

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-ThA

Bridging Gaps in Heterogeneously Catalyzed Reactions

Moderator: Ryan Brown, Clarkson University

2:20pm HC+SS-ThA-1 Hydrogen Adsorption and Reaction on RuO₂(110) Surface, *A Dahal, I Lyubinetsky, Zdenek Dohnalek*, Pacific Northwest National Laboratory

Ruthenium dioxide is used extensively as a co-catalyst in a wide range of photocatalytic water splitting systems. As such, understanding how it promotes the evolution of hydrogen and oxygen is of high importance. In our studies, we employed scanning tunneling microscopy in combination with molecular beam scattering and temperature programmed desorption studies to follow adsorption, reaction, and thermal evolution of hydrogen on a model RuO₂(110). In our temperature-dependent studies, we find that at low coverages ($H_2/Ru < 0.2$) H₂ dissociates heterolytically and forms hydride-hydroxyl pairs below 100 K. At higher coverages ($H_2/Ru > 0.2$), H₂ adsorbed on Ru sites neighboring the hydride-hydroxyl pairs chemisorbs molecularly. Upon annealing the hydride species convert to hydroxyls and most of the chemisorbed H₂ desorbs. Upon heating, the low and high H₂ covered surfaces transform to partially and fully hydroxylated surface, respectively, above 250 K. Molecular beam scattering studies reveal that the adsorption probability of hydrogen on this surface is strongly temperature-dependent, decreasing from ~0.4 at 25 K to <0.01 at 300 K. These combined studies unravel a complete adsorption and dissociation mechanism of H₂ on this model ruthenium dioxide surface.

2:40pm HC+SS-ThA-2 The Role of Oxides for CO Oxidation over Pd and Rh, and How to Deal with Oxygen Poisoning, *Johan Gustafson*, Lund University, Sweden; *O Balmes*, MAX IV Laboratory, Sweden; *C Zhang*, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *A Schaefer*, Chalmers University of Technology, Gothenburg, Sweden; *B Hagman*, Lund University, Sweden; *L Merte*, *N Martin*, *P Carlsson*, Chalmers University of Technology, Gothenburg, Sweden; *M Jankowski*, ESRF, France; *E Crumlin*, Advanced Light Source, Lawrence Berkeley National Laboratory; *E Lundgren*, Lund University, Sweden

Catalytic CO oxidation is a seemingly simple reaction between CO and O₂ molecules, one of the reactions in automotive catalytic converters, and the fruit-fly reaction in model catalysis. Surprisingly, the phase responsible for the catalytic activity is still under debate, despite decades of investigations. We have performed a simple but yet conclusive study of single crystal Rh and Pd model catalysts, resolving this controversy. For Rh, the oxygen covered metallic surface is more active than the oxide, while for Pd, thin oxide films are at least as active as the metallic surface, but a thicker oxide is less active [1]. The difference between these oxide structures is that the thin PdO films expose coordinatively unsaturated (CUS) metal atoms that act as active sites, while Rh oxides and thicker PdO films do not expose such sites and are hence less active. Similar results have also been found for methane oxidation over Pd [2].

Under highly oxidizing conditions, which are, for instance, desirable for optimal efficiency of combustion engines, there is a general problem of deactivation of catalysts due to too high oxygen exposure, so-called oxygen poisoning. With the above results in mind, this problem is likely related to the formation of oxides that do not expose CUS sites. We therefore believe that the problem of oxygen poisoning over Pd catalysts can be solved by growing a PdO film on top of a more inert metal such as Ag or Au, as this will limit the thickness of the oxide film and hence stabilize the active oxide surface.

In this presentation, we will discuss the active phase of Pd and Rh for CO oxidation, and hopefully show the first results of lower degree of oxygen poisoning for CO and methane oxidation over Pd/Au and Pd/Ag systems.

