

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+2D+SS-WeM

Exotic Nanostructured Surfaces for Heterogeneously-Catalyzed Reactions

Moderators: Ashleigh Baber, James Madison University, Erin Iski, University of Tulsa

8:20am **HC+2D+SS-WeM-2 Selective Alkane Chemistry on IrO₂(110) Surfaces, Aravind Asthagiri, M Kim, The Ohio State University; J Weaver, University of Florida**

Selective conversion of alkanes to higher value species using heterogeneous catalysts is of great interest with the increasing availability of light alkanes from shale fracking. We have used a combination of temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) to demonstrate that the stoichiometric terminated IrO₂(110) surface can activate methane and ethane below room temperatures, and furthermore, that this surface can be selective towards ethane dehydrogenation to ethylene. For ethane, DFT shows that adsorption and initial C-H bond cleavage to surface bound C₂H₄* is facile and the selectivity step occurs between further C-H bond breaking leading to complete oxidation versus ethylene desorption. The reactivity of this surface is mediated by the presence of undercoordinated Ir (Ir_{cus}) and adjacent bridge O atoms (O_{br}). Using the combination of TPRS and DFT we find that pre-hydrogenating the IrO₂(110) surface results in the formation of HO_{br} sites that increases the selectivity towards ethylene by increasing the barrier to C-H bond cleavage for C₂H₄* and decreasing the desorption energy of C₂H₄*. We will discuss efforts to use DFT and microkinetic modeling to explore doping strategies of both the Ir_{cus} and O_{br} sites to promote selectivity towards ethylene formation.

8:40am **HC+2D+SS-WeM-3 Design of Nanostructured Catalysts for Better Performance, Francisco Zaera, University of California, Riverside INVITED**

One of the major challenges in heterogeneous catalysis is the preparation of highly selective and robust catalysts. The goal is to be able to synthesize solids with stable surfaces containing a large number of specific surface sites designed for the promotion of a particular reaction. New synergies between surface-science studies and novel nanosynthesis methodology promise to afford new ways to design such highly selective catalysts in a controlled way. In this presentation we will provide a progress report on a couple of projects ongoing in our laboratory based on this approach. Platinum-based catalysts have been prepared for the selective trans-to-cis conversion of olefins, with a design based on early surface-science work with model surfaces and quantum mechanical calculations that indicated a particular preference for (111) facets in promoting the formation of the cis isomers. We are currently extending this research by using the concept of "single-site catalysis" with Pt-Cu bimetallics for the selective hydrogenation of unsaturated aldehydes. In a second example, new metal@TiO₂ yolk-shell nanomaterials conceived for both regular and photo-induced catalytic applications have been used to promote CO oxidation at cryogenic temperatures and to suggest that in photocatalysis the role of the metal may not be to scavenge the excited electrons produced in the semiconductor upon absorption of light, as commonly believed, but rather to promote the recombination of the adsorbed atomic hydrogen initially produced by reduction of H⁺ on the surface of that semiconductor. New mixed-oxide surfaces are being designed using atomic layer deposition (ALD) as well.

9:20am **HC+2D+SS-WeM-5 Characterization of a Pd/Ag(111) Single Atom Alloy Surface Using CO as a Probing Molecule for H₂ Dissociation, Mark Muir, M Trenary, University of Illinois at Chicago**

Tuning catalysts for selective hydrogenation reactions is ultimately determined by the nature of the active site for H₂ dissociation and the adsorption of atomic hydrogen on the surface. Several single atom alloys (SAAs) consisting of small amounts of Pd deposited onto surfaces of metals that do not activate H₂ dissociation, such as Cu(111) and Au(111), have been previously studied. In the present study, we characterize Pd/Ag(111), a possible new single atom alloy surface using reflection absorption infrared spectroscopy (RAIRS) of adsorbed CO as a probe. From 0.01 to 0.04 ML Pd/Ag(111), a ν(CO) stretching peak was seen at 2050 cm⁻¹ corresponding to CO adsorbed on palladium atoms at the on-top site, indicating a single atom alloy surface. By increasing the palladium coverage

to approximately 0.05 ML and above, a second ν(CO) stretching peak was seen at 1950 cm⁻¹ corresponding to CO adsorbed on a palladium bridge site, indicating palladium dimer formation. The surface palladium coverage was determined using temperature programmed desorption (TPD) of CO and Auger electron spectroscopy (AES). By annealing these surfaces to 500 K, the palladium atoms diffuse into the subsurface, and a ν(CO) stretching peak at 2150 cm⁻¹ (CO adsorbed on silver atoms) is greatly enhanced in intensity due to subsurface palladium. The subsurface to surface palladium ratios on the single atom alloy surfaces were varied from capped Ag/Pd/Ag(111), to a 50:50 ratio, to approximately a 60:40 ratio. The ability of subsurface palladium on the Pd/Ag(111) SAA surfaces to facilitate hydrogen dissociation was explored using H₂ and D₂ TPD.

9:40am **HC+2D+SS-WeM-6 Propyne Hydrogenation over a Pd/Cu(111) Single Atom Alloy Catalyst Studied with Infrared Spectroscopy, Mohammed Abdel-Rahman, M Trenary, University of Illinois at Chicago**

The hydrogenation of propyne (C₃H₄) to propylene (C₃H₆) using a Pd/Cu(111) single atom alloy (SAA) has been studied using polarization dependent-reflection absorption infrared spectroscopy. This method allows for simultaneous monitoring of reactants and products in the gas-phase and species adsorbed on the surface during the reaction. The results were compared with the hydrogenation of propyne using Pd-free Cu(111) as well as previous studies on Pd/Cu SAA alumina-supported metal catalysts. Propylene production first occurs at 383 K as indicated by the presence of an infrared peak at 912 cm⁻¹, which is a uniquely characteristic of gas-phase propylene. The presence of propyne oligomers on the surface is indicated by a dramatic increase in the peak intensity at 2968 cm⁻¹ at temperatures above 400 K. The progression of the peaks at 912 and 3322 cm⁻¹ was used to calculate the rate of production of propylene and the rate of consumption of propyne, respectively. This reaction rate was used to determine a turnover frequency (TOF) for the reaction on the Pd/Cu SAA catalyst.

