst primarily used in nanoparticle form for converting toxic gases in automobiles. It is also utilized in organometallic complexes, such as the Wilkinson catalyst, for the hydrogenation of olefins and for converting alkenes to aldehydes through a process known as hydroformylation. So-called “single-atom” catalysis offers an opportunity to reduce the amount of Rh required for traditional heterogeneous catalysis, and a path to heterogenize homogeneous reactions, with the advantage of easy separation of catalyst and product.

Using scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM) and x-ray photoemission spectroscopy (XPS) we compare the stability of Rh adatoms on two different model supports: α-Fe_2O_3(1-102) and TiO_2(110), both after metal deposition in UHV and in a 2 × 10^{-8} mbar water background. We show that the Rh adatoms on α-Fe_2O_3(1-102) sinter in UHV but are stabilized by water up to 150 °C through coordination to 2 – 3 OH ligands. In contrast, Rh adatoms on TiO_2(110) could not be stabilized above room temperature in either environment.

HC-Contributed On Demand-34 Polarons in Single Atom Catalysts: Case Study of Me_1=[Au_1, Pt_1, Rh_1] on TiO_2(110)*, **Panukorn Sombut**, L. Haager, M. Atzmueller, Z. Jakub,* TU Wien, Austria*; M. Reticcioli,* University of Vienna, Austria*; M. Meier, G. Parkinson,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria

Identification of the exact local environment of a single-atom catalysts (SAC) on metal oxide surfaces is crucial for understanding the reactivity as well as the catalytic properties of such systems. On TiO_2(110), the stability and reactivity of adsorbed adatoms is further complicated by the presence of oxygen vacancies and associated polaron charge, as both can affect the energetic, electronic configuration and local geometry of adsorbed adatoms. In this work the adsorption of group 9 to 11 transition metal adatoms (Rh, Pt and Au) are computationally studied by means of density functional theory (DFT, plus on-site Hubbard U), and compared with results obtained by experimental surface techniques such as scanning tunneling microscopy (STM), for Rh_1, and with available literature (Au_1 and Pt_1). Despite the many works on this subject, it is still unclear why Au and Pt are experimentally observed to adsorb in the O vacancy, contrary to Rh. By investigating the most stable adsorption site, oxidation state and intermingled interaction among adatoms, O vacancies and polarons our data attempt to decipher the physical and chemical origin of the observed trend and to provide a conclusive interpretation of the puzzling observation.

HC-Contributed On Demand-37 Conformer-Selective Adsorption of 1-Propanol on Ag(111) from Theoretical Analysis of Experimental Reflection Absorption Infrared Spectra*, **Ravi Ranjan**, M. Trenary,* University of Illinois at Chicago

The experimental reflection absorption infrared spectrum of 1-propanol at 180 K is remarkably simple with usually sharp peaks with FWHM (full-width half maxima) of 1.1, 2.1, 1.6, and 4.0 cm^{-1} for the peaks at 1015, 1051, 1455, and 2948 cm^{-1}, respectively. This suggests that 1-propanol adsorbs as a single conformer, despite the fact that five different conformers of nearly the same energy are known for the gas-phase molecule. The stability of the different 1-propanol conformers on Ag(111) was investigated with DFT using a hybrid density functional (B3LYP) with additional empirical dispersion corrections (B3LYP-D3) using a Ag_{19} cluster model of the Ag(111) surface. The five conformers (Gg, Gg’, Gt, Tg, Tt) are named with a two-letter code. The first letter (G for gauche, T for trans) corresponds to the structure relative to the C-C-C-O dihedral angle, and the second letter (g for gauche, t for trans) refers to the C-C-O-H dihedral angle. In the gas phase, full geometry optimization gives zero-point corrected relative energies of 0.0, 0.06, 0.08, 0.21, and 0.28 kcal/mol respectively for Tt, Tg, Gt, Gg, and Gg’ conformers at the B3LYP/6311++G(2d,2p) level. The global minimum of 1-propanol at this level is for the Tt conformer. On the silver cluster at the B3LYP-D3/6-311++G(2d,2p) level, the adsorption energies with dispersion correction are 17.84, 17.41, 17.01, 16.86, and 16.84 kcal/mol, respectively for Tt, Gg’, Tg, Gg, and Gt conformers. The Tt conformer is the most stable conformer at this level of theory.The theoretical infrared spectra of all conformers are compared to the experimental spectrum. The calculated Tt spectrum best matches the experimental spectrum at 180 K. This reveals that adsorption on the Ag(111) preferentially stabilizes only one of the five possible conformers.

HC-Contributed On Demand-40 Ambient-Pressure CO Driven Restructuring of Cu(111) by Reflection Absorption Infrared Spectroscopy, ***Arephin Islam**,* University of Illinois at Chicago*; C. Kruppe ,* Intel Corporation*; M. Trenary,* University of Illinois at Chicago

Recently, restructuring of surfaces that occur under applicable operating conditions has aroused great interest. The structural changes have been correlated with changes in selectivity and linked to bond scission in heterogeneous catalysis. Metal single-crystals make excellent model systems to study restructuring by adsorbates since they are well defined and can be atomically prepared in ultra-high vacuum. The most popular adsorbates that cause well-defined surface restructuring are atomic oxygen and carbon monoxide. Restructuring due to CO has been seen on Cu(111) before[1], and CO is known to induce segregation in bimetallic materials. Furthermore, CO plays multiple roles including reactant, poison, product, or additive in catalytic processes such as CO hydrogenation, CO oxidation, methanol synthesis, and the water gas-shift (WGS) reaction. We have used reflection absorption infrared spectroscopy (RAIRS) to study the ability of CO to restructure Cu(111) and its subsequent impact on reactivity in the WGS reaction under ambient conditions. With polarized infrared radiation, the gas phase and surface species are easily distinguished. In the presence of ambient pressures of CO at 300 K, peaks at 1800-2100 cm^{-1} were readily observed and the spectral changes were monitored for different time intervals. The results demonstrate that the Cu surfaces have restructured, and new CO binding sites were created. Upon evacuation of the high-pressure CO, a new peak related to strongly bound CO at 2005-2023 cm^{-1} is reported that remains on the surface in UHV at room temperature.