References

1. J. Gustafson et al., The Role of Oxides in Catalytic CO Oxidation over Rhodium and Palladium, *ACS Catal.*, 2018, 8, 4438–4445.
2. A. Hellman et al., The active phase of palladium during methane oxidation, *J. Phys. Chem. Lett.* 2012, 3, 678–682.

3:00pm HC+SS-ThA-3 Simplifying the Relationships between Catalyst Structure and Reaction Rates for Complex Mechanisms, *Charles T. Campbell*, University of Washington

INVITED

Better catalysts and electro-catalysts are essential for many energy and environmental technologies of the future. Designing better catalysts requires knowing the relationships between catalyst structure and catalytic reaction rates, which are in general poorly understood. I will review here some concepts that clarify and simplify these relationships. While a typical catalytic reaction has a dozen or more adsorbed intermediates and elementary-step transition states, Degree of Rate Control (DRC) analysis can be applied to a microkinetic model of the best known catalyst material to show that the net rate really only depends upon the energies of a few (2 to 4) of these. For related materials, one only needs to know how the change in material affects the energies of these few 'rate-controlling species' to understand how rates relate to structure. This offers opportunities for designing better catalysts. DRC analysis also provides a simple way to predict kinetic isotope effects (KIEs), which can be compared to simple KIE experiments to verify the energy accuracy of a microkinetic model (that is often based on DFT energies). Such DFT energies can be used with DRC values to predict faster catalysts.

The chemical potential of metal atoms (μ_m) in supported catalyst nanoparticles provides another simplifying concept for developing structure – rate correlations in catalysis. It has been known for years that this chemical potential enters directly into the rate equations for catalyst deactivation by sintering. I will show here that it also correlates strongly with the strength with which surface metal atoms bind adsorbed reaction intermediates (and transition states), which correlate with rates as outlined above. I will then review what aspects of catalyst structure control metal chemical potential. It can be tuned to lower values (relative to large particles of the pure metal) by mixing the metal with another metal with which it forms an exothermic alloy, and tuned higher by making the nanoparticles smaller and putting them on a support to which they have a smaller adhesion energy (E_{adh}). Quantitative equations that predict how μ_m varies with size and E_{adh} , and how E_{adh} depends on the metal element and the oxide surface used as the catalyst support will be presented. These also offer opportunities for predicting faster catalysts.

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4:00pm HC+SS-ThA-6 Spectroscopic Techniques for Identifying Reactive Intermediate Structures during Decomposition of Formic Acid over Metals and Metal Oxides, *Megan Witzke, D Flaherty*, University of Illinois at Urbana-Champaign

Identifying reactive intermediates within an "organometallic zoo" of species that form on surfaces of metal nanoparticles and metal oxides during reactions is a long standing challenge in heterogeneous catalysis.¹ We use a combination of spectroscopic techniques and data analysis methods to isolate and extract spectral features of the reactive intermediates present under relevant operating conditions. Modulation excitation spectroscopy coupled with phase sensitive detection selectively filters spectra to show only reactive intermediates and suppress features of spectating species.² The combined spectra of all reactive species are deconvoluted using singular value decomposition techniques that provide distinct spectra and estimate surface coverages for independent species.³ Comparisons of spectra obtained at different modulation frequencies exploit differences in intrinsic free energy barriers between reactive intermediates by removing species that are unable to form at higher stimulated frequencies. We combine these techniques to molecularly interpret infrared spectra to identify compositionally similar surface intermediates formed in situ during decomposition of formic acid (HCOOH) over anatase TiO₂ and Au-TiO₂. Operando and transient measurements determine the sequence of elementary steps that decompose HCOOH and identify surface species that do not form CO and CO₂. Transient measurements show that HCOOH adsorbs and deprotonates to form bidentate formates over TiO₂ while monodentate intermediates do not lead to CO or CO₂ formation. Selective inhibition of Au sites with co-fed CO over Au-TiO₂ indicate monodentate reactive intermediates evolve into bidentate formates on Au at higher coverages. Distinguishing the structure, composition, and orientation of reactive intermediates provides complimentary evidence to measured rates and DFT to depict reaction mechanisms and provide insight into how surface properties dictate rate and selectivity.

