

IV.B.3 Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H₂ Storage Materials

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Technical Targets

This project is developing and characterizing new CBN materials for hydrogen storage. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2017 hydrogen storage system targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

FY 2012 Accomplishments

- Identified three classes of CBN materials for synthesis and characterization (liquid, reversible, high-capacity).
- Synthesized a CBN material that is a single-component liquid carrier.
- Developed catalytic conditions for the release of H₂ from the liquid carrier at 80°C



Introduction

Approaches to store H₂ in chemical bonds provide a means for attaining high energy densities. Molecular complexes containing protic and hydridic hydrogen such as ammonia borane (AB) provide between 8 to 16 wt% H₂ at acceptable temperatures in a kinetically controlled decomposition. AB shows promise to meet a number of important technological targets such as high volumetric and gravimetric density of H₂, fast kinetics, thermal stability, facile synthesis at large scale and safe handling under atmospheric conditions. Some of the challenges involving AB include: volatile impurities (e.g., ammonia, diborane, borazine) and the economics of spent fuel regeneration [1-4].

This project is developing hydrogen storage materials that contain the element carbon in addition to boron and nitrogen. The inclusion of carbon can be advantageous for developing chemical H₂ storage materials that are structurally well defined (thus has good potential to be liquid phase), exhibit thermodynamic properties conducive to reversibility, and demonstrate good storage capacities.

Approach

This project will develop new CBN H₂ storage materials that have the potential to meet the DOE goals for motive and non-motive applications. Specifically, we will be focusing on three basic systems: 1) liquid-phase systems that release H₂ in a well-defined and high-yield fashion, minimizing the

Fiscal Year (FY) 2012 Objectives

This project seeks to develop a class of chemical hydrogen storage materials containing the elements carbon, boron, and nitrogen (CBN materials). The project will focus on compounds that show potential to meet the Department of Energy's vehicular technical targets and/or can be applied to near-term market applications. The preferred materials to be developed will exhibit good storage capacity, be liquid, reversible, have good release kinetics at moderate temperature.

Technical Barriers

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

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates

formation of NH_3 and $\text{B}_3\text{N}_3\text{H}_6$, 2) reversible storage systems that could be potentially regenerated onboard, 3) high H_2 -content storage systems that can be used in slurries and regenerated off-board (see Figure 1). Computational chemistry studies will direct our research and reduce risk by accelerating progress. Finally, we will demonstrate the material in conjunction with a fuel cell. These new materials will be prepared and characterized by our interdisciplinary team comprised of the University of Oregon, the University of Alabama, Pacific Northwest National Laboratory, and Protonex (a small business fuel cell manufacturer).

Results

Synthesis of CBN Compounds

We synthesized compound **B** (Figure 1) *via* conditions adapted from our previously reported “first-fill” synthesis of compound **F**. *Bis*-(trimethylsilyl)crotylamine **1** was reacted with borane-triethylamine, producing **2** through intramolecular hydroboration (Scheme 1). The resulting crude mixture containing **2** was reacted with potassium hydride, followed by treatment with $\text{HF}\cdot\text{pyridine}$, yielding carrier **B** in 51% yield from **1**. Compound **B** is indeed a liquid at room temperature (melting point -16°C).

Release of Hydrogen from Liquid Carrier **B**

As with **AB** and other amine-boranes, release of hydrogen from **B** can be induced thermally, or at lower temperatures using catalysts. At 150°C , two equivalents of hydrogen are released from each molecule of **B** within one hour. The release of hydrogen triggers a trimerization reaction (Scheme 1b) and produces trimer **3**, which is also a liquid at room temperature. Thus the hydrogen desorption from liquid material **B** does not involve a phase change. The reaction was monitored by automated gas burette in addition to NMR spectroscopy.

First-row transition metal-halide salts such as CoCl_2 and FeCl_2 can catalyze the hydrogen desorption reaction. The reaction can be

performed at temperatures as low as 50°C in the presence of catalysts. Among the surveyed catalysts, the most active catalyst proved to be CoCl_2 (Figure 2a). At the polymer electrolyte membrane fuel cell waste heat temperature of 80°C , the reaction can be completed in just over five minutes using CoCl_2 as the catalyst. Though cobalt(II) chloride was most effective, we focused further efforts using iron(II) chloride because of its much reduced cost. To demonstrate the potential utility of our material as a simple-to-operate, single-component liquid system, we performed a large-scale dehydrogenation of liquid fuel **B** without additional solvent using 5 mol% FeCl_2 as a catalyst. Figure 2b shows that 2 equiv of H_2 were released from the neat material in ca. 20 min at 80°C . At the conclusion of the reaction, the spent fuel trimer was isolated in 95% yield.

