
IV.B.4h Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation

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Objectives

- Efficient production of hydrogen from a chemical hydrogen storage material suitable for on-board automotive applications.
- Development of mechanistic understanding to guide catalyst discovery for efficient hydrogen release.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (I) Dispensing Technology
- (R) Regeneration Processes

Technical Targets

This project is working to develop efficient catalysts for the dehydrogenation of amineboranes. Amineboranes are promising substances for chemical

hydrogen storage, provided that efficient catalysts can be developed to liberate the stored hydrogen rapidly.

Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Discovered several homogeneous catalysts for dehydrogenation of boron nitride (BN) compounds.
- Discovered that an iridium pincer complex is a very active catalyst for dehydrogenation of amine borane (NH_3BH_3). This is by far the most effective catalyst for this reaction discovered to date.

Introduction

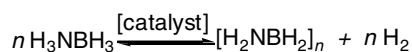
The storage of hydrogen in chemical form requires substances which have a high weight percentage of hydrogen. This limits the possibilities to light elements such as boron, nitrogen, carbon etc. Compounds containing boron (B) and nitrogen (N) are very promising in this regard. A key requirement for this technology is the development of catalysts to accelerate the rate of hydrogen release to make it sufficiently rapid to meet the needs of a vehicle. The final problem which needs to be solved is the regeneration or rehydrogenation of the storage substance. This step may ultimately be carried out off board at a centralized facility.

Approach

We sought to build upon the prior art reported for homogeneous catalysis of the dehydrogenation of hydrocarbons. To this end, we tested catalysts using so-called pincer ligands, which have three ligating atoms in a meridional arrangement. The transition metals employed are from the platinum metals group, which includes Rh, Ir, Ru, Os, Pt and Pd.

Results

The reaction that we seek to accelerate via a metal catalyst is:



We have discovered a highly effective catalyst for the dehydrogenation of NH_3BH_3 . The iridium complex POCOPIrH_2 (complex **1**) dehydrogenates the substrate very rapidly. Once the substrate is consumed, the catalytic activity can be restored by adding further substrate. One equivalent of hydrogen is released. The BN containing product has been tentatively identified as the cyclic pentamer $(\text{NH}_2\text{BH}_2)_5$. This catalyst is unique in that it works very rapidly and a single product is generated.

The rate of the reaction is dependent on catalyst loading. As shown in Figure 1, with the same initial ammonia borane concentration, a 0.25 mol % catalyst loading increases the time required to consume the substrate to at least 30 minutes, while a 1 mol % catalyst loading, reduces the time to ca. 4 minutes.

The catalytic activity of complex **1** in the dehydrogenation of ammonia borane is substantially higher than the current best reported catalyst. The rhodium catalyzed reaction reported by Manners and

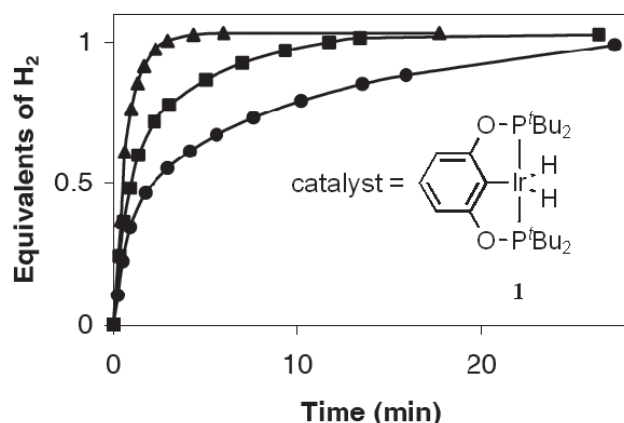


FIGURE 1. Amount of Hydrogen Gas Evolved per Mole NH_3BH_3 using 0.25 mol % (●), 0.5 mol % (■) and 1.0 mol % (▲) of **1** as Catalyst

coworkers (*J. Am. Chem. Soc.* **2004**, *126*, 9776) required two to four days at 45°C with a catalyst loading of 0.6 mol % to produce two equivalents of hydrogen gas and borazine. By contrast, the reaction catalyzed by a comparable loading of the iridium catalyst **1** (0.5 mol %) is complete within 14 minutes at room temperature.

The dehydrogenation of H_3NBH_3 catalyzed by 0.5 mol % of **1** occurs at the same rate in the presence or absence of elemental mercury. This observation strongly suggests that the iridium catalyst remains homogeneous throughout the reaction. In comparison, elemental mercury completely inhibited a similar reaction using the previously reported rhodium catalyst system, suggesting a heterogeneous environment for that catalyst.

Conclusions and Future Directions

The iridium catalyst described above is very effective for dehydrogenation, but iridium is too rare and expensive to be practical on a large scale. It is anticipated, however, that the insight gained in detailed studies of the mechanism by which this catalyst operates will assist in the design of non-precious metal catalysts. Ultimately, the goal is to generalize our iridium results to prepare effective catalysts comprised of less expensive metals, such as iron, cobalt and nickel.

We will also be investigating catalysts that may yield greater amounts of hydrogen by weight from ammonia borane and various substituted amine borane complexes.

FY 2006 Publications/Presentations

- Efficient Catalysis of Ammonia Borane dehydrogenation.* Melanie C. Denney, Vincent Pons, Travis J. Hebden, D. M. Heinekey and Karen I. Goldberg, accepted (pending minor revision) for publication in *J. Am. Chem. Soc.*
- Novel Catalysts for hydrogen production.* Melanie C. Denney, Vincent Pons, Travis J. Hebden, Denis Mery, D. M. Heinekey and Karen I. Goldberg. Paper to be presented at the 32nd ACS National Meeting, San Francisco, CA, September 10-14, 2006.