References

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HC-Contributed On Demand-43 Metal Vapor Adsorption Calorimetry on Clean Surfaces of Oxide and Mixed-Oxide Single Crystals and Powdered Catalyst Support Materials*, **Charles T. Campbell**, Z. Mao, W. Zhang,* University of Washington, Seattle

Many important catalysts and electrocatalysts for energy and environmental technologies involve late transition metal atoms and nanoparticles dispersed across the surface of some powdered oxide support material.The long-term stability of these materials depends strongly on the strength of bonding of the metal atom and nanoparticles to the support surface. This talk will review recent studies were we have measured these bond strengths to clean and well-defined surfaces using metal vapor adsorption calorimetry.This includes planar single crystal surfaces, as well as the clean surfaces of high-surface-area powdered support materials of the type used industrially. Specifically, we measured the heat of adsorption versus coverage of Ni on MgO(100) and CeO_2(111) surfaces, from which we extracted the adhesion energy (E_{adh}) at these Ni/oxide interfaces. The results proved the predictive ability of our earlier linear correlation of E_{adh} with metal oxophilicity based on earlier measurements with metals that are less oxophilic than Ni. We also describe measurements of the adsorption energies of Ag atoms and the adhesion energies of Ag nanoparticles to drop-cast powders of anatase TiO_2 and to the (001) surface of calcium niobate nanosheets deposited in thin films by Langmuir-Blodgett (LB) techniques. This second application shows that LB deposition of multilayer films of such perovskite nanosheets, followed by their annealing in ultrahigh vacuum, provides a powerful new approach for studying surface of mixed oxides that are as clean and well-ordered as typical surfaces of single crystal oxides studied in surface science. The new calorimeter used for the study of these high-area support materials offers the potential for rapid screening of technical support materials for the strength with which they bond metal atoms and nanoparticles, which may aid in discovering better catalyst support materials.

Work supported by DOE-OBES Chemical Sciences Division.

HC-Contributed On Demand-46 Sum Is Better Than the Parts: CrCoFeNi High Entropy Alloy as Hydrogen Evolution Catalyst in Acidic Solution*, **Frank McKay,*** Louisiana State University*; Y. Fang,* Louisiana State Universityt*; O. Kizilkaya,* Louisiana State University*; P. Singh,* Ames Laboratory*; D. Johnson,* Iowa State University*; A. Roy, D. Young, P. Sprunger, J. Flake, W. Shelton, Y. Xu,* Louisiana State University

Pt plays a central role in industrial and technological catalytic applications, but limitations on sourcing and availability make reliance on it a potential weakness of modern economies. Alloying base metals with Pt has long been practiced to enhance catalytic performance and reduce use of Pt. Alloys of 3d base metals, e.g. Cr, Fe, Co, and Ni, with Pt have been extensively studied as electrocatalysts for reactions including oxygen reduction. Here we report that a random, equimolar alloy (or high entropy alloy, HEA) of the four base metals, being entirely free of Pt, can catalyze the electrochemical hydrogen evolution reaction in 0.5 M H2SO4 with an overpotential that is ca. 60 mV more than Pt at 1 mA/cm2 that is smaller than any of the component metals. While the HEA is not immune to dissolution, its activity remains stable with respect to repeated cycling up to 1000 times. DFT calculations based on a Super-Cell Random Approximates model of the HEA predict its surface to be partially oxidized under the given conditions, and the un-oxidized sites to adsorb atomic hydrogen with an average strength that is closer to that on Pt than on all the component metals. Hydrogen adsorption is further investigated via HREELS and compared with calculations. Changes in the surface and near-surface composition of the HEA are probed with XPS through increasing exposure to oxygen at room temperature. The results show that the elements preferentially oxidize in the order of Cr >> Fe > Co, with nearly no Ni oxidation up to 1,000 L of O2. Moreover, angle-dependent XPS and UPS measurements show that oxygen forms a passive surface layer, but the elemental metal concentration remains unchanged upon oxidation. Our findings provide tantalizing evidence for the potential of HEAs for chemical and catalytic applications.

HC-Contributed On Demand-49 The Influence of Palladium on the Hydrogenation of Acetylene on Ag(111)*, **David Molina**, M. Muir, M. Abdel-Rahman, M. Trenary,* University of Illinois - Chicago

We have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction (TPR) to study the selective hydrogenation of acetylene on both a clean Ag(111) surface and on a Pd/Ag(111) single-atom-alloy surface. The partial hydrogenation of acetylene to ethylene is an important catalytic process that is often carried out using PdAg alloys. It is challenging to study the reaction with ultrahigh vacuum techniques because H_2 does not dissociate on Ag(111) and while H_2 will dissociate at Pd sites, H-atom spillover from Pd to Ag sites does not generally occur. We bypassed the H_2 dissociation step by exposing the surfaces to atomic hydrogen generated by the hot filament of an ion gauge. We find that hydrogen atoms react with acetylene to produce adsorbed ethylene at 85 K, the lowest temperature studied. This is revealed by the appearance of a RAIRS peak at 950 cm^{-1} due to the out-of-plane wagging mode of adsorbed ethylene when acetylene is exposed to a surface on which H atoms are pre-adsorbed. The formation of both ethylene and ethane are detected with TPR, but no acetylene coupling products, such as benzene, were found. From quantitative analysis of the TPR results, the percent conversion and selectivities to ethylene and ethane were determined. Low coverages of Pd enhance the conversion but do so mainly by increasing ethane formation.

