Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room B113 - Session HC+SS-WeA

Advances in Complex Catalytic Systems

Moderators: Zdenek Dohnalek, Pacific Northwest National Laboratory, **Dan Killelea**, Loyola University Chicago

2:20pm HC+SS-WeA-1 Computational Studies of Selective Reduction Reactions on Metal and Metal Compounds Electrocatalysts, *J.R. Schmidt,* UW Madison **INVITED**
Understanding and controlling the factors that govern selectivity in electrocatalysis is key to enabling a wide range of electrochemical transformations. I will highlights efforts from two ongoing collaborative studies, focusing on the selective 2e- reduction of oxygen to hydrogen peroxide over a series of transition metal dichalcogenides; and the selective reduction of highly functionalized biomass molecules using traditional metallic electrocatalysts. In both cases, I will demonstrate how emerging computational electrocatalysis approaches yield a rich picture for the factors that govern catalytic selectivity in these systems. In addition, I will briefly discuss recent work focused on increase the long-term stability of these electrocatalysts, opening the doors to potential commercial applications.

3:00pm HC+SS-WeA-3 Metal Atom Chemical Potential: A Key Descriptor for Predicting Particle Size Effects on Catalyst Performance, and How to Estimate It, *Charles T. Campbell, K. Zhao, N. Janulaitis,* University of Washington
Many important catalysts and electrocatalysts for energy and environmental technologies involve late transition metal nanoparticles dispersed across the surface of some oxide or carbon support.The activity and long-term stability of these materials depend strongly on particle size below 7 nm, and, in this size range, upon the composition and atomic-level structure of the support surface. We show here that the chemical potential of the metal atoms in such supported catalysts provides a convenient descriptor of their performance as heterogeneous catalysts that captures many of the effects of particle size, metal-metal alloying and support on catalyst performance. Based on microcalorimetric measurements of metal adsorption energies, the metal chemical potential is shown to be predictable as a function of metal particle size and the adhesion energy of the particle to the support. For oxide supports, this adhesion energy correlates predictably with metal oxophilicity, as we defined based on heats of oxide formation from gaseous metal atoms. For carbon supports, this adhesion energy correlates predictably with metal carbophilicity, as we defined based on DFT estimates of C atom adsorption energies. These correlations provide predictions of metal chemical potential that can enable catalyst design.

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3:20pm HC+SS-WeA-4 Size-Dependent Properties of Cobalt Nanoclusters on CeO_2(111), *M. Rahman,* Louisiana State University; *T. Ara,* University of Wyoming; *Ye Xu,* Louisiana State University; *J. Zhou,* University of Wyoming
Cobalt is a versatile catalytic metal. It has been used to catalyze many reactions of technological importance, including Fischer-Tropsch synthesis, reforming, and ammonia synthesis, where oxidic Co and metallic Co lead to different catalytic pathways. Meanwhile, ceria offers a desirable set of properties as catalyst support, including the abilities to stabilize nanoclusters, undergo redox interaction with metals, and enhance oxygen availability. Nanoparticles of Co supported on ceria have therefore been the mainstay of many heterogeneous catalysis studies. We have carried out an investigation of Co nanoclusters supported on stoichiometric CeO_2(111) using computational modeling and scanning tunneling microscopy (STM). Various sizes up to ca. 20 Co atoms have been optimized using a minima hopping algorithm combined with density functional theory (DFT) calculations, which identifies many compact, symmetric structures as minimum-energy for the sizes that are considered. Theory predicts that in this size regime, the Co clusters prefer to be notably wider than they are high. A significant fraction of the Co atoms in each cluster are oxidized, and most of those are located on the periphery between the clusters and ceria. Co atoms that are not directly in contact with the surface are effectively screened and remain neutral. The large aspect ratios and high fractions of oxidic Co in small clusters at low Co metal coverages are corroborated by STM studies of Co deposited on CeO_2(111) thin film surfaces at ambient temperature. Our findings shed light on atomic-level characteristics of Co nanoclusters on ceria that are relevant to catalytic applications.

