IV.B.5h Kinetic and Mechanistic Studies of BN Hydrogenation/Dehydrogenation

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Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric densities of H_2.
- Develop catalysts to meet DOE target goals for H_2 charging/discharging rates from boron/nitrogen (BN) materials.
- Optimize system to obtain cost-effective catalysts.
- Optimize BN materials for potential in effective regeneration processes.

Technical Barriers

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

(A) System Weight and Volume
(E) Charging/Discharging Rate
(B) System Cost
(R) Regeneration Processes

Technical Targets

Amineboranes are promising substances for chemical hydrogen storage, provided that efficient catalysts can be developed to liberate the stored hydrogen rapidly. This project is working to develop catalysts for the dehydrogenation of amineboranes. Insights gained from these studies will be applied toward the design 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

- Identified Ir catalyst (reported in 2006) [1] and other modified platinum group metal (PGM) catalysts as effective for the dehydrogenation of several different amineboranes.
- Identified dormant form of 2006 Ir catalyst and established mild conditions for catalyst regeneration.
- Discovered several non-PGM catalysts for the dehydrogenation of amineboranes.
- Identified the fastest PGM and non-PGM catalysts for ammoniaborane (AB) dehydrogenation.
- Demonstrated an amineborane system that is within a factor of 10 of the 2010 DOE target goals for system gravimetric and volumetric densities of H_2.
- Developed a PGM catalyst for the dehydrogenation of neat amineborane mixtures.
- Experimentally measured enthalpy of reaction for the dehydrogenation of AB.

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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 B and 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, making it sufficiently rapid to meet the needs of a vehicle.

Amineboranes and other BN compounds have potential for high H_2 storage capacities. Thermal H_2 release from BN materials is slow and inefficient. Effective catalysts for dehydrogenation/hydrogenation

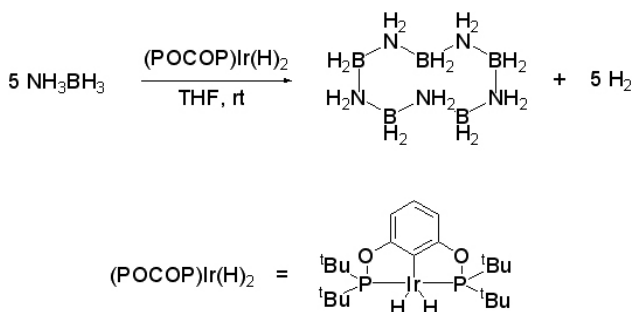will be needed. The scale of project requires inexpensive and widely available components.

The final problem which needs to be solved is the regeneration or hydrogenation of the depleted storage substance. Efficient regeneration of spent BN materials is critical. This step may ultimately be carried out off-board at a centralized facility.

Approach

Our approach to meeting the DOE targets is to develop cost effective and efficient catalysts for the dehydrogenation of amineborane compounds. We are attempting to understand how our previously identified iridium catalyst, reported in 2006 [1], dehydrogenates AB and test its effectiveness for the dehydrogenation of other amineborane compounds. The knowledge gained in the studies of PGM catalysts will be applied to develop efficient non-PGM catalysts for dehydrogenation of amineborane compounds. We will investigate the potential for facile regeneration of a variety of amineborane materials in order to meet the target of efficient regeneration. Using the highly efficient Ir catalyst, the thermodynamics of dehydrogenation/ hydrogenation can be easily measured and the potential for regeneration of new materials reliably evaluated.

Results

We have discovered a highly effective catalyst for the dehydrogenation of AB (Scheme 1), with results recently reported [1]. $(POCOP)IrH_2$ is the fastest reported transition metal catalyst for hydrogen release from AB. The rate with this Ir catalyst is 200 times faster than the previous best catalyst [2]. This catalyst is also impressive in that a single BN product is generated. The spectral data for the BN product is consistent with previous reports of the cyclic pentamer (NH_2BH_2) [3]. Unfortunately, the BN product is insoluble, which hinders the release of any further equivalents of hydrogen gas. The generation of only one equivalent of H_2 limits the weight % of the system.

The rates of dehydrogenation of AB with $(POCOP)IrH_2$ catalyst were observed to decrease with subsequent additions of AB substrate, indicating catalyst deactivation. The dormant form of the catalyst has been characterized by X-ray crystallography and ^1H nuclear magnetic resonance (NMR) spectroscopy. As shown in Scheme 2, further investigations have shown that the active Ir catalyst can be regenerated from the dormant form under moderate H_2 pressure.