HC-Contributed On Demand-52 In Situ Investigation of the Oxidation of Cu(111) and Reduction of Cu_2O Doped with Single Pt Atoms*, A. Schilling,* Tufts University*; K. Groden,* Washington State University*; J. Simonovis, A. Hunt,* Brookhaven National Laboratory*; R. Hannagan, V. Cinar,* Tufts University*; J. McEwen,* Washington State University*; E. Sykes,* Tufts University*; **Iradwikanari Waluyo,*** Brookhaven National Laboratory

The redox behavior of metal oxides, either as catalyst supports or as the active sites themselves, plays an important role in heterogeneous catalytic reactions. In many cases, the redox behavior of a metal oxide can be significantly affected by the presence of a dopant atom due to the introduction of additional active sites as well as new interfaces. In this talk, I will present recent results from the IOS (23-ID-2) beamline at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, in which we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to study the oxidation and reduction behavior of Cu(111) doped by single Pt atoms on the surface, initially forming a PtCu single-atom alloy. Complementary data from temperature-programmed desorption (TPD) experiments and results from density functional theory (DFT) calculations will also be presented. By probing the Pt 4f core level, we were able to clearly distinguish Pt atoms in different chemical and physical environments as well as monitor their evolution under oxidizing and reducing environments. XPS revealed that a mild oxidizing condition ($5x10^{-6}$ Torr O_2 at 400 K) can result in the formation of a complete Cu_2O thin film on the surface of the sample that covers the Pt atoms. TPD results show that the oxidized Pt/Cu_2O surface is inert and the Pt atoms are inactive in H_2 dissociation. AP-XPS was used to monitor the evolution of the oxide O 1s peak in 1 Torr H_2 at room temperature, which revealed that the presence of a small amount of Pt, at the single atom limit, significantly accelerates the reduction of Cu_2O by H_2, even when the Pt atoms are covered by an oxide layer. DFT calculations show that the presence of Pt atoms under the oxide layer weakens the Cu-O bonds in its immediate vicinity. This work highlights the role of the metal-oxide interface in heterogeneous catalysis in terms of its ability to influence the catalyst's ability to maintain a reduced state during a reaction.

HC-Contributed On Demand-55 Kinetics of the Thermal Oxidation of Ir(100) toward IrO2 Studied by Ambient-Pressure X–ray Photoelectron Spectroscopy*, **Zbynek Novotny,*** University of of Zürich & Paul Scherrer Institute, Switzerland*; B. Tobler,* University of Zürich, Switzerland*; L. Artiglia,* Paul Scherrer Institut, Switzerland*; M. Fischer, M. Schreck,* Universität Augsburg, Germany*; J. Raabe,* Paul Scherrer Institut, Switzerland*; J. Osterwalder,* Universität Zürich, Switzerland

Using time-lapsed ambient-pressure X-ray photoelectron spectroscopy, we investigate the thermal oxidation of single-crystalline Ir(100) films toward rutile IrO_2(110) in situ [1]. We initially observe the formation of a carbon-free surface covered with a complete monolayer of oxygen, based on the binding energies of the Ir 4f and O 1s core level peaks. During a rather long induction period with nearly constant oxygen coverage, the work function of the surface changes continuously as sensed by the gas phase O 1s signal. The sudden and rapid formation of the IrO_2 rutile phase with a thickness above 3 nm, manifested by distinct binding energy changes and substantiated by quantitative XPS analysis, provides direct evidence that the oxide film is formed via an autocatalytic growth mechanism that was previously proposed for PbO and RuO_2.

[1] Z. Novotny, B. Tobler, L. Artiglia, M. Fischer, M. Schreck, J. Raabe, J. Osterwalder, *J. Phys. Chem. Lett.*2020, 11, 9, 3601–3607.

HC-Contributed On Demand-58 A Study of Subsurface Oxygen on Ag(111) Using Density Functional Theory and Monte Carlo Simulations*, **Carson Mize,*** University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; S. Isbill,* Oak Ridge National Laboratory*; S. Roy,* University of Tennessee Knoxville

Transition metals are commonly employed as heterogeneous catalysts for the functionalization of molecules, as well as the synthesis of many bulk materials and useful commodities. One well-studied catalytic application involves the use of an oxygen rich silver surface to induce partial oxidation of ethylene to ethylene oxide. While this reaction is required as a precursor to sterilization procedures and the synthesis of ethylene glycol, the structure of the active catalyst, specifically how oxygen is adsorbed to the silver surface, has not yet been fully elucidated. Past studies suggest that atomic oxygen adsorbs to the surface as well as the region below the surface, the subsurface. To investigate the formation of subsurface oxygen at different oxygen temperatures and surface coverages, we have theoretically studied the adsorption of atomic oxygen to the surface and subsurface of Ag(111) using a combination of density functional theory (DFT), a pairwise-additive site-adsorption model, and Monte Carlo simulations. Results show that oxygen accumulates in the subsurface at surface temperatures greater than ~500 K and oxygen coverages greater than ~1/3 ML, strongly suggesting that subsurface oxygen participates in industrial oxidative catalysis. Future studies will explore the role of subsurface oxygen in surface reconstruction and catalytic mechanisms of Ag(111), as well as the formation of subsurface oxygen on Ag(110) and Ag(100) surfaces.

