Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-ThM

Bridging Gaps III: Combined Theory and Experiment in Catalysis

Moderators: Liney Arnadottir, Oregon State University, **Sharani Roy**, University of Tennessee Knoxville

8:00am **HC+AS+SS-ThM-1 Mechanistic Understanding and Catalyst Design for Selective Methane Activations*, Ping Liu,*** Brookhaven National Laboratory **INVITED**

The development of variable catalysts to promote the activation of methane and control the conversion selectivity has long been a challenge in catalysis. One of the obstacles is the lacking in fundamental understanding of reaction network due to the complexity. Here, the mechanistic study of methane activation to carbon monoxide and/or methanol on metal/oxide and oxide/oxide will be presented using combined Density Functional Theory and kinetic Monte Carlo simulation. Our results not only provide new insight into the mechanism and active sites, but also highlight the importance of confined active site in tuning the binding of intermediates and promoting the catalytic performance.

8:40am **HC+AS+SS-ThM-3 A First Principles Study of Propane Dehydrogenation Reactions on Hydroxyl-Terminated Al_2O_3 Decorated Platinum Surfaces*, Sumandeep Kaur,*** *H. Nguyen, L. Árnadóttir,* Oregon State University

Propylene is precursor of many complex chemicals such as polypropylene, propylene oxide, acrylonitrile etc. which are used in the fabrication of numerous consumer and industrial products. Catalytic dehydrogenation of propane has been proposed as a practical route for propylene production and metal catalysts such as Pt, Pd and Sn have been extensively employed for this purpose. Recent experimental studies have shown that tailoring metal-active sites with atomic layer deposition (ALD) can increase the selectivity of propane dehydrogenation (PDH) towards propylene.[1] Herein we use DFT and microkinetic modeling to study PDH on Pt surfaces covered with Al_2O_3 to investigate the effect of ALD on PDH. Our primary results show that alumina ALD covers 1/6 of the planar surface Pt(111) blocking all the active sites for propane dehydrogenation while on the step or kink surfaces, (Pt(211), Pt(321), Pt(533)) alumina ALD forms a one-dimensional ribbon like structure along the step or kink atoms, leaning over the lower terrace and leaves room on the upper terrace for the reaction intermediates to interact with the ALD layer and the metal catalyst. These studies on PDH reactions on ALD covered Pt can lead to better understanding on how ALD can be used to tailor catalytic active sites and improve selectivity.

[1] Lu et al. ACS Catal. 2020, 10,23, 13957

9:00am **HC+AS+SS-ThM-4 Atomic-Level Studies of C_2H_4 on clean and Rh_1-Decorated $Fe_3O_4(001)$*, Panukorn Sombut,*** *L. Puntscher, C. Wang, M. Ulreich,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; J. Pavelec, Z. Jakub, F. Kraushofer, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; G. Parkinson,* TU Wien, Austria

The local binding environment of metal-oxide supported single-atom catalysts (SACs) determines how reactants adsorb and therefore plays a decisive role in catalysis. Here, we study how $Fe_3O_4(001)$-supported Rh_1 adatoms interact with ethylene (C_2H_4) using density functional theory, combined with temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. C_2H_4 is the simplest alkene molecule, and thus a model reactant for hydrogenation and hydroformylation reactions. Our study begins with the clean $Fe_3O_4(001)$ surface[1], where C_2H_4 binds weakly. We identify and model different molecule orderings at different coverages that agree nicely with STM images, as well as explain the experimental TPD data. Then, we study C_2H_4 adsorption at 2- and 5-fold coordinated Rh sites at the $Fe_3O_4(001)$ surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two C_2H_4 molecules, while 5-fold Rh can only host a single C_2H_4 molecule. Finally, we investigate coadsorption of C_2H_4 with CO, a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

1. Bliem, R. *et al.* Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science* **346**, 1215–1218 (2014).

9:20am **HC+AS+SS-ThM-5 How the Support Dictates the Reactivity of FeO_x-Based Single-Atom Catalysts*, Matthias Meier,*** TU Wien, Austria **INVITED**

Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system[1], magnetite (Fe_3O_4), specifically its (001) facet has been used because it offers stable sites for single-atom adsorption up to high temperatures[2]. Here, I will demonstrate how important the support is for the stability of single-atoms, as well as their catalytic properties.

Rh and Ir single-atoms utilize Fe vacancies in the subsurface of the reconstructed $Fe_3O_4(001)$ unit cell to incorporate into the surface layer. Changing the positions of Fe atoms in the support as part of the incorporation process enables the single-atoms to be accommodated in a more favorable configuration than if they were adsorbing on top of the surface. Their catalytic properties are drastically affected by changes in the atomic environment. Incorporation temperatures vary depending on both coverage and the presence or absence of adsorbates, such as CO.

Changes in the support can affect not only ground states, but also reaction mechanisms and activation barriers. Pt single-atoms become mobile upon CO adsorption, forming dimers, which oxidize CO via a Mars van Krevelen reaction using a surface oxygen atom[3]. The support is temporarily altered, reducing overall activation barriers and permitting CO oxidation otherwise inaccessible at the observed experimental temperatures.