11:00am **HC+2D+SS-WeM-10 "Single-Atom" Catalysis: How Structure Influences Reactivity, Gareth S. Parkinson, TU Wien, Austria INVITED**

The field of „single-atom“ catalysis (SAC) [1-2] emerged as the ultimate limit of attempts to minimize the amount of precious metal used in heterogeneous catalysis. Over time, it has become clear that metal adatoms behave differently to supported nanoparticles [3-4], primarily because they form chemical bonds with the support and become charged. In this sense, SAC systems resemble the mononuclear coordination complexes used in homogeneous catalysis, and there is much excitement that SAC could achieve similar levels of selectivity, and even heterogenize problematic reactions currently performed in solution. It is important to note, however, that homogeneous catalysts are designed for purpose based on well-understood structure-function relationships, but the complexity of real SAC systems means that the structure of the active site is difficult to determine, never mind design. In this talk, I will describe how we are using precisely-defined model supports [5] to unravel the fundamentals of SAC. I will show a selection of our latest results in this area, including scanning probe microscopy, x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) data to show how the local structure of Ir₁/Fe₃O₄(001) and Rh₁/Fe₃O₄(001) single atom catalysts changes based on preparation and adsorption of reactants, and how the structures obtained can be rationalised by analogy to Ir(I) and Ir(IV) complexes, respectively. If time permits, I will also show that CO oxidation activity in the Pt₁/Fe₃O₄(001) system is promoted by water.

[1] Qiao, B., et al., Single-atom catalysis of CO oxidation using Pt₁/FeOx. *Nature Chemistry* **3** (2011) 634-41.

[2] Liu, J., Catalysis by supported single metal atoms. *ACS Catalysis* **7** (2016) 34-59.

[3] Gates, B.C., et al., Atomically dispersed supported metal catalysts: perspectives and suggestions for future research. *Catalysis Science & Technology* **7** (2017) 4259-4275.

[4] Parkinson GS, *Catalysis Letters* **149** (2019), 1137-1146

[5] Bliem, R., et al., Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science*, **346** (2014) 1215-8.

11:40am **HC+2D+SS-WeM-12 Oxidation Reactions on Rh(111), Marie Turano, G Hildebrandt, Loyola University Chicago; R Farber, The University of Chicago; D Killelea, Loyola University Chicago**

The uptake and subsequent surface structures of oxygen on transition metal surfaces reveal much about the reactivity of the metal catalyst. On clean Rh(111) at room temperatures in ultra high vacuum (UHV), oxygen molecules (O₂) readily dissociate into two adsorbed oxygen atoms,

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asymptotically approaching a saturation coverage of 0.5 monolayers (ML, 1 ML= 1.5×10^{15} O atoms cm^{-2}). However, exposing Rh(111) to gas-phase oxygen atoms (atomic oxygen, AO) generated by thermally cracking molecular oxygen over a hot Ir filament, allows for higher oxygen coverages. In addition, oxygen not only adsorbs to the surface, but it may also penetrate into the subsurface region of the crystal. After atomic oxygen exposures at elevated temperatures, the Rh(111) surface is covered in a combination of oxides, adsorbed surface oxygen, and subsurface oxygen (O_{sub}). The coexistence of a variety of structures allows for the determination of which species is reactive to the oxidation of carbon monoxide (CO) on highly oxidized Rh(111) surfaces. Using scanning tunneling microscopy (STM), we have determined that CO oxidation occurs mainly at the interface between the metallic and oxidic surface phases on Rh(111) where the O_{sub} , upon emergence from the bulk, replenishes the surface oxygen. Once O_{sub} is depleted, CO consumes the oxide and the surface quickly degrades into the (2x2)-O+CO adlayer.

12:00pm **HC+2D+SS-WeM-13 Adsorption and Motion of Atomic Oxygen on the Surface and Subsurface of Ag(111) and Ag(110)**, *S Isbill, C Mize, L Crosby, Sharani Roy*, University of Tennessee Knoxville

Silver surfaces act as important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards understanding the mechanism of heterogeneous catalytic oxidation by silver, the role of subsurface oxygen in such catalysis has yet to be elucidated. Subsurface oxygen is adsorbed just beneath the surface of the metal and is believed to play an important role in surface reconstruction and oxidation catalysis. In the present study, density functional theory (DFT) was used to study the interactions of atomic oxygen with the surface and subsurface of the Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption of atomic oxygen at different coverages and examine its effects on the structural and catalytic properties of silver. Our study of O/Ag(111) showed that adsorption of atomic oxygen was strong at low coverage but became weaker with an increase in coverage, much more so for surface oxygen than for subsurface oxygen. Therefore, at higher and industrially relevant oxygen coverages, oxygen preferred to bind to the subsurface than to the surface. In contrast, atomic oxygen bound more strongly to the surface than to the subsurface at all studied coverages. Based on the results from DFT, we constructed analytic models for adsorption in O/Ag(111) and O/Ag(110) as well as performed kinetic Monte Carlo simulations to explain the differences in coverage dependence of surface adsorption versus subsurface adsorption on the two surfaces. The results provide qualitative insight on why surface and subsurface oxygen might have qualitatively different effects on the electronic, geometric, and catalytic properties of silver.

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