

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-MoA

Advances in Materials and Analysis in Heterogeneous Catalysis I

Moderators: Dan Killelea, Loyola University Chicago, Svetlana Schauermann, Christian-Albrechts-University Kiel, Germany

2:00pm **HC+AS+SS-MoA-2 Electrochemical Activity of Size-Selected Sub-nano Pt Clusters Toward the Hydrogen Evolution Reaction, Tsugunosuke Masubuchi**, University of Utah; S. Kumari, Z. Zhang, P. Sautet, A. Alexandrova, University of California at Los Angeles; H. White, S. Anderson, University of Utah

Platinum is known to exhibit high electrocatalytic activity toward the hydrogen evolution reaction (HER). From a sustainable point of view, sub-nano Pt clusters can be promising HER electrocatalysts because their electrochemically active surface area per mass is much larger than that of bulk Pt or larger Pt nanoparticles. There are fundamental questions, however, about the nature of the HER mechanism, including the electronic and structural properties of the catalytic sites required.

To this end, we studied the HER activity of atomically size-selected sub-nano Pt clusters deposited on conductive oxide supports. The electrodes of sub-nano Pt clusters were prepared using a home-built cluster beam deposition instrument, which consists of a laser vaporization cluster source, a mass-selecting ion beamline, and an ultrahigh vacuum (UHV) end station for cluster deposition. The oxide substrates were cleaned in advance by Ar⁺ sputtering and annealing and tested to ensure that they are electrochemically inactive. Ions of size-selected sub-nano Pt clusters were deposited on the substrates until a certain coverage was reached. The sample electrodes prepared in this way were exposed to an O₂-free HClO₄ electrolyte solution, and electrochemical measurements were performed.

In this contribution, we will discuss how every Pt atom counts for the HER activity of size-selected sub-nano Pt clusters. We will particularly show that by the interplay between the experiment and quantum chemical calculations, certain Pt clusters, composed of only several atoms, can reduce protons and adsorb hydrogen atoms very efficiently, which leads to their superior HER activity.

2:20pm **HC+AS+SS-MoA-3 In situ X-ray Absorption Spectroscopy to Probe the Dynamics of Ni₃Fe catalysts: Implications for Dry Methane Reforming,**

L. Cruz, University of California, Riverside; J. Hong, Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; S. Shah, University of California - Riverside; S. Bare, Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; **Kandis Leslie Gilliard-AbdulAziz**, University of California - Riverside **INVITED**
The exsolution of nanoparticles from perovskite precursors has been explored as a route to synthesize firmly anchored catalysts. The characteristics of these exsolved nanoparticles, such as size, composition, and morphology, are highly dynamic depending on the redox nature of the reactive environment. Their dynamic nature warrants a study that tracks the changes with in-situ and ex-situ characterization to benchmark states. In this talk, we will discuss the use of operando X-ray Absorption Spectroscopy (XAS) to study the formation, evolution, and regeneration of exsolved NiFe nanoparticles from LaFe_{0.8}Ni_{0.2}O₃ perovskite oxide precursors. STEM-HAADF with EDS analysis was used to measure the nanoparticle composition and morphology after exposure to dry methane reforming (CH₄, CO₂, CO, H₂, H₂O), reductive (H₂) or oxidative (O₂) conditions. Our findings show that the nanoparticle formation in 5%H₂/He occurs in sequential exsolution mechanisms where Ni exsolves first and then Fe. During DRM conditions, the Ni composition transforms from predominantly Fe-rich to Ni-rich NiFe catalysts. Lastly, we will discuss the regeneration of bimetallic alloys and implications for future work in exsolved bimetallic alloys.