We have extended our dehydrogenation studies to include the dehydrogenation of methylamine borane $CH_3NH_2BH_3$ (MeAB) using the iridium catalyst $(POCOP)IrH_2$. Similar to the results seen with the ammonia borane, we observe the release of one equivalent of hydrogen gas, however, the reaction yields a soluble BN product $(MeNHBH_2)_n$. Characterization of the product is in progress but NMR spectroscopy suggests that it is a single product. The $(POCOP)IrH_2$ was also used as a catalyst for a 1:1 mixture of AB: MeAB. Again, one equivalent of H_2 was released and a single soluble product observed. The fact that the products obtained with MeAB and AB:MeAB mixtures are soluble provides greater potential that further optimization will lead to the release of more than one equivalent of H_2. Remarkably, the $(POCOP)IrH_2$ catalyzed dehydrogenations of AB and MeAB, as well as of the mixed AB:MeAB material proceed at essentially the same rate (Figure 1). That the Ir catalyst promotes the release of H_2 from different BN systems at similar
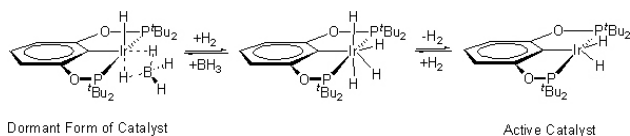
SCHEME 2. Regeneration of Active Catalyst from Dormant form under H_2 Pressure

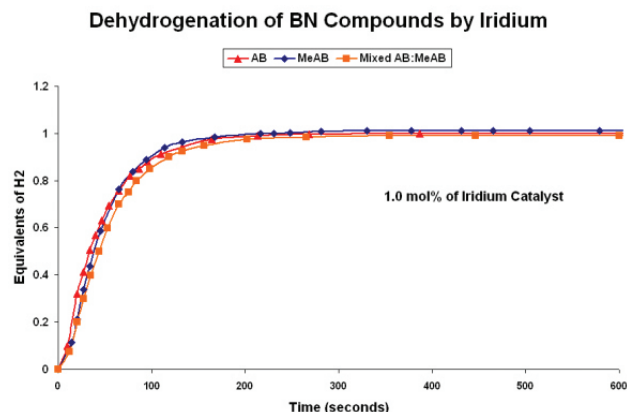**SCHEME 1.** Dehydrogenation of Ammonia Borane by $(POCOP)IrH_2$

FIGURE 1. Comparison Plot of Dehydrogenation of AB, MeAB and 1:1 mixtures of AB:MeAB by $(POCOP)IrH_2$

rates allows for the potential development of mixtures of BN materials for hydrogen storage applications.

From a concentrated mixture of 1:1 AB:MeAB in tetrahydrofuran (THF) at room temperature with 0.5 mol% Ir catalyst, 0.5 L of H_2 (1 eq.) was produced in 60 seconds. This unoptimized system generated 0.4 wt% H_2 which is within a factor of 10 of several DOE targets (Table 1). A 1:1 mixture of AB:MeAB forms a liquid at 60°C. Knowledge gained from the (POCOP)IrH$_2$ system was used to identify a PGM catalyst that can dehydrogenate the liquid AB/MeAB mixture. Preliminary results show that 0.25 equivalents of H_2 were released in 10 minutes and up to 1.25 equivalents of H_2 was released in 16 hours. Dehydrogenation of AB/MeAB mixtures with no solvent can lead to systems with a gravimetric density of up to 11.0 wt%.

Knowledge gained from the study of PGM catalysts has been used to guide the development of several non-PGM catalysts that dehydrogenate BN compounds. PGMs are expensive, making the identification of non-PGM catalysts a priority. Several complexes of iron, cobalt and nickel have been prepared and tested for catalytic activity. Data from two cobalt catalysts are shown in Figure 2. These catalysts were verified as homogeneous using mercury poisoning experiments. Co catalyst B is the fastest known base metal catalyst for AB dehydrogenation.

