

## V.G.4 Multifunctional Catalysis to Synthesize and Utilize Energy Carriers

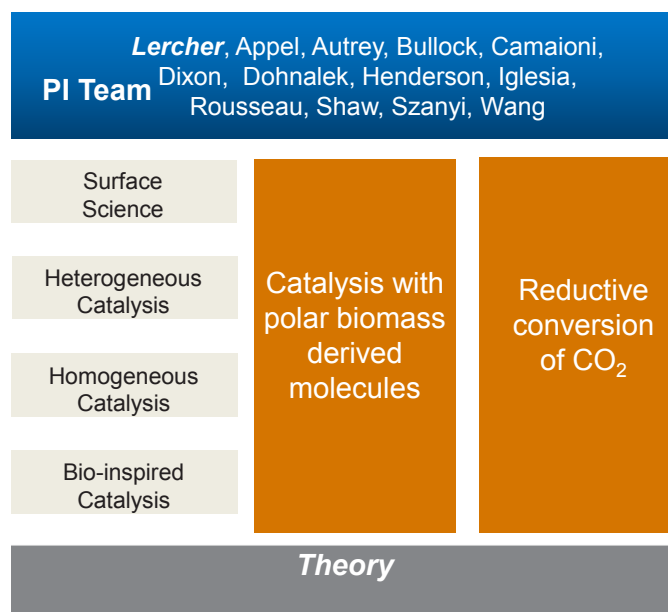
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### Program Scope

The goal of the Institute for Integrated Catalysis (structure shown in Figure 1) is the development of the fundamental science basis for a significant step forward in the way we catalytically transform common carbon resources, such as bio-derived molecules and CO<sub>2</sub>, and how we access and activate H<sub>2</sub> at lower temperatures and with higher rates than practiced today. We are convinced that gaining fundamental understanding of the basic steps of the individual reactions involved will enable us to achieve



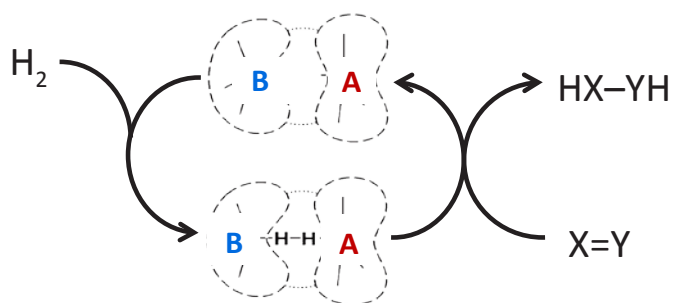
**FIGURE 1.** The goal structure of the Institute for Integrated Catalysis.

the knowledge-based development of catalysts essential to realize these transformations. The strategy is to focus on a few chemical transformations and to explore, in depth, the molecular and atomistic pathways of these selected reactions on catalysts spanning from single-crystal surfaces to molecular complexes.

### FY 2016 Highlights

*Activation of Small Molecules with Bifunctional Ambiphilic Catalyst Complexes:* Catalytic activation of molecular hydrogen is critical for the efficient upgrading of energy carriers ranging from conventional hydrocarbons to renewables such as biomass. Metals are often used to activate H<sub>2</sub>, however, a number of research groups have shown that frustrated Lewis pairs (FLPs) can be used to mimic the chemistry of transition metals and provide an alternate pathway for the catalytic reduction of polar and polarizable substrates. FLPs are of interest as they provide an approach to heterolytically activate H<sub>2</sub> catalytically, at moderate pressures and temperatures. The heterolytic activation of H<sub>2</sub>, i.e., H<sup>+</sup>/H<sup>-</sup>, using a combination of a spatially oriented Lewis acid, A, and Lewis base, B, will provide a route that favors the reduction of polar and polarizable substrates H<sub>2</sub> + X=Y → HX-YH.