HC-Contributed On Demand-61 Measuring Adhesion Energies and Using them to Bridge the Gaps between Gas-Phase and Liquid-Phase Surface Chemistry, and Between Single-Crystal Metal Surfaces and Metal Nanoparticles*, **S. Elizabeth Harman**, G. Ruehl, J. Rumptz, C. Campbell,* University of Washington

Understanding how solvents affect the adsorption energies of catalytic reaction intermediates compared to their better-known values in gas phase is crucial for understanding liquid-phase catalysis and electrocatalysis. It has been shown that the dominant effect is a decrease in adsorption energy compared to the gas phase by an amount equal to the solvents' adhesion energies to the solid multiplied by the area per adsorbate.[1]Therefore, knowing values for solvent / solid adhesion energies is critical for understanding solvent effects in catalysis and electrocatalysis.We report here adhesion energies of liquid solvents to clean Pt(111), estimated using single crystal adsorption calorimetry (SCAC) measurements of heats of adsorption versus coverage integrated from zero coverage up to thick (bulk-like) multilayer solid films. We also present new values estimated from temperature-programmed desorption (TPD) measurements.

The adhesion energy is also the key factor that determines how strongly metal nanoparticles bind to different catalyst support materials.[2] We present SCAC measurements of the heat of adsorption of azulene to Pt(111) and show that it binds ~100 kJ/mol more strongly than naphthalene to Pt(111). Azulene has been shown to have very similar electronic character to the pentagon-heptagon (5-7)-type defects in graphene, while naphthalene resembles perfect graphene. This SCAC result therefore implies that Pt(111) binds ~100 kJ/mol more strongly to (5-7) type defects in graphene than to perfect regions of graphene.From this we estimate that the adhesion energy of Pt nanoparticles to such (5-7)-type defects in graphene will be ~0.63 J/m^2 higher (locally) than to perfect graphene surfaces.This will greatly stabilize Pt nanoparticles at such defects on graphene-like and graphite-like catalyst support materials.For example, all the Pt atoms in a 1 nm particle would be ~30 kJ/mol more stable, and have an activation energy for sintering that is ~30 kJ/mol higher, when attached to such a defect.

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Supported by the National Science Foundation.

1. *ACS Catalysis***9** (2019) 8116.

1. 2.Charles T. Campbell and Zhongtian Mao, *ACS Catalysis***7** (2017) 8460 (2017).

HC-Contributed On Demand-64 Carbon Dissolution via Beam Reflectivity Measurements on Nickel Single Crystal Catalysts*, Daniel Tinney,* Tufts University*; E. High,* Rowland Institute at Harvard*; E. Dombrowski,* Commonwealth Fusion Systems*; L. Joseph, A. Utz,* Tufts University

Carbon atom diffusion on the surface and into the bulk of metal particles can modulate catalytic reactivity and film growth. Subsurface carbon diffusion is a primary step in graphene, carbon nanotube (CNT) and carbon nanofiber (CNF) growth on Ni substrates via chemical vapor deposition (CVD). Carbon build-up in the subsurface of nickel steam reforming catalysts gradually reduces catalytic activity and ultimately deactivates the metal catalyst. Traditionally, carbon diffusion is monitored using post-dose spectroscopic techniques. These methods require long wait times, temperature changes during the measurement, and correction and fitting of the spectroscopic peaks. Here, we use a novel molecular beam reflectivity approach to measure carbon diffusion and site-blocking kinetics in real time quantified on a flat Ni(111) and stepped Ni(997) surfaces. We track carbon uptake onto and into the Ni single crystal while holding surface temperature constant throughout the measurement. This new application of molecular beams allows for real-time, surface-sensitive detection of carbon dissolution into the crystal bulk at the elevated temperatures used in steam reforming (650-1000K). The onset of carbon dissolution occurs over a relatively narrow temperature range. Diffusion was found to be well fit by a Fickian model and we report bulk diffusion barriers, ED, of 137 ± 1.03 kJ mol-1 and 124 ± 0.73 kJ mol-1 for Ni(111) and Ni(997), respectively. We are also able to use the diffusion model to trace carbon and probe coverage dependent reaction trends at these elevated temperatures.

HC-Contributed On Demand-67 Trimetallic Alloys for Enhanced Ethanol Conversion to Hydrogen*, Paul Kress,* *Y. Wang, L. Cramer,* Tufts University*; M. Montemore,* Tulane University*; E. Sykes,* Tufts University

Understanding and controlling the structure and electronic properties of active sites is a central goal in modern catalyst research. We use a well-defined surface science and microcopy approach to characterize the structure of active sites in dilute metal alloys for a range of important reactions. Moving beyond the bimetallic paradigm, trimetallic alloys offer an additional variable with which to control active site type and properties. In this work we seek to identify a new type of catalytic site in dilute alloys - the heteronuclear dimer and small ensembles comprised of two dopant metal atoms. The reaction of interest is ethanol decomposition to acetaldehyde, hydrogen and other products with the goal of understanding the elementary steps and what sites are required for ethanol activation and conversion. Specifically, small amounts of Pt atoms in a Ag(111) host are unable to activate ethanol. Cr, which is not often investigated in model systems, also leads to limited reactivity. However, combining these two metals into an Ag host surface, as shown here at the single-atom limit, leads to cooperativity and a much higher conversion for the ethanol dehydrogenation reaction. We further understand and explain this synergy with density functional theory calculations that reveal that the mixed dimer sites have the lowest barriers for the reaction. This work demonstrates that more complex trimetallic alloys offer new and potentially useful properties with a great degree of tunability derived from their high degree of composition and structure space

HC-Contributed On Demand-70 Investigating the Alloying Mechanism of RhCu(100) and RhCu(110)*, Yicheng Wang,* Tufts University*; K. Papanikolaou ,* University College London, UK*; R. Hannagan,* Tufts university*; J. Schumann, M. Stamatakis,* University College London, UK*; C. Sykes,* Tufts University