Similarly, subsurface vacancies are also present in $Fe_3O_4(111)$, modifying electronic surface states and allowing again for easy incorporation of single-atoms already at low temperatures, in line with experimental observations.

References

[1] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M. A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, and G. S. Parkinson, Science **346**, 1215 (2014). [2] R. Bliem, R. Kosak, L. Perneczky, Z. Novotny, O. Gamba, D. Fobes, Z. Mao, M. Schmid, P. Blaha, U. Diebold, and G. S. Parkinson, ACS Nano **8**, 7531 (2014). [3] M. Meier, J. Hulva, Z. Jakub, F. Kraushofer, M. Bobić, R. Bliem, M. Setvin, M. Schmid, U. Diebold, C. Franchini, and G. S. Parkinson, Sci. Adv. **8**, 4580 (2022).

11:00am **HC+AS+SS-ThM-10 Modifying Ethane Oxidation Selectivity on the stoichiometric $IrO_2(110)$ surface through anion substitution*, 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. DFT derived microkinetic simulations show that the selectivity of ethylene peaks at ~60% Cl substitution with increasing Cl substitution reducing the reactivity of ethane. Extending this work to other halogen anion substitutions (F, Br, I) shows that Cl is the optimal dopant. While Br and I favor ethylene desorption over further reaction, these dopants decrease ethane reactivity. In contrast, F dopant does not promote ethylene desorption versus reactivity as effectively as Cl. Current efforts to develop a microkinetic model to explore ethylene selectivity under reaction conditions will be discussed.

11:40am **HC+AS+SS-ThM-12 HC Graduate Student Finalist Talk: Insight into Subsurface Adsorption and Reconstruction of Ag(111) Deduced from a Lattice-Gas Model and Monte Carlo Simulations***, **Carson Mize,*** University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; E. Lander, S. Roy,* University of Tennessee Knoxville

Gas-phase surface models are a beneficial, theoretical tool for providing qualitative insight into elementary steps of surface chemistry. Elementary steps, like adsorption, play a crucial role in many chemical phenomena like surface reconstruction and industrial heterogeneous catalysis. While there exist many previously developed gas-phase adsorption models, most models are limited to low adsorbate coverages due to the computational cost required to produce high coverage models. To investigate adsorption over a broad range of adsorbate coverages on a crystalline solid, we have developed a lattice-gas adsorption model that includes surface and subsurface adsorption, tunable interaction parameters calculated with density functional theory, and larger scale modeling with Monte Carlo simulations. This model has been applied to study oxygen adsorption on a Ag(111) surface, due to experimental findings suggesting the possibility of subsurface-adsorbed oxygen species. Our first model iteration included only strongest binding sites for each region and our simulations indicated greater oxygen accumulation in the second subsurface than the first subsurface in total coverages in excess of 0.375 monolayer (ML). Our second model iteration included all high symmetry sites in each region and found the same qualitative results as the first model using canonical Monte Carlo distributions. Additionally, current grand canonical distributions suggest some subsurface oxygen adsorption exists under temperatures of 475 – 550 K and pressures of 1 – 2 bar, which are typical industrial conditions for catalysis with these systems. Our current model includes adding Ag – Ag and Ag – O interactions to model surface reconstruction, as our previous models only included the unreconstructed silver lattice. This iteration will allow us to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4 × 4) and c(4 × 8) lattices, as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

12:00pm **HC+AS+SS-ThM-13 Measuring and Predicting a Key Catalyst-Performance Descriptor for Supported Metal Nanoparticle Catalysts: Metal Chemical Potential***, **Charles T. Campbell,** J. Rumptz, K. Zhao,* University of Washington

Metal nanoparticles supported on high-area oxides and carbons form the basis for many catalysts and electrocatalysts. Their activity and stability depend on both particle size and choice of support. The chemical potential of the metal atoms in the catalyst material quantifies their stability and is a convenient descriptor that captures the effects of both the nanoparticle size and the support material on both surface reactivity and sinter resistance.[1,2] This chemical potential enters quantitatively into the rate equations for sintering, making a negative contribution to the activation energy.[2] Numerous experimental and theoretical studies have also found that the stability of metal atoms in catalyst materials, including alloys, correlates with their binding energies to adsorbates, whereby surface metal atoms that are more weakly bound to the solid interact more strongly with small adsorbates like O, CO, -OH and $-CH_3$.[1-3] It is thus desirable to develop methods to predict how metal chemical potential depends on particle size and support. Herein, we report calorimetric measurements of: (1) metal chemical potential as a function of particle size and support, and (2) the adhesion energy of the solid metals to different oxide and carbon supports.From these, we have identified predictive correlations of: (1) metal chemical potential in supported nanoparticles as a function of the particle size and the adhesion energy of the particle to the support, and (2) the dependence of this adhesion energy upon the metal element in the catalyst for oxide supports.

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1. Campbell, C. T.; Sellers, J. R. V., *Faraday Discussions,* 162, 9 (2013).
2. Campbell, C. T. and Mao, Z. *ACS Catalysis*, 7, 8460 (2017). See also correction 2018.
3. Mao, Z. and Campbell, C. T., *ACS* Catalysis, 11, 8284 (2021). See also correction 2021.

Author Index

Bold page numbers indicate presenter