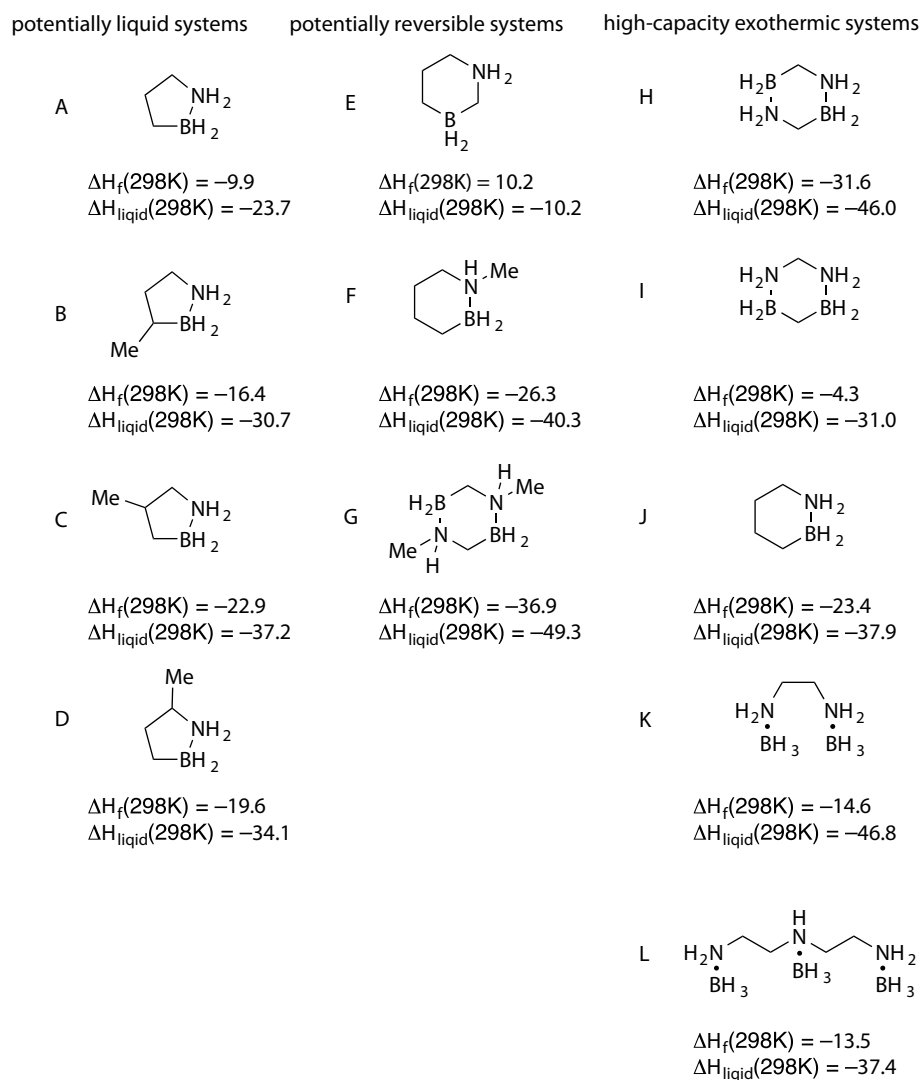
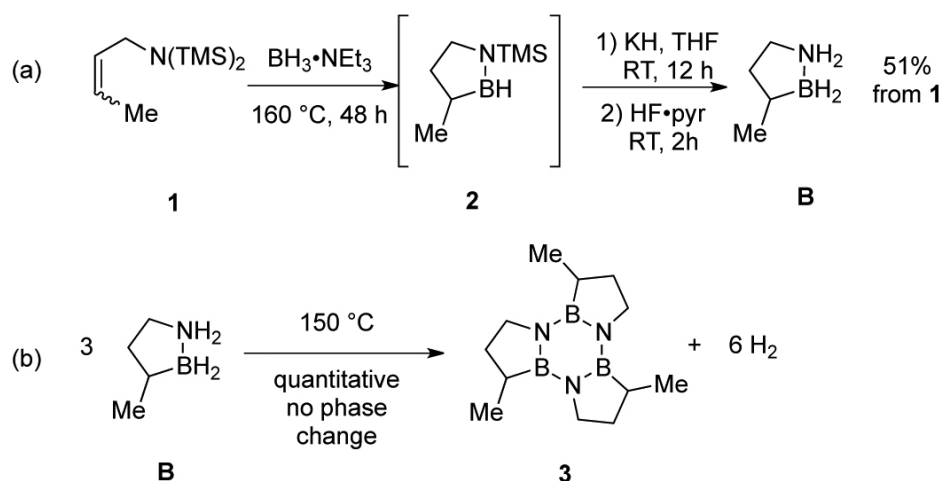