References:

- (1) Burwell, R. L. The mechanism of heterogeneous catalysis, *C&EN Magazine*, 22 August, 1966, 56.

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(2) Urakawa, A.; Burgi, T.; Baiker, A. *Chem. Eng. Sci.* 2008, 63, 4902.

(3) Jaumot, J.; de Juan, A.; Tauler, R. *Chemometr. Intell. Lab.* 2015, 140, 1.

4:20pm **HC+SS-ThA-7 Self-sustained Reaction Oscillations in a New Light, Uta Hejral, S Albertin, J Zhou, S Pfaff**, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *S Blomberg*, Lund University, Sweden; *O Gutowski, A Dippel*, Deutsches Elektronen-Synchrotron DESY, Germany; *J Gustafson, J Zetterberg, E Lundgren*, Lund University, Sweden

Catalysts are complex material systems accelerating desired chemical reactions in chemical industry, fuel cells and car exhaust treatment. To improve their performance, an atomic-scale understanding of the interplay between catalyst structure, the surrounding gas composition and the catalyst activity under realistic reaction conditions is inevitable. Self-sustained reaction oscillations, in which the catalyst shuts its activity periodically off, have been studied for many years [1, 2] with the aim (1) to avoid reactor instabilities or even reactor explosions, and (2) to understand and make use of the underlying catalyst structures leading to higher conversion rates and selectivities often present during the oscillations. However, no general mechanism, especially for the structure leading to the activity increase and decrease, has been put forward.

Here we combined High Energy Surface X-Ray Diffraction (HESXRD) [3, 4], Planar Laser Induced Fluorescence (PLIF) [5], in-situ Mass Spectrometry (MS) and optical LED reflectance [6] at beamline P07 (DESY) at a photon energy of 77 keV to study self-sustained reaction oscillations during CO oxidation over Pd(001). This allowed, with sub-second time resolution, for correlating the catalyst structure (HESXRD) to the sample's CO₂ production (PLIF, MS) and hence its catalytic activity. The LED light, reflected from the sample surface, provided in addition immediate information on the surface roughness. Our data indicate that the oxidation and reduction of (111)-oriented Pd islands on top of an epitaxial PdO(101) oxide layer, previously reported under reducing conditions close to UHV [7], play a crucial role in the underlying mechanism for the self-sustained reaction oscillations.

References:

- [1] F. Schüth et al., *Adv. Catal.* **39**, 51 (1993).
- [2] B. L. M. Hendriksen et al., *Nature Chem.* **2**, 730 (2010).
- [3] J. Gustafson et al., *Science* **343**, 758 (2014).
- [4] U. Hejral et al., *Phys. Rev. B* **96**, 195433 (2017).
- [5] S. Blomberg et al., *J. Phys.: Condens. Matter* **28**, 2222 (2016).
- [6] J. Zhou et al., *J. Phys. Chem. C* **121**, 23511 (2017)
- [7] J. F. Weaver, *ACS Catal.* **7**, 7319 (2017).

4:40pm **HC+SS-ThA-8 Operando Catalysis--A First-Principles Perspective, William Schneider**, University of Notre Dame **INVITED**

First-principles computational methods have had a profound impact on the science of heterogeneous catalysis. One of the challenges in making these models more rigorous, for instance to establish quantitative relationships between experimental observations of rates, rate orders, and models, is to faithfully account for the influence of the catalytic reaction conditions on the state of a catalytic material and on mechanism. "Operando"

experiments interrogate catalysts at the conditions at which they are functioning. In the same way, by incorporating finite temperatures and pressures through statistical mechanical and ab initio dynamics models, and by recognizing that a catalytic material may present a heterogeneous array of sites, it is in principle to model a catalyst "operando" from first principles. In this presentation I first discuss our efforts to model finite-temperature adsorption behavior at metal surfaces, including the translational motions that control adsorption free energies and the interactions between adsorbates that can modify surface reaction kinetics.

