

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeA

Bridging Gaps II: Single Atom Alloys and Desirable Defects

Moderators: Rachel Farber, University of Chicago, Gareth Parkinson, TU Wien, Austria

3:00pm HC+AS+SS-WeA-3 Atomic-Scale Structure-Function Relationships of Pt-based Copper Oxide Single-Atom Catalysts, *Audrey Dannar, A. Schilling, G. Giannakakis, A. Therrien, E. Sykes*, Tufts University

Single-atom catalysts comprised of isolated metal atoms anchored on oxide supports have recently gained considerable attention for their potential to improve the activity and or selectivity of important industrial reactions. We have previously shown that single Pt atoms on a copper oxide thin-film are able to perform low-temperature CO oxidation without sintering, a common deactivation mechanism of single-atom catalysts. Using a combination of scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopy, and temperature programmed desorption we elucidated the atomic-scale surface structure of these model catalysts and related that structure to catalytic function. We found that Pt atoms have a preferred binding site on the oxide surface and that they can oxidize CO, but not H₂. These fundamental surface results were leveraged in the design of nanoparticle analogs that were active and selective for the preferential oxidation of CO. In order to extend this approach to bulk oxides we have begun characterizing the 111 facet of a Cu₂O single-crystal which better mimics the Cu₂O particles present in high surface area catalysts. Scanning tunneling microscopy images of the Cu₂O(111) surface reveal atomic-scale structures that may be responsible for the reactivity observed in real catalysts. Low-energy electron diffraction patterns reveal reconstructions in the model catalyst surface induced by exposure to reducing or oxidizing conditions, which is important in terms of how the active sites, and their coordination to the oxide support evolve under relevant reaction conditions. Taken together, our thin-film and bulk copper oxide surfaces decorated with isolated Pt atoms provide useful model systems with which to parse out atomic-scale structure-function relationships that inform the rational design of novel catalysts.

4:20pm HC+AS+SS-WeA-7 Comparison Study of Several Transition Metals on Two Different TiO₂ Model Supports: Anatase TiO₂ (101) and Rutile TiO₂ (110), *Lena Puntscher, K. Daninger, P. Sombut*, TU Wien, Austria; *M. Meier*, University of Vienna, Austria; *M. Schmid*, TU Wien, Austria; *C. Franchini*, Alma Mater Studiorum, Università di Bologna, Bologna, Italy; *U. Diebold, G. Parkinson*, TU Wien, Austria

Single-atom catalysis (SAC) offers an opportunity to minimize the amount of precious catalyst material required for traditional heterogeneous catalysis and to “heterogenize” reactions presently requiring homogeneous catalysis; this would eliminate the problem of separating catalyst and product, while retaining the excellent selectivity and activity of homogeneous catalysts [1].

Unravelling how metal atoms bind to oxide supports is crucial for a better understanding of the SAC’s catalytic properties. Using STM and XPS, we compare the adsorption geometry and stability of several transition metals on TiO₂ model supports: anatase TiO₂(101) and rutile TiO₂(110) [2] and the influence of water on the dispersion of these systems.

This study points out the importance of metal-support interaction and the surprisingly different behaviour of the transition metals Pt, Rh, Ir and Ni on TiO₂ model supports.

1. Parkinson, G.S., *Single-atom catalysis: how structure influences catalytic performance*. Catalysis Letters, 2019. **149**(5): p. 1137-1146.
2. Sombut, P., et al., *Role of Polarons in Single-Atom Catalysts: Case Study of Me₁ [Au₁, Pt₁, and Rh₁] on TiO₂ (110)*. arXiv preprint arXiv:2204.06991, 2022.

4:40pm HC+AS+SS-WeA-8 Boron Effect Improves Catalytic Performance on Supported Pt/SiO₂ Catalysts for Dry Reforming of Methane at Reduced Temperatures, *Carly Byron*, University of Delaware; *M. Ferrandon, A. Kropf*, Argonne National Laboratory; *S. Bai*, University of Delaware; *M. Delferro*, Argonne National Laboratory; *A. Tepyakov*, University of Delaware