FIGURE 1. Selected synthetic targets and their gas phase heats of formation calculated at the G3MP2 level. Liquid phase heats of formation obtained from calculated boiling points using COSMO-RS. Energy values are in kcal/mol.



SCHEME 1. Synthesis of liquid fuel **B** and its thermal H_2 desorption reaction

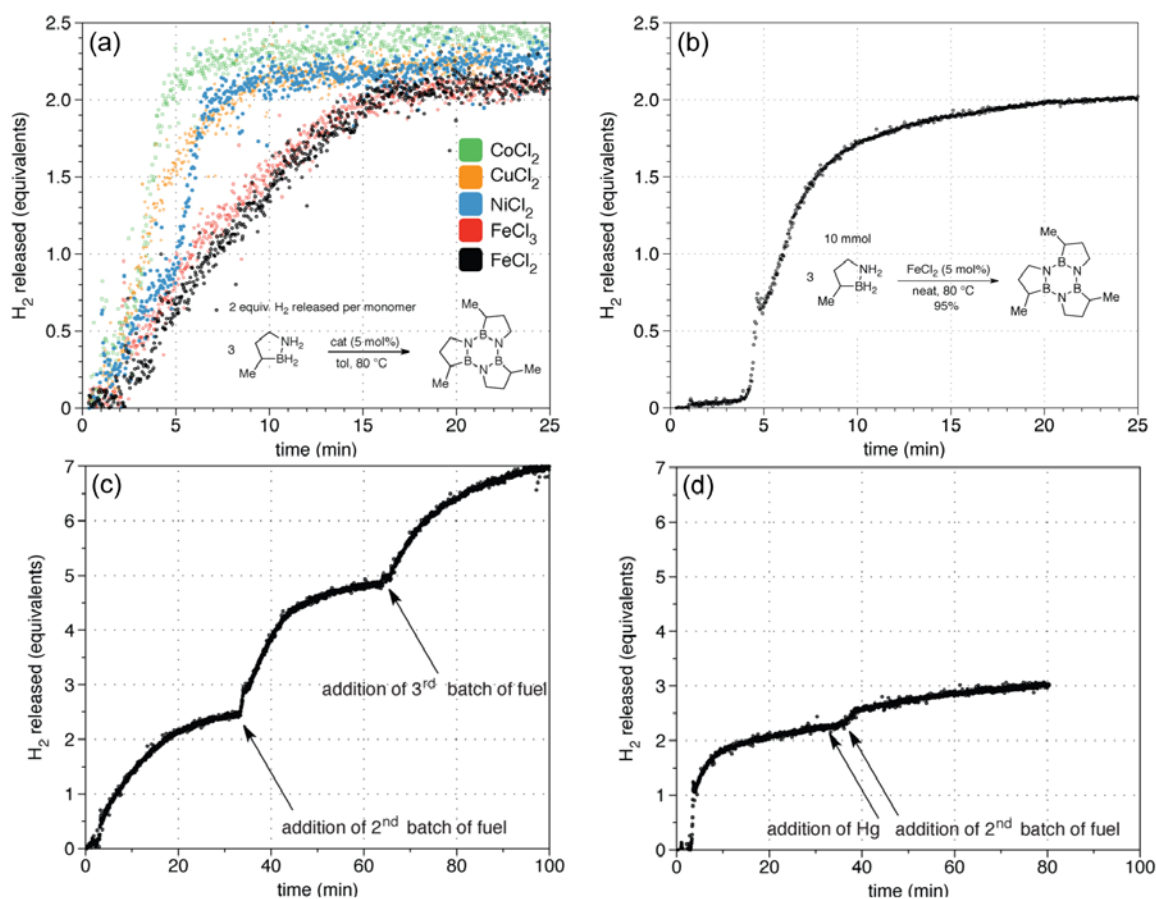
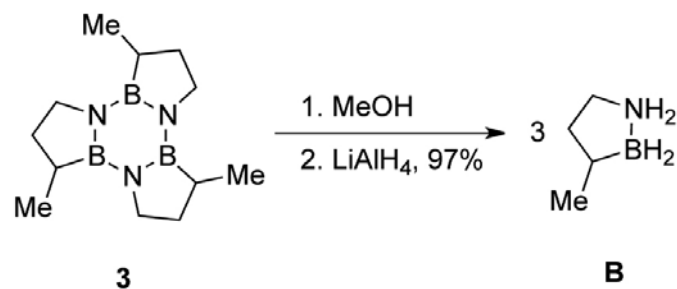


