

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

### Room B113 - Session HC+SS-ThA

#### Closing in on Reality & HC Discovery Reception

**Moderators:** *Liney Arnadottir*, Oregon State University, *Ashleigh Baber*, James Madison University, *Dan Killelea*, Loyola University Chicago

#### 2:20pm HC+SS-ThA-1 Ion Imaging applied to Heterogeneous Catalysis on Metals, *Theofanis Kitsopoulos*, University of Southern Mississippi **INVITED**

I will discuss how to implement ion imaging methods to measure the kinetics and dynamics of elementary reaction on metal surfaces. I will discuss the recombination of H atoms on Pt and Pd, followed by a discussion on the kinetics of formic acid adsorption on Pt and Pd

#### 3:00pm HC+SS-ThA-3 Structure-Sensitive Metal-Support Interactions – Applications to Selective Hydrogenation Reactions, *Helena Hagelin Weaver*, *H. Zhao*, *M. Lapak*, *L. Hsiao*, *D. Choi*, *C. Bowers*, University of Florida **INVITED**

Producing hyperpolarized molecules is important for increasing signal intensities in nuclear magnetic resonance (NMR) or magnetic resonance imaging (MRI) applications, and one efficient strategy is to add a parahydrogen molecule, where the nuclei have antiparallel spins, to an unsaturated substrate. The requirements for the production of a hyperpolarized molecule are that the added hydrogens must come from the same hydrogen molecule, i.e. a pairwise addition, the spins must be preserved, and the hydrogens in the generated product must be inequivalent. While this is efficient over homogeneous organometallic catalysts, heterogeneous catalysts would be preferred to facilitate separation of hyperpolarized product from the catalyst and allow continuous operation. However, over typical heterogeneous catalysts, i.e. oxide-supported metal nanoparticles, the pairwise addition of parahydrogen is challenging due to facile and reversible dissociation of dihydrogen, rapid diffusion of hydrogen atoms across the metal surface, step-wise addition of hydrogen atoms to the unsaturated molecule, and spillover of hydrogen from the active metal to the oxide support, as these are all mechanisms that can lead to a rapid loss in the singlet spin-correlation of the original parahydrogen molecule. Therefore, the pairwise selectivity in hydrogenation reactions over supported metal catalysts is often very low (< 1%).

To limit diffusion of hydrogen across the metal surface and improve the pairwise selectivity in the hydrogenation of propene, the metal particle size was first reduced to the limit, i.e. single atoms on the support. Single atoms on an oxide support are indeed more selective to pairwise addition of parahydrogen than larger nanoparticles of the same metal, but the activity is low and stability is an issue during reaction conditions. Another approach is to limit diffusion by blocking metal sites with an oxide overlayer. This was done by inducing strong metal-support interactions via a high-temperature reduction of titania-supported catalysts. The structure of the titania support, anatase versus rutile, influenced the metal-support interactions, and active metals, such as Rh and Ir, exhibited different behavior in the pairwise selective addition of parahydrogen to propene. However, in all cases, the high temperature reduction increased the pairwise selectivity regardless of whether geometric (migration of titania over metal) or electronic metal-support interactions were induced. Preliminary data reveal that oxide layers deposited by ALD can also improve the pairwise selectivity in hydrogenation reactions.

#### 3:40pm HC+SS-ThA-5 High Activity and Selectivity of Dilute Ti-Cu(111) Alloys Toward the Deoxygenation of Ethanol to Ethylene, *J. Shi*, University of Florida; *H. Ngan*, *P. Sautet*, University of California at Los Angeles; *Jason Weaver*, University of Florida

Alloys comprised of an early transition metal dispersed in a coinage metal can provide opportunities for effecting selective chemical transformations of organic oxygenates and other compounds. In this talk, I will discuss our recent work to synthesize dilute Ti-Cu(111) surface alloys in ultrahigh vacuum and characterize their structural and chemical properties using experiments and DFT. We find that Cu-capped, Ti-containing islands are preferentially generated on step edges of Cu(111) during Ti deposition below ~500 K, whereas Ti atoms alloy into the step edges during deposition above 500 K. These dilute Ti-Cu(111) surfaces are highly selective for the deoxygenation of ethanol, resulting in the production of only C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> near 400 K during temperature programmed reaction spectroscopy. DFT

calculations corroborate the high selectivity of metallic Ti-Cu(111) surfaces toward ethanol deoxygenation and predict that C<sub>2</sub>H<sub>4</sub> production becomes significantly favored as the Ti ensemble size is increased from monomer to trimer, and that the O released to Ti during C-O bond cleavage promotes desorption of the C<sub>2</sub>H<sub>4</sub> product by destabilizing its adsorbed state.

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