3:00pm **HC+AS+SS-MoA-5 Photocatalysis between High-Purity and Applied Reaction Conditions: Understanding Carbon Dioxide Reduction on the Molecular Level, Jennifer Strunk**, Leibniz Institute for Catalysis, Germany **INVITED**

Reducing carbon dioxide just with the energy of (sun)light to platform chemicals for the chemical industry (e.g. carbon monoxide, methane) is still a highly desirable process to enable a recycling of this greenhouse gas. Yet, despite more than 40 years of research, the achievable yields in

photocatalytic carbon dioxide reduction have not increased significantly, thereby clearly failing to meet demands for industrial implementation. One significant hurdle is our limited understanding of the chemical processes on the molecular scale, in particular under reaction conditions relevant to a future application. This is to a large extent due to the vastly different, and in part badly described, reaction conditions applied in published works, making it practically impossible to compare the different studies.

Our approach is the design of a reactor and a research methodology to enable highly reproducible studies in photocatalytic carbon dioxide reduction. Using solely construction parts suitable for high vacuum applications, we have developed the so-called "high-purity gas-phase photoreactor" with gas chromatographic trace gas analysis, allowing to obtain reproducible results on the ppm level. It can also function as bridge between true single-crystal studies and possible reaction conditions in practical applications.

Using this device, fair comparisons of different photocatalysts suggested in literature has been possible. This revealed the well-known titanium dioxide as one of the best materials, despite its large bandgap. Reliable apparent quantum yields have been determined. Focusing our studies on titania, it has been possible to obtain a rather complete picture of the reaction progress on the molecular scale. The reaction from carbon dioxide to methane is likely not a linear sequence of reduction steps but involves also oxidative steps by a reaction with holes. Even if methane as one-carbon product is formed, intermediates involving a C-C bond are involved. The limiting step is the water oxidation reaction, which does not run to completion. Instead, oxygen-related species are stored on or in titania until the material is saturated and the reaction ceases. These findings indicate that (i) completely other materials, possibly Z scheme systems with suitable cocatalysts, need to be developed that allow a less complex surface reaction pathway, and (ii) that (biogenic) methane may be a better co-reactant than water in a "photo dry reforming" reaction.

4:00pm **HC+AS+SS-MoA-8 Electrochemical Nitrate Reduction: Controlling Adsorbate Affinity to Tailor Reaction Products, Kelsey Stoerzinger**, Oregon State University **INVITED**

The electrochemical nitrate reduction reaction (NO₃RR) represents a distributed approach for water treatment and chemical synthesis (ammonia) as an alternative to conventional carbon-intensive processes (Haber-Bosch). Catalysts requirements for this reaction, however, are immense: water/protons are required to reduce nitrate but compete with NO₃RR to evolve hydrogen gas at comparable potentials, and selectivity along an 8 e⁻/10 h⁺ process is required to produce ammonium. Here we investigate NO₃RR activity and ammonium selectivity across 3d and select 4d transition metals in neutral conditions prototypical of nitrate-containing source waters, developing fundamental understanding of the competitive processes that give rise to these trends to guide future catalyst design. We develop a microkinetic model capturing the potential-dependent nitrate rate order, arising from competitive adsorption between nitrate and hydrogen. Competition with the hydrogen evolution reaction is manifest in the NO₃RR Faradaic efficiency, described by catalyst work function. Selectivity to ammonium nominally increases as transition metal d-band center energy approaches and overcomes the Fermi level, with Co representing an optimal catalyst. Density functional theory calculations identify a Sabatier-like relationship between ammonium selectivity and the driving forces for nitrite reduction to nitric oxide and the dissociation of nitric oxide, where Co represents a local optimum between these two processes. These results identify competing design considerations – linking electronic structure to mechanistic selectivity-limiting steps – offering strategies to improve existing catalysts and design new alloy compositions for NO₃RR to ammonium.