FIGURE 2. Automated gas burette analysis of a) catalyst screening survey for hydrogen desorption of **B** at 80 °C, b) large scale dehydrogenation of **B** using $FeCl_2$ as a catalyst, c) hydrogen desorption via sequential addition of charged fuel to $FeCl_2$ catalyst, d) hydrogen desorption with Hg poisoning of the $FeCl_2$ catalyst.

The $FeCl_2$ pre-catalyst changed form during the course of the reaction, becoming an amorphous black powder. At 5 mol% loading, the catalyst could be reused without loss of

activity (Figure 2c). Adding fresh fuel **B** to the reaction flask after dehydrogenation of the old batch had completed resulted in immediate H_2 desorption from the new batch of fuel



SCHEME 2. Conversion of spent fuel trimer **3** back to the charged fuel **B**

(tested up to three times). To probe the nature of the active catalyst species, Hg was added to the reaction mixture, and a reduced rate of hydrogen release was observed, suggesting a heterogeneous catalysis mechanism (Figure 2d vs 2c).

Regeneration of B from Spent Fuel Trimer

We determined that trimer **3** can be “digested” at room temperature by stirring with methanol then reduced with lithium aluminum hydride to furnish the charged liquid fuel **B** in high yield (Scheme 2). The described regeneration scheme is not yet optimal from an energetic point of view (i.e., the use of highly energetic LiAlH_4 ultimately needs to be avoided).

Conclusions and Future Directions

In summary, we developed the synthesis of a new single-component liquid phase hydrogen storage material **B** based on the CBN heterocycle approach. We found that liquid carrier **B** released two equivalents of hydrogen in less than 20 minutes at 80°C in the presence of catalytic amounts of first-row transition metals without a phase change. A preliminary regeneration scheme was also demonstrated.

Future work includes:

- Continue develop and demonstrate the synthesis of remaining CBN heterocycle targets illustrated in Figure 1.
- Provide detailed characterization for compound **B** (e.g., thermogravimetric analysis, residual gas analysis, viscosity, thermodynamic parameters).
- Investigate the dehydrogenation mechanism of CBN heterocycles.

Selected FY 2012 Publications/Presentations

1. Luo, W.; Campbell, P.G.; Zakharov, L.N.; Liu, S.-Y. “A Single-Component Liquid-Phase Hydrogen Storage Material” *J. Am. Chem. Soc.* **2011**, *133*, 19326-19329.

* This paper is included for completeness sake. It was published before the grant was funded. Highlighted in *Chemical & Engineering News (C&EN)* (2011, November 28, page 35), C&EN online (2011, <http://cen.acs.org/articles/89/web/2011/11/Liquid-Future-Hydrogen-Fuel.html>), in *Nature Chemistry* **2012**, *4*, 5, and in *Nature Climate Change* **2012**, *2*, 23.

2. “Hydrogen Storage by Novel CBN Heterocycle Materials”; Heidelberg, Germany, *International Energy Agency, Hydrogen Implementing Agreement, Task 22 Expert Meeting*, May 8, 2012.

3. “Hydrogen Storage by Novel CBN Heterocycle Materials”; Washington, DC, *DOE Annual Merit Review*, May 17, 2012.

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2. A. Staubitz, A.P. Robertson, I. Manners. “Ammonia-borane and related compounds as dihydrogen sources” *Chem. Rev.* **2010**, *110*, 4079-4124.
3. C.L. Aardahl, D. Rassat. “Overview of systems considerations for on-board chemical hydrogen storage” *Int. J. Hydrogen. Energy.* **2009**, *34*, 6676-6683.
4. A.D. Sutton, A.K. Burrell, D.A. Dixon, E.B. Garner, III, J.C. Gordon, T. Nakagawa, K.C. Ott, J.P. Robinson, and M. Vasiliu. “Regeneration of Ammonia Borane Spent Fuel by Direct Reaction with Hydrazine and Liquid Ammonia” *Science*, **2011**, *331*, 1426-1429.