Metal nanoparticles supported on metal oxides are studied as catalysts for a variety of applications, most notably catalytic hydrocarbon reforming reactions. Platinum has shown to be a highly active catalyst for the dry reforming of methane (DRM), which converts CO₂ and CH₄ into “synthesis gas”, which can be further processed to produce biofuel. However, the DRM process requires further optimization before large scale use. Our prior studies have shown that boron has a positive effect on platinum/silica catalyst for butane dehydrogenation, due to the reduction in carbon contaminant (coke) on the surface and migration of carbon deposit away from platinum active sites. Based on these findings, Pt/B/SiO₂ catalysts were prepared for DRM catalysis and compared with Pt/SiO₂ catalysts without boron promotion. Both catalysts had similar concentrations of platinum, but the catalytic activity after 14 hours for boron-containing catalyst was drastically improved, resulting in nearly 100% CO₂ conversion compared to 12% without boron. The reacted catalysts were investigated with synchrotron x-ray adsorption spectroscopy (XAS), transmission electron microscopy (TEM), x-ray electron spectroscopy (XPS), and Raman spectroscopy to identify the deactivating factor. It was determined that neither sintering nor coking was a significant factor in Pt/SiO₂ catalyst deactivation, instead that platinum and boron interact electronically to optimize DRM catalysis, which results in high activity at relatively low DRM operating temperatures.

5:00pm HC+AS+SS-WeA-9 Facet Dependence of RhCu Single-Atom Alloy Structure and Reactivity, *Yicheng Wang, R. Hannagan*, Tufts University; *J. Schumann, M. Stamatakis*, University College London, UK; *C. Sykes*, Tufts University, UK

Direct propane dehydrogenation is a promising way to address the current propene shortage. RhCu single-atom alloys (SAAs), predicted by first-principal calculations, have recently been demonstrated to be efficient propane dehydrogenation catalysts. While RhCu model catalysts have been conducted on the (111) facet of Cu to understand the C-H activation mechanism, other facets have not been explored which is important fundamental information needed to bridge the structure gap between model catalyst and nanoparticle studies. In order to better understand the effect of the more open (100) facet, we investigated the RhCu(100) SAA surface using a combination of scanning tunneling microscopy (STM), temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT). Our STM results reveal a striking difference between the alloying mechanism of Rh atoms in Cu(111) versus Cu(100) surface facets. Unlike RhCu(111) where Rh atoms tend to form dense brim in the regions above the step edges, homogeneously dispersed Rh atoms can be observed across the whole Cu(100) surface. DFT modeling indicates that the starkly different Rh distribution can be attributed to the different alloying mechanisms between the Cu(111) and Cu(100) where Rh atom place exchange into the terraces is facile on Cu(100). CO TPD and RAIRS experiments were conducted to study the Rh active sites in the RhCu(100) alloys. CO TPD experiments revealed CO desorption at both low and high temperature hinting at the existence of dicarbonyls, which had not previously been observed on SAAs. RAIRS was used to demonstrate that the low temperature peak corresponded to the transition from dicarbonyls to monocarbonyls and the high temperature peak involved the desorption of the monocarbonyls, which was further confirmed by DFT. Together, these results help us to understand the active sites in RhCu(100) SAAs and the influence of the coordination environment on the binding to Rh sites. These results will further shed light on the structural characterization of high surface area SAA catalysts.

5:20pm HC+AS+SS-WeA-10 Crossing the Great Divide Again: Pseudo-Molecular Beams at Atmospheric Pressure, *E. High, Christian Reece*, Harvard University

In order to reliably predict catalytic activity, we require accurate and robust kinetic models. Fundamental surface science studies on model catalysts are generally considered the “gold standard” for measuring in-depth kinetic and mechanistic information. However, there is often a perceived difficulty in transferring this knowledge from ultra-high vacuum surface science to applied reactor conditions i.e., at elevated temperature and pressure. This misunderstanding led to the development of terms such as pressure gap. In

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reality this so-called pressure gap is in fact a pressure continuum, with the caveat that the catalyst state (i.e., the structure and composition) must be kept consistent across the pressure regimes [1,2]. Herein we demonstrate a high-pressure analogue to classic molecular beam experiments utilising a home-built transient flow reactor in order to directly compare results measured at UHV and at atmospheric pressure. Using CO oxidation over polycrystalline Pd as a test reaction, we find that the transient behaviour observed at UHV [3] is recreated in the transient flow reactor. Further, the fundamentally derived kinetic model that is used to describe the molecular beam experiments also recreates the transient behaviour observed at atmospheric pressure when fed into a packed bed reactor simulation.

[1] Reece, C., Redekop, E.A., Karakalos, S., Friend, C.M. and Madix, R., 2018. Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients. *Nature Catalysis*, 1(11), pp.852-859.

[2] Reece, C. and Madix, R.J., 2021. Moving from Fundamental Knowledge of Kinetics and Mechanisms on Surfaces to Prediction of Catalyst Performance in Reactors. *ACS Catalysis*, 11(5), pp.3048-3066.