Metal alloys plays a crucial role in heterogeneous catalysis and it is now fairly well established that the local coordination environment of an alloy can have a profound influence on its chemical reactivity. However, these effects can be difficult to probe in nanoparticle studies given the complexity of the active sites, nanoparticle shape and different predominantly exposed facets. On the other hand, model studies using well defined single crystal surfaces alloyed with dopants can achieve fundamental understanding of the structure-function relationship. The first step in this approach involves understanding the alloying mechanism and the type of ensembles formed. We report a combined scanning tunneling microscopy (STM) and density functional theory (DFT) study which was applied to understand the alloying behavior of Rh atoms in Cu(111), Cu(100) and Cu(110) surfaces. The STM results show a striking difference between Rh atoms alloying in Cu(111) versus the more open Cu(100) and Cu(110) surface facets.Unlike RhCu(111) where Rh atoms tend to form brim above the step edges, homogeneously dispersed Rh atoms can be observed in the terrace of Cu(100) and Cu(110). The stark different Rh distribution can be attributed to the dominance of different alloying mechanism in the Cu(111) versus Cu(100) and Cu(110) surfaces. DFT calculations show that direct atomic place exchange alloying mechanism prevails in Cu(100) and Cu(100) while Rh atoms tend to hop to a preferred sites (like step edges) before alloying in the Cu(111) surface. These model systems will serve as useful platforms for examining structure sensitive chemistry on single-atom alloys

HC-Contributed On Demand-73 2020 AVS Russell & Sigurd Varian Award Talk: Rhodium Copper Single-Atom Alloys for Selective and Coke-Free C-H Activation*, Ryan Hannagan*[1], *E. Sykes,* Tufts University

Due to the recent prevalence of small hydrocarbons, there has been renewed interest in direct dehydrogenation of small alkanes to the corresponding alkenes. One of the major issues in this reaction is the deactivation of catalysts due to coke formation. Here, we report a new RhCu single-atom alloy which displays considerable activity for C-H activation without coke formation. First, using a combination of scanning tunneling microscopy, temperature programmed desorption, and infrared spectroscopy, we characterize the model catalyst surface. We find that Rh atoms exist as isolated sites in the Cu host. We correlate this structure with the binding energy and vibrational frequency of CO on the isolated Rh sites. With knowledge of the atomic-scale structure, we then examine how the isolated Rh sites promote C-H activation. Using methyl iodide as a reporter on C-H activation, we find the isolated Rh sites promote C-H activation at a significantly lower temperature than Cu(111). We observe the formation of methane (from the hydrogenation of methyl groups) in addition to the formation of ethene (via coupling of CH_2 to CH_3 followed by beta-dehydrogenation). This is in strong contrast to extended Rh ensembles where coke formation is apparent. Together, these results indicate that RhCu single-atom alloys offer significant opportunities for efficient and coke-free C-H activation.

HC-Contributed On Demand-76 Beam Reflectivity Measurements of Ethane Dissociation on High Temperature Nickel Single-Crystal Surfaces*, Molly Powers*, *D. Tinney, L. Joseph, A. Utz,* Tufts University

Dissociative chemisorption of methane on a Ni catalyst via C-H bond cleavage is generally believed to be the rate-limiting step in the industrial steam reforming reaction. The commercial importance of this reaction, and methane's role as a model system for unravelling the energetics and dynamics of dissociative chemisorption, has resulted in extensive experimental and theoretical study including efforts to improve the absolute accuracy of DFT-based calculations of catalytically important

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[1] **AVS 2020 Russell and Sigurd Varian Awardee**

reactions. While methane is the majority component of natural gas feedstock, ethane (C_2H_6) can also represent a significant fraction.

Previously, we used energy and vibrationally state-selected methane molecules in a supersonic molecular beam to quantify reaction probability over a wide range of energies and energetic configurations (i.e. the distribution of energy among translational, vibrational, rotational, and surface degrees of freedom). Here, we report on the extension of that approach to ethane molecules prepared with similar energy configurations. Our goal is to understand how reactivity patterns observed in the smaller methane molecule may extend to larger molecules as well as to provide accurate benchmark data for computational studies of increasingly larger and more complex molecule-surface reaction systems.

For this work, energy-resolved reaction probabilities were measured for supersonically-expanded ethane gas molecules impinging on an atomically flat Ni(111) surface. Experimental variables include a range of surface temperatures (550 K $\leq T_S \leq$ 1000 K), varying incident energies (E_i = 35 kJ/mol to > 140 kJ/mol), incidence angle, and both vibrational state-averaged and vibrational state-resolved ensembles of ethane molecules. The data provide benchmarks for computational efforts to extend chemically accurate DFT calculations to larger chemical systems, and comparisons with prior methane reactivity data on the Ni(111) surface will shed light on the role that the additional molecular complexity may play in energy flow and reactivity in larger molecules.

HC-Contributed On Demand-79 Elucidating the effect of Oxidation on the Structure and Reactivity of Rhodium Copper Single-Atom Alloys, ***Volkan Cinar,*** Tufts University; *D. Guo,* Washington State University; *A. Schilling,* Seagate Technology; *I. Waluyo,* Brookhaven National Laboratory; *J. McEwen,* Washington State University; *C. Sykes,* Tufts University