Our research interests are focused on the development of tools and approaches that use a combination of theory and experiment to understanding how molecular hydrogen is activated heterolytically without using metals in frustrated Lewis pairs. We have developed novel approaches to using reaction calorimetry to measure both kinetic and thermodynamics of H<sub>2</sub> activation and transfer to a series of polar substrates to gain a quantitative measure of both activation barriers and enthalpic driving force under catalytic

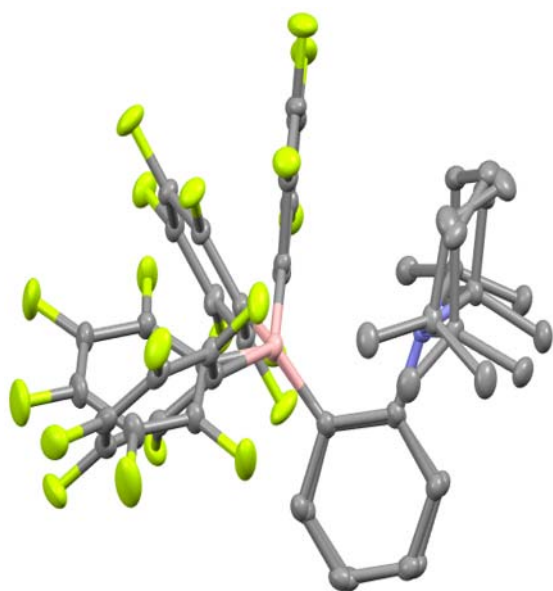


**SCHEME 1.** Illustration of a catalytic cycle for the reduction of polar substrate X=Y using a bifunctional Lewis acid Lewis base pair. Optimal spatial alignment prevents quenching of Lewis acid and Lewis base resulting in novel reactivity that mimics transition metals.

reaction conditions. This approach has provided the first experimental measure of the activation barrier for the heterolysis of  $H_2$  by FLPs. Surprisingly these results show that the barrier for heterolysis is quite small, 15–20 kJ/mol for a reaction with a moderate driving force.

Inspired by this insight we began to investigate the reactivity of crystal FLPs over the past year. We hypothesized that the crystalline molecular complex, 1-{2-[bis(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine, abbreviated KCAT, could react with gaseous  $H_2$  for the corresponding ion pair, KCATH2. Our theory calculations suggest the driving force is greater in the crystalline state than in solution. Figure 2 shows the crystallographic overlay of KCAT and KCATH2. Note the minute change in structure suggesting the possibility of a single crystal–single crystal transformation.

Optical microscopy was used to follow the transformation of the colored KCAT crystals to form the

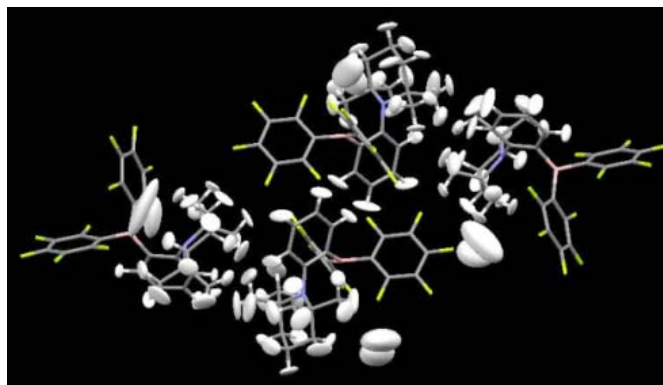


**FIGURE 2.** Crystallographic overlay of KCAT and KCATH2.

colorless KCATH2 in the presence of  $H_2$  gas at room temperature. The results show that some regions of the crystal react faster than other regions, but the boundaries between these regions are diffuse, showing there is not a clear preference for reactivity at surface or interior sites.

Inelastic neutron scattering spectroscopy (INS) provides a unique approach to study both the energetics and dynamics of hydrogen interactions in condensed phase materials. Using the VISION spectrometer at the Spallation Neutron Source we were able to investigate the single crystal–single crystal transformation of solid KCAT, to the corresponding ion pair, KCATH2, quantitatively upon exposure to gaseous  $H_2$ . The reaction does not occur until temperatures exceeded 200 K. Ab initio molecular dynamics approaches used to calculate the INS spectra are in excellent agreement with the experimentally measured spectra.

The chemical transformation of a crystalline FLP to the corresponding crystalline ion pair provides the first example of a non-metal activation of  $H_2$  in the solid state. Insight from these studies will permit the development of new approaches to *heterogenize* Lewis acid Lewis base pairs on conventional catalyst supports, e.g., metal oxides, metal organic frameworks, or high surface area carbons. The reactivity of these novel complexes is currently under investigation.



**FIGURE 4.** Thermal ellipsoids predicted from harmonic calculations of  $H_2$  interacting with KCAT.



**FIGURE 3.** Optical micrographs of KCAT crystals exposed to  $H_2$  gas for (a) 0 min, (b) 55 min, (c) 85 min, (d) 112 min, (e) 150 min. Scale bar = 100  $\mu$ m.