

IV.B.1 Hydrogen Storage by Novel CBN Heterocycle Materials

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- (E) Charging/Discharging Rates
- (R) Regeneration Processes

Technical Targets

This project is developing new liquid phase materials for hydrogen storage that can be readily regenerated. 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 targets:

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

FY 2012 Accomplishments

- Optimized first-fill synthesis of 6-membered N-Me fuel system (**1'**).
- Characterized thermodynamics of H₂ release from N-Me (**1'**).
- Optimized dehydrogenation/trimerization reaction of **1** with cheap and relatively environmentally benign FeCl₂.
- Explored various strategies to regenerate spent fuel materials using less energetically costly reagents.



Fiscal Year (FY) 2012 Objectives

The objective of this project is to develop novel boron-nitrogen heterocycles as liquid-phase hydrogen storage materials with storage capacities and thermodynamic properties that have the potential to lead to rechargeable systems capable of meeting DOE targets. We seek to:

- Develop new materials that:
 - are structurally well-defined along the desorption/absorption processes
 - exhibit appropriate enthalpy of H₂ desorption
 - are liquids at operating temperatures
 - possess high H₂ storage capacities
- Identify catalysts that will release hydrogen from these materials at temperatures <200°C.
- Develop conditions that will readily recharge the spent fuel.

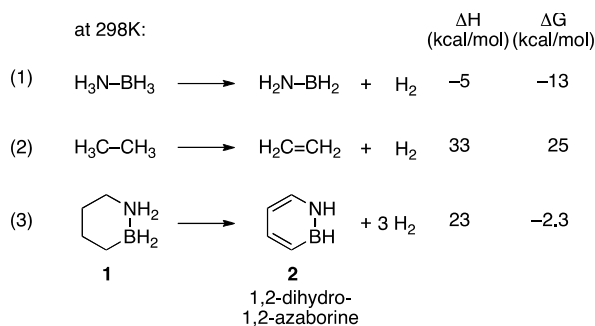
Technical Barriers

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

Introduction

Hydrogen storage is a vital component in the development of a hydrogen-based energy infrastructure. Boron nitrogen containing compounds, e.g., ammonia-borane (H₃N–BH₃ or AB), have attracted much attention as chemical H₂ storage materials because of their high gravimetric hydrogen densities and fast kinetics of H₂ release. This project is developing structurally well-defined liquid carbon-boron-nitrogen (CBN) hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that have the potential to be reversibly regenerated using molecular hydrogen. A liquid phase, hydrogen storage system that can be regenerated using molecular hydrogen is highly desired for many reasons, including versatility, lower cost and improved efficiency, and durability. Such a storage material will allow onboard hydrogen storage. It can also be applied as an off-board energy carrier for vehicle and stationary applications that takes advantage of the existing liquid fuels infrastructure.



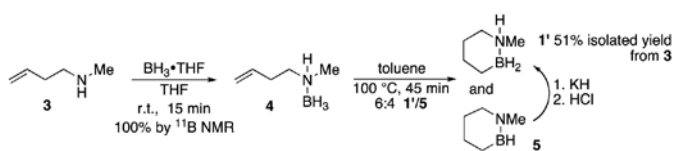
Approach

In order to accomplish reversibility, neutrality in free energy of the hydrogen release process (i.e., $\Delta G \sim 0$ kcal/mol) at the operating temperature is pivotal. The dehydrogenation of AB is exergonic by -13 kcal/mol at 298 K (eq 1). In contrast to AB, the dehydrogenation of its isoelectronic organic counterpart, ethane (CH_3-CH_3), is endergonic by $+25$ kcal/mol (eq 2). The coupling of endothermic dehydrogenation from CC with exothermic dehydrogenation from BN in a cyclic six-membered framework could lead to a reversible H_2 storage system. Indeed, high-level computational analysis indicates that the release of H_2 from CBN heterocycles such as **1** has favorable overall thermodynamics conducive to reversibility, (e.g., see eq 3). The potential for reversible hydrogen release/uptake and the relatively high gravimetric hydrogen density of CBN heterocycle materials (e.g. 7.1 wt% for **1**) render their preparation and development an important goal. This project is investigating several CBN heterocycle materials for H_2 storage applications using a synergistic theoretical and experimental approach. Synthesis will be a crucial component of this project given the relatively unexplored nature of these CBN heterocycles. The structurally well-defined nature of these CBN heterocycle materials will facilitate their characterization and mechanistic investigation of the proposed desorption/absorption processes.