Single-atom catalysts (SACs) consisting of late-transition metals on oxide supports have recently gained significant world-wide attention due to their well-defined sites that enable more selective chemistry and the fact that they use precious metals at the ultimate limit of atom efficiency. SACs involving reducible oxide supports are good catalysts for oxidation reactions, but they tend to deactivate by sintering under reducing conditions. On the other hand, single-atom alloys (SAAs) are robust towards sintering and exhibit exceptional catalytic performance for a wide range of reactions under reducing conditions, but some SAAs deactivate under oxidizing environments. This project is aimed at systematically exploring catalytic reactivity between the SAC and SAA oxidation state extremes. Historically, bimetallic RhCu and supported Rh systems have been investigated for several reactions including CO oxidation, NO_x reduction, and the hydrogenation of hydrocarbons. Recent studies conducted on RhCu SAAs have shown that while the Rh sites bind CO strongly, CO desorbs reversibly. In contrast, model Rh/CuO_x SACs perform CO oxidation just above room temperature. However, there is a lack of understanding of structure-function relationships between these two extremes when the surface is partially oxidized. We report a study of CO oxidation on partially oxidized RhCu alloys using temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS), and low energy electron diffraction (LEED). The TPD results demonstrate that CO oxidation occurs around 456 K on an oxidized RhCu SAA. Increasing the Rh coverage led to gradual decrease of the CO oxidation temperature to 362 K at 25% of a monolayer of Rh. Isotopic TPD experiments provided evidence of a Mars van Krevelen (MvK) CO oxidation mechanism. Furthermore, more fully oxidized RhCu SAAs were inactive for CO oxidation meaning that intermediate oxidation states of the SAA are most efficient for CO oxidation. LEED and IR results provide evidence for how the incorporation of Rh in the system affects its structure and the accessibility of the Rh sites to reactants. Together, these results begin to shed light on the effect of surface oxidation on the structure and reactivity of Rh sites in Cu-based SACs.

HC-Contributed On Demand-82 Investigation of CO oxidation on Rh(111) with IRRAS, ***Elizabeth Jamka,*** *D. Killelea,* Loyola University Chicago

Fourier-transform Infrared (FTIR) spectroscopy is a powerful technique for identification of small molecules adsorbed to metal surfaces. We have added FTIR to an ultra-high vacuum (UHV) chamber as a non-destructive and highly sensitive surface analysis technique. Because IR measurements can be performed in UHV conditions, interference from atmospheric species are avoided, while enabling investigation of catalytic systems, like carbon monoxide (CO) to carbon dioxide (CO_2) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO_2on oxidized Rhodium (Rh) will be utilized as a probe reaction. We will be able to determine the chemical significance of various oxygen phases on different Rh surfaces, and the CO coverage and binding sites on the different oxygenaceous phases. Studying CO oxidation on different Rh surfaces will provide atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes. Past exposure conditions determined that at low temperatures, CO was observed to adsorb along (2x1)-O and RhO2 domain boundaries, and O_{sub} replenished the reacted oxygen at these boundaries at higher temperatures. When CO was prolonged exposure it consumed all O_{sub} and reacted with oxides at the defects. In recent studies, it was determined that there are multiple reaction pathways available for CO oxidation, but at temperatures at or below 350K reaction sites are not regenerate. Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.Methods developed for Rh can also be applied to other metal surfaces and small molecules of interest.

HC-Contributed On Demand-85 Study of the Effects of Co-Adsorbed Water on Acetic Acid Decomposition on Metal Surfaces, *K. Chukwu,* ***Hoan K.K. Nguyen,*** *L. Arnadottir,* Oregon State University

Acetic acid decomposition on metal surfaces and the effects of water on the decomposition are good model systems for solvent effects on small oxygenates with applications in biomass conversion. Numerous studies have found that solvents influence the selectivity and rate of heterogeneous catalytic reactions. Fundamental understanding of how water affects acetic decomposition on metal surfaces gives us valuable insight into how water changes the selectivity of decomposition reactions on different metals, further enabling bottom up design of effective catalyst and catalyst system. Here we present a combined density functional theory (DFT) calculations, microkinetic analysis and AP-XPS study of the effects of co-adsorbed water on acetic acid decomposition over Pd (111). The combination of theory and experiments is used to improve the AP-XPS analysis as well as providing atomistic insights into the mechanism. AP-XPS data show an increase in surface coverage of both chemisorbed acetic acid and acetate, while coverage of CO decreases in the presence of co-adsorbed water. MS-RGA data collected concurrently during the exposure also show an increase in the ratio of CO2(g)/CO(g) up to 80% for exposure of acetic acid with water. This supports the microkinetic analysis, where we show that in the absence of co-adsorbed water, the decarboxylation pathway (CO2) is more favorable than the decarbonylation pathway (CO) but in the presence of co-adsorbed water, the decarboxylation pathway is more favored. On Pd (111), the shift in selectivity is mostly due to changes in the OC-O bond cleavage. Water has a similar effect on the selectivity for this reaction on Pt(111) but the water has a larger effect on OC-OH bond cleavage on Pt than Pd.

HC-Contributed On Demand-88 Structure and Chemistry of Metal Surfaces at High Oxygen Coverages, ***Dan Killelea,*** *M. Turano,* Loyola University Chicago; *R. Farber,* The University of Chicago; *L. Juurlink,* Leiden University, Netherlands

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O_{sub}); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O_{sub}into the selvedge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O_2. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of O_{sub} and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O_{sub} is present. This enhanced reactivity is located at the interface between the less reactive RhO_2 oxide and O-covered metallic Rh. These results reveal the conditions under which O_{sub} is formed and stable, and show that O_{sub} also leads to enhanced reactivity of oxidized metal surfaces.

HC-Contributed On Demand-91 Surface Science at Atmospheric Pressure: Measuring Intrinsic Kinetics on Metallic Systems*, **Eric High**, E. Lee, C. Reece,* Rowland Institute at Harvard

Ultra-high vacuum surface science remains the gold standard for monitoring the elementary steps that define activity and conversion in catalysis. When combined with microkinetic modeling, these measurements have been successfully used to rationalize catalytic behavior at industrially relevant conditions. However, this method has been applied to a limited number of reactions and such pressure transferability is seen as the exception rather than the norm. We approach this problem by employing techniques with a long history of application in surface science (isotopic labeling, pulse transient measurements and model catalysis) to probe kinetic parameters at atmospheric pressure and elevated temperatures. To that end, we have built a flow system comprised of two parallel gas streams that has demonstrated a reproducible sub-second rise time upon switching. The set-up is capable of multiple experimental methodologies (steady-state flow, SSITKA, CTK, atm-TAP, atm-K&W, etc.) with no changes in configuration and the rapid rise time enables direct observation of transients inaccessible on traditional flow systems. Initial measurements have been made investigating CO oxidation on pure Pt particles to validate the instrument and to allow for a thorough and direct comparison with results from traditional surface science kinetic measurements.