[3] Libuda, J., Meusel, I., Hoffmann, J., Hartmann, J., Piccolo, L., Henry, C.R. and Freund, H.J., 2001. The CO oxidation kinetics on supported Pd model catalysts: A molecular beam/in situ time-resolved infrared reflection absorption spectroscopy study. *The Journal of Chemical Physics*, 114(10), pp.4669-4684.

5:40pm **HC+AS+SS-WeA-11 Self-Propagating High Temperature Synthesis of Chevrel Phase Sulfides from Elemental Precursors**, *Tessa Gilmore, M. Pawar, P. Gouma*, The Ohio State University

Self-propagating high temperature synthesis (SHS) is a spontaneous, irreversible, combustion process that requires close to no energy to produce complex materials at high temperature through self-sustained reactions. Little is known about the mechanistic nature of this versatile process, which limits its controllability and applicability. Chevrel Phase (CP) compounds ($MxMo_6S_8$ -CPs) constitute a class of multifunctional, ceramic, designer materials targeted for catalysis, battery electrodes, quantum computing, and other applications. In this research, the successful and rapid processing of the sulfide Chevrel compound $Cu_4Mo_6S_8$ via SHS is demonstrated, and a mechanism is provided. Thermochemical measurements identify an atypical behavior for this SHS process where the overall reaction temperature does not surpass that of the materials with the lowest melting point. This result is attributed to intercalation assisted massive phase transformation facilitated by the use of a MoS_2 precursor. Further work to synthesize the Chevrel phase using other cations is continuing.

6:00pm **HC+AS+SS-WeA-12 Growth and Activity of Ni Catalysts Supported over Ti-doped Ceria from Single Crystal Thin Films to Nanocrystals**, *J. Miao, T. Ara, Jing Zhou*, University of Wyoming

Ceria-supported nickel catalysts have been of great interest in many important applications such as dry reforming of methane (DRM).[1] They can exhibit promising catalytic behavior owing to the unique redox properties of ceria as well as strong metal-support interactions. To enhance the thermal stability of ceria as well as improve its redox properties as a catalytic support for practical applications in catalysis, metal dopants such as Ti can be introduced into ceria. Our previous studies have shown that well-ordered (111)-oriented $Ce_{1-x}Ti_xO_{2-δ}$ thin films can be prepared by simultaneous introduction of Ce and Ti onto Ru(0001) at 700 K in an oxygen environment.[2] The incorporation of Ti in ceria causes the partial reduction of Ce from +4 to +3 state. The films are of high quality consisting of flat terraces with surface features of ceria lattices, oxygen vacancies, Ti dopants, as well as domain boundaries. The extent of the Ce reduction and the nature of the surface structure correlate with the amount of Ti dopants in ceria. Compared to pure $CeO_2(111)$, addition of Ti dopant in $Ce_{1-x}Ti_xO_{2-δ}(111)$ can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as smaller particles upon heating.[3] To study as practical catalysts, powder materials of 5 wt.% Ni dispersed over a series of $Ce_{1-x}Ti_xO_{2-δ}$ (x : 0-0.5) were prepared using sol-gel and impregnation methods and investigated for the DRM reaction with a fixed-bed flow reactor, monitored by on-line mass spectrometer and GC instruments. Incorporation of Ti into the ceria lattice forming $Ce_{1-x}Ti_xO_{2-δ}$ was observed with Ti/Ce ratios less than 3/7 and NiO is formed over these supports. The formation of segregated titania domains was also detected in $Ce_{1-x}Ti_xO_{2-δ}$ with higher Ti/Ce ratios ($Ce_{0.6}Ti_{0.4}O_{2-δ}$ and $Ce_{0.5}Ti_{0.5}O_{2-δ}$). Both NiO

and $NiTiO_3$ can be formed in these Ti-rich ceria supports. Our results demonstrate that doping Ti can enhance the reducibility of ceria and tune the Ni-support interaction, which result in an enhanced coke resistance and catalytic performance of Ni in DRM. The research is sponsored by the Carbon Engineering Initiative from School of Energy Resources at the University of Wyoming.

[1] Z.Y. Liu, D.C. Grinter, P.G. Lustemberg, T.-D. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E.J. Crumlin, D.J. Stacchiola, J. Zhou, J. Carrasco, H.F. Busnengo, M.V. Ganduglia-Pirovano, S.D. Senanayake, J.A. Rodriguez, *Angew. Chem. Int. Ed.* **55**, (26), 7455-7459 (2016).

[2] Y. Zhou, J. Zhou, *J. Phys. Chem. Lett.* **1**, (11), 1714-1720 (2010).

[3] Y. Zhou, J. M. Perket, A. B. Crooks, J. Zhou, *J. Phys. Chem. Lett.* **1**, (9), 1447-1453 (2010).

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