Results

Optimized First-Fill Synthesis of **1'**

We have further optimized the synthesis of **1'** and now report the gram-scale overall yield from amine **3** to be 51% (Scheme 1). This was achieved by careful monitoring of the “ring-closing” step: utilizing a shorter reaction time (45 min vs 1 hour) and a slightly lower temperature (100°C vs 110°C) promoted the formation of **1'** and reduced the formation of the species **5**. The resulting mixture could be separated by distillation and **5** could be converted to **1'** by sequential treatment with KH and HCl.



SCHEME 1. Optimized synthesis of **1'**

Experimental Measurement of Thermodynamics of H_2 Release from **1'**

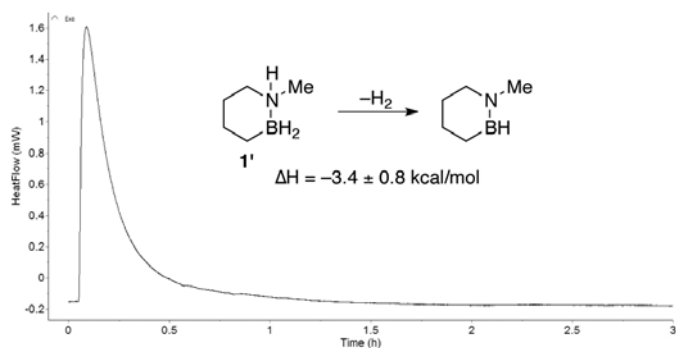
We have found the optimal catalyst for our calorimetric dehydrogenation experiments, $\text{Cl}_2(\text{PPh}_3)_3\text{Ru}$ at 10 mol % loading, and used it to perform thermodynamic measurements for the dehydrogenation of the N-Me model fuel **1'** (Scheme 2). We measured the enthalpy of dehydrogenation to be -3.4 ± 0.8 kcal/mol compared to a predicted $\Delta H = -4.9$ kcal/mol (G3/MP2). This is more exothermic by 2.02 kcal/mol than the value we previously measured for the N-tBu substituted model fuel (-1.38 ± 0.12 kcal/mol).

Dehydrogenation of **1** Using FeCl_2

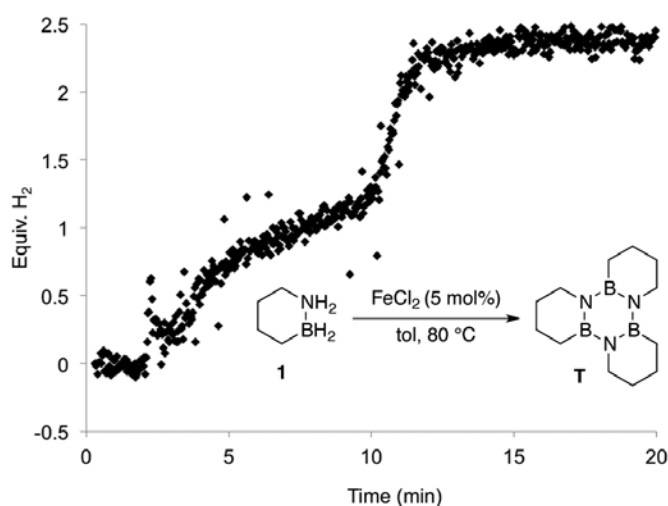
Last year we reported the discovery that CoCl_2 , efficiently promoted hydrogen loss from our CBN fuel materials. More recently, we were pleased to find that FeCl_2 enabled clean dehydrogenation and trimer formation from **1** at a reasonable rate and yield under the same conditions (80°C , 5 mol% catalyst loading). Interestingly, the shape of the FeCl_2 promoted H_2 release curve shown in Scheme 3 differs considerably from CoCl_2 . The loss of the first equivalent of H_2 takes place within seven minutes of the start of the reaction, slow compared to cobalt. The loss of the second equivalent of H_2 proceeds more quickly and the reaction is complete within 12 minutes.