HC-Contributed On Demand-94 Catalytic Enhancement Due to Coke Formation: Investigation of the Bimetallic Effect on Carbon Nanotubes Formed during Dry Reforming of Methane*, **Carly Byron**,* University of Delaware*; M. Ferrandon,* Argonne National Laboratory, USA*; G. Çelik,* Middle East Technical University, Turkey*; R. McCormick, J. Sloppy, K. Booksh,* University of Delaware*; M. Delferro,* Argonne National Laboratory, USA*; C. Ni, A. Teplyakov,* University of Delaware

Metal nanoparticles supported on metal oxides are excellent catalysts for a variety of applications, and nickel supported on MgO and Al_2O_3 has shown to be a highly active catalyst for the dry reforming of methane (DRM). Nickel is typically deposited with another transition metal to hinder surface carbon (coke) formation, often in the form of carbon nanotubes, which is assumed to deactivate the catalyst. However, recent advancements have shown that carbon nanotube formation does not always deactivate the catalyst. An in-depth analysis of the coke formation on bimetallic nickel catalysts may help us better understand the chemistry behind this phenomenon, therefore this work provides microscopic and spectroscopic characterization of the carbon nanotubes formed on various bimetallic nickel catalysts during the DRM reaction. It was determined that bimetallic promotion of nickel significantly altered the morphology of the coke formed, and that the carbon nanotubes did not affect catalytic activity due to the orientation of the nickel nanoparticle at the tips. In fact, the high catalytic activity of the nickel nanoparticles may be partially attributed to the morphology of the coke formation.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room On Demand - Session HC-Invited On Demand

Fundamental Discoveries in Heterogenous Catalysis Invited On Demand Session

HC-Invited On Demand-1 Low Temperature Selective Alkane Conversion on IrO_2(110) Surfaces*, **Aravind Asthagiri**,* The Ohio State University**INVITED**

Selective alkane conversion to high value fuels or chemicals, such as methanol or ethylene, has drawn increasing interest due to abundance of natural gas. Recently, we reported a combined temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) study of below room temperature (T ~ 120 K) activation of methane on the stoichiometric IrO_2(110) surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on IrO_2(110) by creating some proportion of hydrogenated bridging oxygen (O_{br}-H) sites, which limit the oxidative capacity of the surface. This past work suggests that substitution of O_{br} sites with inert species may be an avenue to control selectivity between full and partial oxidation. We have used DFT to explore the effects of Cl substitution of O_{br}. Chlorine is isoelectronic to O_{br}-H and selective Cl substitution of O_{br} has been demonstrated on RuO_2(110) by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped IrO_2(110). We find that the Cl-doped IrO_2(110) is still facile in converting ethane to ethylene. In contrast, the ethylene selectivity step shows a strong effect due to Cl doping. Specifically, we find that H atom transfer from ethylene to the saturated O_{br} sites is unfavorable and therefore Cl doping will promote ethylene desorption over further reaction. Current efforts to develop a microkinetic model to explore ethylene selectivity under both TPRS and reaction conditions will be discussed.

HC-Invited On Demand-7 Alkali-promoted Copper-based Catalysts for CO_2 Activation*, W. Liao,* Stony Brook University*; **Ping Liu**,* Brookhaven National Laboratory **INVITED**

Alkalis have been reported as a promotor in the heterogeneous catalysis, being able to enhance the activity and selectivity of catalysts. The effective utilization of alkalis in catalyst optimization requires the fundamental understanding of underlying mechanism. This presentation will take potassium (K)-modified Cu_xO/Cu(111) (x≤2) model surface as a case study to rationalize the nature of K during the carbon dioxide hydrogenation using combined density functional theory (DFT) calculation and the kinetic Monte-Carlo (KMC) simulation. The result demonstrates the significant tuning of selectivity from carbon monoxide to methanol on going from Cu(111) to K-modified Cu_xO/Cu(111). The deposited K^+ stabilizes the Cu_xO thin film under the reducing condition of carbon dioxide hydrogenation. More importantly, our study reveals that K^+ acts as an active center for selective tuning in the binding, an accelerator for charge transfer, and a mediator for the electron tunneling. As a result, the K-modified Cu_xO/Cu(111) opens a methanediol [$H_2C(OH)_2$]-mediated Formate pathway to facilitate the selective conversion of carbon dioxide to methanol. Our study develops the intrinsic rules of design to tune the catalytic performance using alkali metals.

HC-Invited On Demand-13 Influence of Water on C-O Hydrogenolysis Catalyzed by Ru/TiO_2*, D. Stuck, A. Mahdavi-Shakib,* University of Maine*; R. Austin,* Barnard College*; L. Grabow,* University of Houston*; B. Frederick, **Thomas J. Schwartz**,* University of Maine **INVITED**

Several groups have recently shown the importance of metal-TiO_2 interfacial sties for selective activation of oxygen in a variety of reactions, including hydrodeoxygenation of phenolics.Our team has previously shown that TiO_2-supported catalysts containing small Ru nanoparticles are highly active for the conversion of phenol to benzene, which is consistent with the results from Crossley and coworkers, who have shown the reaction to occur at the Ru-TiO_2 interface.Both observations can be explained by a mechanism wherein surface hydroxyls present on the TiO_2 surface in the immediate vicinity of the Ru nanoparticles are protonated during heterolytic H_2 dissociation, leading to acidic Ti-OH_{2-} surface species.Phenol then adsorbs across the Ru-TiO_2 interface, and the acidic proton from Ti-OH_2 facilitates C-O scission, regenerating the Ti-OH moiety and leaving a phenyl ring to be hydrogenated on the Ru surface.This mechanism is predicted to be favorable in the presence of water, and reports from the literature indicate an enhancement in the amount of benzene produced ranging from 30% to 200%, depending on the fugacity of water in the system. In this work, we seek to clarify the role of water in C-O hydrogenolysis catalyzed by Ru/TiO_{2}- materials.