4:20pm HC+SS-WeA-7 on-Surface Synthesis of Porous Planar-Carbon-Lattices: Fundamental Properties and Applications, *Abner de Siervo,* Institute of Physics Gleb Wataghin, University of Campinas (UNICAMP), Brazil **INVITED**
Materials science in the nanoscale domain has become a reality for several applications, from integrated circuits, sensors, catalysts, medicines, and data-storage devices, among others [1]. We achieved the ability to understand materials and, more importantly, command the materials' properties at the atomic level using precise synthesis and growth methods. Therefore, during the last decades, enormous efforts have been made to develop new processes for the fabrication, characterization, and manipulation of materials in complex nanoarchitectures with atomic precision, making it possible to express emergent new chemical, electronic, photonic, magnetic, and structural properties. On-surface synthesis becomes a powerful bottom-up technique to fabricate such nanostructures using organic and organometallic precursors as molecular building blocks [2]. In this talk, I will present some strategies we have adopted to produce planar carbon lattices nanostructures, for example, porous nanoribbons and nanomembranes [3-5]. For a complete understanding of the atomic and electronic properties of the materials, we have combined scanning tunneling microscopy and spectroscopy (STM/STS), X-ray photoelectron spectroscopy (XPS), and numerical simulations based on density functional theory (DFT) calculations.

Acknowledgments:

References:

[1] G Ali Mansoori and TA Fauzi Soelaiman. Nanotechnology—An introduction for the standards community. ASTM International,

2005.

[2] Johannes V. Barth. Annual Review of Physical Chemistry, 58(1):375–407,

2007.

[3] Alisson Ceccatto dos Santos, et al., Chemistry of Materials 32 (5), 2114-2122 (2020).

[4] Nataly Herrera-Reinoza, et al., Chemistry of Materials 33, 2871-2882 (2021).

[5] Alisson Ceccatto dos Santos, et al., J. Phys. Chem. C 125, 31, 17164–17173 (2021).

5:00pm HC+SS-WeA-9 2D Surface Optical Reflectance for Surface Studies in Harsh Environments, *A. Larsson,* Lund University, Sweden; *S. Pfaff,* Sandia National Laboratories; *L. Ramisch, S. Gericke, A. Grespi, J. Zetterberg, Edvin Lundgren,* Lund University, Sweden
During recent years, 2D Surface Optical Reflectance (2D-SOR) [1,2] microscopy [3] has emerged as a valuable surface characterization tool for model catalysts or electrodes [4] when performing operando investigations in harsh environments. In particular, 2D-SOR microscopy is favorably used as a complementary technique to other photon-in-photon-out techniques which do not carry direct information on the surface 2D morphology. In this presentation we will present the development and examples of 2D-SOR instrumentation and investigations from single and poly-crystalline samples in combination with Planar Laser Induced Fluorescence (PLIF) [2, 3], High Energy Surface X-ray Diffraction (HESXRD) [5,6,7] and Polarization Modulation-Infrared Reflection Absorption Spectroscopy (PM-IRRAS) [8] coupled to Mass Spectrometry (MS) and Cyclic Voltammetry (CV) in thermal catalysis, electrocatalysis and corrosion. Illustrating examples of the versatility of the technique will be shown including reflectance changes during the thermal CO oxidation over Pd(100) and Pd polycrystalline

surfaces. We show that reflectance changes during the reaction can be associated with the formation of thin Pd oxides by the combination of 2D-SOR and Surface X-Ray Diffraction (SXRD). The combined measurements demonstrate a sensitivity of 2D-SOR to the formation of a 2-3 Å thin Pd oxide film. During Cyclic Voltammetry (CV) in an acidic electrolyte using a Au(111) surface as an electrode, we show that the differential of the change in 2D-SOR reflectance correlate to various current features in the CV curve. This observation can be used to differentiate current features in the CV curve from a polycrystalline Au surface, demonstrating that the different grains contribute to the current at different potentials due to the different surface orientations. Finally, we show that 2D-SOR is a cheap and useful technique to investigate the corrosion of applied materials such as duplex stainless steels and Ni alloys.

[1] W. G. Onderwaater et al Rev. Sci. Instrum., **88** (2017) 023704.

[2] J. Zhou et al, J. Phys. Chem. C **121** (2017) 23511.

[3] S. Pfaff et al, ACS Appl. Mater. Interfaces **13** (2021) 19530.

[4] W. Linpe, et al, Rev. Sci. Instrum., **91** (2020) 044101.