Potential Regeneration Pathways

We previously reported conditions to regenerate the spent fuel trimer **T** via treatment with excess MeOH and



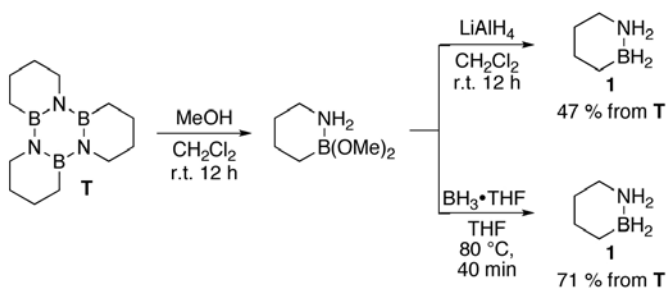
SCHEME 2. Representative calorimeter heat flow trace for the dehydrogenation of **1'**



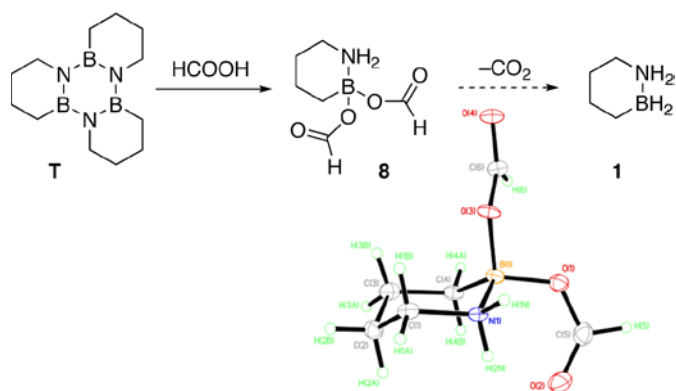
SCHEME 3. Burette measurement of hydrogen release from **1** catalyzed by FeCl_2

subsequent addition of 2 equivalents LiAlH_4 to generate the parent fuel **1** in 47% overall yield (Scheme 4). In an effort to optimize the yield of the regeneration sequence and utilize milder hydride sources, we found that treatment of the $\text{B}(\text{OMe})_2$ intermediate with $\text{BH}_3\cdot\text{THF}$ at 80°C for 40 minutes afforded the fully charged fuel **1** in 71% yield over two steps. We also attempted digestion of the trimer with formic acid, which is synthetically available from the hydrogenation of CO_2 . We found that treatment of **T** with 7 equiv. formic acid smoothly generated the monomeric bisformate adduct **8** (Scheme 5). We are currently working to find conditions to regenerate the fully charged fuel **1** by decarboxylation (i.e., loss of CO_2) of species **8** and thus eliminate the need for high-energy reagents (e.g., LAH, KH, BH_3).