We measured reaction orders for phenol hydrogenolysis over Ru nanoparticles supported on two different TiO_2 materials: pure anatase TiO_2 and pure rutile TiO_2.The phase of water and phenol is verified based on thermodynamic calculations, which show that 85% of the material exists as a vapor.The 15% which exists as a liquid is hypothesized to be trapped in the pore structure of the catalyst, indicating that the reaction should occur in the liquid phase.The reaction is positive-order with respect to water for Ru/rutile and negative-order for Ru/anatase, which correlates with differential heats of irreversible water adsorption on TiO_2 powders that show stronger binding of water to anatase TiO_2 than to rutile TiO_{2-}. The kinetics are consistent with a rate expression in which water inhibits the reaction by strong binding to Ru-TiO_2 interface sites. Kinetic Monte Carlo results for a catalyst consisting of a Ru nanorod supported on a rutile TiO_2 surface suggest that water-related species are abundant at the Ru-TiO_2 interface at high water pressures, and that as the temperature is lowered these abundant species can lead to the inhibitory effect observed in our kinetics data.The observed reactivity trends are correlated with the surface hydroxyl features of the TiO_2 support, as we have recently observed using FTIR spectroscopy.

HC-Invited On Demand-19 Reversible Surface Transformation Enables the Revivification of Mixed Metal Hydroxide Water Oxidation Catalysts*, C. Kuai,* ***Feng Lin,*** Virginia Tech **INVITED**

The electrode-electrolyte interfacial reactivity and stability govern the efficiency and lifetime of electrochemical devices, especially under aggressive reaction conditions such as high temperature, high potential, and corrosive environments. Modulating the metal-oxygen bonding environment at the electrode surface offers an effective path towards enhancing the interfacial reactivity. However, the high interfacial reactivity can trigger undesired interfacial reactions that lead to local structural changes, phase segregation and dissolution, and ultimately the complete degradation of the pre-designed metal-oxygen bonding environment. The rational design of a highly active and stable electrocatalyst is largely hindered by this dilemma. Understanding how the electrocatalyst-electrolyte interface transforms under operating conditions can generate mechanistic insights into identifying the catalytically active motif and establishing methodologies to circumvent the dilemma by repairing the degraded structure. In this presentation, we report that *operando* synchrotron spectroscopic and microscopic analyses suggest that the interfacial degradation can be reversible between catalytic oxidation and reduction potentials. Such reversibility allows us to develop an intermittent reduction methodology to revivify the catalytic activity under operating conditions, enhancing catalyst durability.

HC-Invited On Demand-25 Designed Metal Release from Complex Metal Oxides*,* ***Sara Mason,*** University of Iowa **INVITED**

Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. This is a pressing problem because the environmental and biological impact of complex metal oxide nanomaterials are most times unknown, since they are subject to transform rapidly with changes in pH and concentration. This brings us to a looming problem that needs to be solved on a global scale. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. We have adapted and developed a method that combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the cation release of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO2 (LCO) and compositionally tuned variants with general chemical formula Li(NixMnyCoz)O2 (NMC). We find that adjusting surface terminations, compositions and pH will change the dissolution properties of this family of materials, and ultimately lead to increased favorability of metal release. We go on to propose a new set of materials, with maintained function, based on non-toxic and abundant metals, thereby reducing the biological impact. We then predict the thermodynamics of metal release to give insight on tailorable properties that can be used to formulate sustainable design principles for future generations of functional complex metal oxide materials.

HC-Invited On Demand-31 Hydrogenation of CO_2 to Methanol on Metal-Oxide and Metal-Carbide Interfaces*,* ***Jose Rodriguez,*** Brookhaven National Laboratory **INVITED**

The high thermochemical stability of CO_2 makes very difficult the catalytic conversion of the molecule into alcohols or other hydrocarbon compounds which can be used as fuels or the starting point for the generation of fine chemicals. Pure metals and bimetallic systems used for the CO_2 → CH_3OH conversion usually bind CO_2 too weakly and, thus, show low catalytic activity. Here, I will discuss a series of recent studies that illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 into methanol. CeO_x/Cu(111), Cu/CeO_x/TiO_2(110) and Au/CeO_x/TiO_2(110) exhibit an activity for the CO_2 → CH_3OH conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Au-ceria interfaces, the multifunctional combination of metal and oxide centers leads to complementary chemical properties that open active reaction pathways for methanol synthesis. Efficient catalysts are also generated after depositing Cu and Au on TiC(001). In these cases, strong-metal support interactions modify the electronic properties of the admetals and make them active for the binding of CO_2 and its subsequent transformation into CH_3OH at the metal-carbide interfaces.

HC-Invited On Demand-37 Chirality Detection of Surface Desorption Products using Photoelectron Circular Dichroism*, J. Wega,* ***Tim Schäfer****, G. Westphal,* University Göttingen, Germany **INVITED**

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule (multiphoton photoelectron circular dichro-ism (MP-PECD)). In the talk, I will present the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We recorded velocity resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measured temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combined both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

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