[5] S. Pfaff, et al Rev. Sci. Instrum. **90** (2019) 033703.

[6] S. Albertin, et al, J. Phys. D: Appl. Phys. **53** (2020) 224001.

[7] W. Linpé, et al J. Electrochem. Soc. **168** (2021) 096511.

[8] L. Rämisch et al, Appl. Surf. Sci. **578** (2022) 152048

5:20pm **HC+SS-WeA-10 Interrogating Reactive Sites with Intrinsic Kinetics Over Well-Defined Supported Pt Nanoparticles**, *T. Kim, C. O'connor, Christian Reece,* Harvard University

The chemical industry is the primary consumer of energy and fossil fuels in the industrial sector and relies almost entirely on complex heterogenous catalytic systems. Yet our ability to employ these systems far outweighs our understanding. While a detailed understanding of heterogeneous catalysts does exist for model systems (e.g., 2D single crystals) at ultra-high vacuum, our understanding of applied catalytic materials (e.g., metal nanoparticles deposited on a metal oxide support) under reaction conditions is still lacking. Herein we utilise the Temporal Analysis of Products (TAP) technique to precisely resolve the intrinsic kinetics of CO oxidation of size selected 2nm Pt nanoparticles supported on SiO_2. Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) we identify multiple types of well-coordinated, undercoordinated, and bridge-bound CO sites exist on the Pt nanoparticles However, through a combination of isotopic labelling and microkinetic modelling, we find that only two pathways for CO oxidation exist over the catalyst surface under the entire range of reaction conditions studied: a fast and a slow pathway. The fast pathway follows typical catalytic behaviour and shows a strong temperature dependence and a linear dependence on CO coverage, but the slow pathway is independent of both temperature and CO coverage which is unexpected for a slow catalytic process. This study demonstrates the importance of being able to precisely resolve kinetics over applied catalytic materials using techniques such as TAP. Further, it also hints that under reaction conditions the highly dynamic nature of catalytic surfaces implies that our classical understanding of structure-activity-relationships may not hold as strong as originally hoped.

5:40pm **HC+SS-WeA-11 The Effects of Catalytic Cluster Size on Catalysis and Electrocatalysis**, *Scott Anderson,* University of Utah **INVITED**

Supported sub-nano clusters are potentially a metals-efficient approach to catalysis, where all the expensive catalytic atoms (Pt, Pd, etc.) are exposed in the surface layer.In addition, because the properties of small clusters are highly size dependent, varying the cluster size provides a parameter that can be used to tune activity and selectivity.The problem with small clusters is that they tend to sinter and poison easily, and much of our work is in developing approaches to stabilize the supported clusters under thermal or electro-catalytic conditions.

Deposition of mass-selected clusters in UHV is used to prepare model catalysts and electrocatalysts with catalytic centers that all start out being the same size.We have developed an in-vacuum ALD-like self-limiting reaction approach to dope or alloy the clusters with elements like B, Sn, or Ge, with the goal of stabilizing the clusters against both poisoning and sintering.Two types of catalysis experiments will be described.

Gas-surface catalysis is studied in the UHV system by mass spectrometric methods, but we also have new microreactor system that allows clusters deposited on alumina or silica surfaces to be exposed to reactant flows at pressures up to 1 atm, with mass spectrometric product detection.This part of the talk will focus on using Ge doping to stabilize small Pt clusters against deactivation by both carbon deposition (coking) and sintering at

temperatures up to 700 K.To goal is to make stable and selective alkane dehydrogenation and cracking catalysts.

Electrocatalysis is studied either *in situ*, using an electrochemical cell housed in an antechamber to the UHV system, or in conventional benchtop electrochemical cells.The *in situ* experiments allow us to study aqueous electrochemistry with minimal air exposure, while the *ex situ* setups allow more elaborate types of electrochemical measurements.Results for the hydrogen evolution reaction (HER), oxygen evolution reaction (ORR), and alcohol electro-oxidation will be presented for catalytic Pt_n clusters deposited on indium tin oxide (ITO), fluorine tin oxide (FTO), and graphite (HOPG).For ITO/FTO, electrodes were prepared by soft landing the clusters.For HOPG, the effects of deposition energy on electrocatalytic activity and stability, and on physical properties measured by XPS and ISS will be discussed.

Author Index

Bold page numbers indicate presenter