Using differential scanning calorimetry (DSC) and the (POCOP)IrH$_2$ catalyst, measurements for the enthalpy of AB dehydrogenation to produce hydrogen and $(BH_2NH_2)_5$ were obtained. In collaboration with

Tom Autrey and Dave Linehan at Pacific Northwest National Laboratory, an enthalpy of -6.7 ± 0.6 kcal/mol was found for this reaction. This is in good agreement with previous experimental work [4] and computational work [5] on closely related dehydrogenations of AB. These results imply that direct rehydrogenation of spent AB will not be possible and alternate regeneration routes will be required. The methodology of using DSC and the (POCOP)IrH$_2$ catalyst will allow us to investigate the potential of new amineborane and related BN compounds for reversibility of hydrogen release.

Conclusions and Future Directions

The iridium catalyst described is very effective for dehydrogenation, not only of AB, but of MeAB and mixed AB:MeAB systems as well. However, iridium is too expensive for use on a large scale.

It was anticipated that the insight gained in studies of this catalyst system would assist in the design of base metal catalysts as well as in the selection of appropriate amineborane materials. Promising leads using less expensive metals, such as iron, cobalt, and nickel, are being pursued and the fast Ir catalyst allows for the assessment of the suitability and reversibility of hydrogen generation from amineborane compounds and mixtures. We will also be investigating catalysts and reaction conditions that have potential to yield greater amounts of hydrogen by weight from ammonia borane and various substituted amine borane complexes.

FY 2007 Publications/Presentations

1. Melanie C. Denney, Vincent Pons, Travis J. Hebden, D. Michael Heinekey and Karen I. Goldberg, "Efficient Catalysis of Ammonia Borane Dehydrogenation," *J. Am. Chem. Soc.* **2006**, *128*, 12048.

2. Melanie C. Denney, Vincent Pons, Travis J. Hebden, Denise Méry, D. Michael Heinekey and Karen I. Goldberg, "Novel Catalysts for Hydrogen Production," presented at the ACS National Meeting, San Francisco, CA, September 10–14, 2006.

3. Melanie C. Denny, Vincent Pons, Travis J. Hebden, D. Michael Heinekey, Karen I. Goldberg , "Fueling the Hydrogen Economy: Efficient Dehydrogenation of Ammonia Borane," poster presented at the Gordon Research Conference on Organometallic Chemistry, Newport, RI, July 2006.

4. Melanie C. Denny, Travis J. Hebden, Vincent Pons, Karen I. Goldberg, Paula M.B. Piccoli, Arthur J. Schultz, Thomas F. Koetzle and D. Michael Heinekey, "Catalysts for Hydrogen Release from Amine Borane Compounds," presented at the Argonne National Laboratory Users Meeting, May 2007, Argonne, Illinois

TABLE 1. Gravimetric/Volumetric Density of Concentrated 1:1 Mixture of AB:MeAB and Comparison to DOE Goals

	Concentrated AB/MeAB Mixture	DOE 2010 Target
Gravimetric Density (wt% H_2)	0.4%	6.0%
Volumetric Density (kg H_2/L)	0.005	0.045

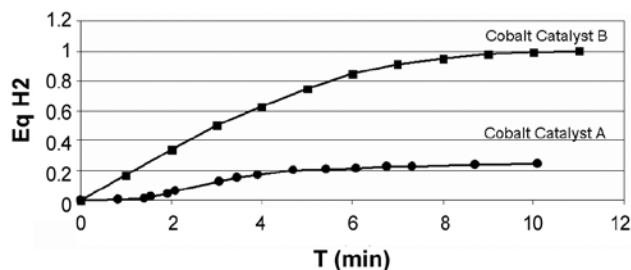**FIGURE 2.** Dehydrogenation of AB at room temperature in THF solution, 2% catalyst loading. Squares: Co catalyst A; diamonds: Co catalyst B.

5. Nathan Bennette, Brandon Dietrich, Travis Hebden, Denise Méry, D. Michael Heinekey, Karen Goldberg, "Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds," poster presented at the D.O.E. Hydrogen Program Annual Review, Washington, D.C., May 2007.

6. D. M. Heinekey, Denise Méry, Melanie C. Denny, Karen I. Goldberg, Brandon L. Dietrich, Nathan A. Bennette, Travis Hebden, "New Catalysts for Dehydrogenation of Amine Boranes," paper to be presented at the ACS National Meeting, Boston, MA, August 2007.

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4. Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P., *Thermochimica Acta* **2000**, *343*, 19.

5. Dixon, D. A.; Gutowski, M., *Journal of Physical Chemistry A* **2005**, *109*, 5129.