I then discuss our recent work to describe how the rates of surface reactions might be altered by the imposition of an external plasma, showing how changing the "environment" is an alternative and promising way to control catalytic reactivity.

5:20pm **HC+SS-ThA-10 Chiral Selectivity in Heterogeneous Catalysis, R Chapleski, Sharani Roy**, University of Tennessee Knoxville

Developing powerful next-generation technologies for catalysis, energy conversion, and energy storage relies on understanding and controlling molecular transformations at complex interfaces. However, relatively little is known about the fundamental molecular-scale phenomena driving

chemical selectivity at functional and complex interfaces. Our work aims to investigate mechanisms of enantioselectivity in heterogeneous catalysis. Specifically, by investigating hydrogenation reactions of both the (R)- and (S)- enantiomers of limonene on the chiral Pt(532) surface, we will provide insight into the adsorbate-surface interactions that lead to enantiomeric excess in the formation of the chiral product, menthene. Here, we report our initial results of this work, which uses computational methods to probe molecular adsorption of limonene followed by catalytic hydrogenation. Our approach utilizing density functional theory combined with the results of recent experimental sum-frequency generation experiments, reveals likely adsorption orientations and reaction pathways of both enantiomers on the Pt(532) surface. A comparison of adsorption and reaction mechanisms across both enantiomers leads to a fundamental description of the atomic-scale interactions that produce enantioselectivity in adsorption and reactions of limonene on a chiral platinum surface. We hope that these results provide qualitative insight into how enantioselectivity is achieved in heterogeneous catalysis at intrinsically chiral metal surfaces.

5:40pm **HC+SS-ThA-11 Combining in situ Environmental TEM and Multiscale Simulations to Study the Dynamic Processes of Copper Oxidation, Meng Li, M Curnan, W Saidi, J Yang**, University of Pittsburgh

Cu-based materials are widely used in industrial catalysts applications, including methanol synthesis and H₂ production from the water-gas shift reaction. Across these applications, maximizing the Cu surface area improves the catalytic performance. However, side effects such as poor stability and deactivation also occur due to oxide formation at active sites over long-term use. Therefore, developing a fundamental understanding of the nanoscale mechanisms initiating Cu surface oxidation is essential to addressing these issues. The process of surface oxidation can be divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Of these three stages, the initial stage – which spans from the oxygen chemisorption to the onset of oxide nucleation – is least understood, as it is inaccessible to traditional surface science and bulk material experimental methods. Despite recent improvements in computational methods, current computational capabilities have yet to simulate O chemisorption directly leading to oxide nucleation, given the resources required to complete such simulations over sufficiently large time and size scales.

In this work, by combining Environmental TEM (ETEM) with multiscale atomistic simulation, the dynamical processes enabling initial stage copper oxidation were explored. Our ETEM (Hitachi H-9500, 300 kV, LaB₆) results show that over surface step defects of various facet orientations, oxide nucleation preferences vary over adjacent facet edges, potentially leading to known differences in observed reconstructions on differently oriented surfaces. Surface reconstructions on Cu(100) and Cu(110) facets were observed, followed by Cu₂O island nucleation and growth in a layer-by-layer manner. Investigation of the dynamical processes leading to oxide nucleation on these reconstructed surfaces is done via a multiscale computational approach. Single initial oxidation stage events from oxygen chemisorption to surface reconstruction are first modeled using the Nudged Elastic Band (NEB) method on systems modeled with Reactive Force Field (RFF) potentials. Oxide nucleation and growth is then affordably modeled at size and time scales consistent with ETEM results, applying structures and energies resolved in RFF NEB calculations to rate tables used by adaptive kinetic Monte Carlo simulations. This simulation methodology forms a feedback loop with ETEM results, allowing computational and experimental results to validate one other. Ultimately, this cross-validation will be used to explain how oxide nucleation can be prevented by controlling factors like surface and defect orientation, temperature and pressure.

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