4:40pm **HC+AS+SS-MoA-10 Energetics and Growth Modes of Ni and Pd Nanoparticles on Graphene / Ni(111), Kun Zhao, J. Rumpitz, N. Janulaitis, C. Campbell**, University of Washington

The use of carbon supports for late transition metal nanoparticle catalysts has grown substantially in recent years due to efforts to develop electrocatalysts for clean energy applications and catalysts for new aqueous-phase biomass-related conversions, and due to the evolution of new carbon materials with unique properties (e.g., graphene, carbon nanotubes, etc.). However, much less is known about the bonding energetics of catalytic metal nanoparticles on carbon supports in comparison with oxide supports, which are more common for thermal catalysis. Here we investigated the growth morphologies and heats of adsorption of Ni and Pd vapor deposited onto graphene/Ni(111) at 300 K and 100 K using He⁺ low-energy ion scattering (LEIS) and single crystal

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adsorption calorimetry (SCAC). For Ni/graphene/Ni(111), the SCAC results showed at 300 K the heat of adsorption of Ni vapor increases rapidly from 336 kJ/mol initially to the heat of sublimation (430 kJ/mol) by 2 ML, and at 100 K from 230 kJ/mol to the heat of sublimation slower by 3.5 ML. The growth models derived from LEIS results suggested that Ni grows as flat-topped islands with a thickness of ~1.5 nm when deposited at 300 K, and small hemispherical cap shape with a number density of 2×10^{16} particles/m² when deposited at 100 K. The particle size and morphology account for the differences in the heat of adsorption versus coverage at these two temperatures. The Ni chemical potential as a function of average particle diameter in the 0.5 to 4 nm range at 100 K was determined from the LEIS and SCAC measurements, and an adhesion energy of 3.6 J/m² was determined from fitting the chemical potential vs diameter to a theoretical model. For Pd/graphene/Ni(111), the heats of adsorption of Pd increase with coverage similarly to Ni at 300 K and 100 K and reach the heat of sublimation (370 kJ/mol) by 2.8 ML, with an initial heat of adsorption at 300 K (272 kJ/mol) that is 47 kJ/mol higher than at 100 K. The trends in the heat of adsorption are supported by the growth model from the LEIS results. Similar to Ni growth, however with much smaller particle size and larger particle density, Pd grows as flat-topped islands at 300 K with a thickness of ~0.85 nm, and hemispherical cap shape at 100 K with a number density of 6×10^{16} particles/m². The evolution of Pd chemical potential along with particle size was determined in the average particle diameter range of 0.6 – 2.5 nm at 100 K and the adhesion energy was found to be 3.8 J/m².

5:00pm **HC+AS+SS-MoA-11 Size Dependent CO₂ Reduction Activity and Selectivity of Ag Nanoparticle Electrocatalysts in sub-5 nm Regime**, *Xingyi Deng*, NETL/LRST; *D. Alfonso*, NETL; *T. Nguyen-Phan*, NETL/LRST; *D. Kauffman*, NETL

Coinage metals (Au, Cu and Ag) are state-of-the-art electrocatalysts for the CO₂ reduction reaction (CO₂RR). Size-dependent CO₂RR activity of Au and Cu has been studied, and increased H₂ evolution reaction (HER) activity is expected for small catalyst particles with high population of undercoordinated corner sites. A similar level of consensus is lacking for Ag catalysts because the ligands, capping agents, or stabilizers typically used to control particle size and crystallographic orientation can block specific active sites and mask inherent activity trends. We used a combination of ultrahigh vacuum surface science techniques, electrochemical measurements, density functional theory, and microkinetic modeling to finely resolve the size dependent CO₂RR activity and selectivity of Ag nanoparticle electrocatalysts in the sub-5 nm range. Experimental results identified CO₂RR selectivity increased with average particle diameter between 2 to 6 nm with 3.7 ± 0.7 nm diameter Ag particles demonstrating the highest combination of CO₂RR activity and selectivity. A nearly identical size-dependent trend was also predicted in computational modeling: smaller diameter particles favored H₂ evolution reaction (HER) due to a high population of Ag edge sites, whereas larger diameter particles favored CO₂RR as the population of Ag(100) surface sites grew. Our results resolve the CO₂RR behavior of Ag in the crucial sub-5 nm range and establish an effective minimum size limit for balancing activity and selectivity. Particles below a critical diameter suffered from poor selectivity, while larger particles above the critical diameter demonstrated bulk-like activity that led to reduced catalyst utilization. These results provide insight into the size-dependent CO₂RR activity of pristine Ag catalysts and will help guide future catalyst development efforts.

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