We have also pursued lower-energy regeneration strategies predicated on avoiding the formation of strong B-O bonds. Hydrazine has been used to “digest” and regenerate the polymeric reaction products (e.g. polyborazylene) of the dehydrogenation of ammonia borane [1]. When excess hydrazine was added to **T** without additional solvent and heated to 90°C overnight, approximately 25% conversion to the bishydrazine adduct was observed by ^{11}B NMR. When



SCHEME 4. Regeneration of spent-fuel trimer **T**



SCHEME 5. Digestion of trimer **T** with formic acid

two equivalents of hydrazine (per B equivalent) were added to a toluene solution of **T** and heated at 150°C overnight, approximately 25% of conversion to monohydrazine adduct was observed. In both cases, no other boron-containing products formed, but we were unable to increase the yield to useable levels. *Ortho*-benzenedithiol has also been used for the digestion of polyborazylene [2]. Treatment of **T** with one equiv. benzenedithiol (per boron equivalent) in tetrahydrofuran at 90°C for 24 hours resulted in $<10\%$ conversion to the boron-sulfur adduct **8** (identified by ^{11}B NMR comparison to a sample of **8** synthesized from **1**) in addition to $\sim 5\%$ of an unidentified boron-containing product.

Conclusions and Future Directions

In summary, we have optimized the synthesis of 6-membered N-substituted material **1'** concluding the materials optimization portion of our Phase II goals. We measured the enthalpy of hydrogen release from **1'** and found it to be -3.4 ± 0.8 kcal/mol compared to a predicted $\Delta H = -4.9$ kcal/mol (G3/MP2). We also pursued alternative spent-fuel regeneration strategies using less energy-intensive reagents. We successfully digested the spent fuel trimer using formic acid, which is synthetically available from the hydrogenation of CO_2 and may enable regeneration of fully charged fuel by a decarboxylation reaction.

Future work includes:

- Continue develop/optimize conditions/catalysts for H_2 desorption, specifically the H_2 desorption from the carbon portions of the fuel.
- Continue develop more efficient conditions for recharging the spent fuel material.

Selected FY 2012 Publications/Presentations

1. Luo, W.; Zakharov, L.N.; Liu, S.-Y. "1,2-BN Cyclohexane: Synthesis, Structure, Dynamics, and Reactivity" *J. Am. Chem. Soc.* 2011, *133*, 13006-13009.
2. Campbell, P.G.; Marwitz, A.J.V.; Liu, S.-Y. "Recent Advances in Azaborine Chemistry" *Angew. Chem. Int. Ed.* 2012, *51*, 6074-6092.
3. "Hydrogen Storage by Novel CBN Heterocycle Materials"; Copenhagen, Denmark, *International Energy Agency, Hydrogen Implementing Agreement, Task 22 Expert Meeting*, September 5, 2011.
4. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; Université de Pau, Pau, France, *Seminar*, November 24, 2011.
5. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; Université Paul Sabatier, Toulouse, France, *Seminar*, November 28, 2011.
6. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; Okayama, Japan, 6th *International Green Elements Science Symposium*, December 3, 2011.
7. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; The University of Tokyo, Tokyo, Japan, *Seminar*, December 6, 2011.
8. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; San Diego, CA, *American Chemical Society National Meeting 243 Session "ACS Award for Creative Work in Synthetic Organic Chemistry: Symposium in Honor of Gregory C. Fu"* (ORGN 442); *Invited Lecture*, March 27, 2012.
9. "Hydrogen Storage by Novel CBN Heterocycle Materials"; Washington DC, *DOE Annual Merit Review*, May 17, 2012.
10. "Hydrogen Storage by CBN Heterocycle Materials"; Calgary, Canada, *National Meeting of the Canadian Society for Chemistry Session "Recent Advances in Hydrogen Activation, Production and Storage"*; *Invited Lecture*, May 30, 2012.
11. "Hydrogen Storage by CBN Heterocycle Materials"; Baltimore, MD, *Remsen Symposium; Invited Lecture*, May 31, 2012.

References

1. Sutton, A.D.; Burrell, A.K.; Dixon, D.A.; Garner, E.B.; Gordon, J.C.; Nakagawa, T.; Ott, K.C.; Robinson, J.P.; Vasiliu, M. *Science* **2011**, *331*, 1426–1429.
2. Davis, B.L.; Dixon, D.A.; Garner, E.B.; Gordon, J.C.; Matus, M.H.; Scott, B.; Stephens, F.H. *Angew. Chem. Int. Ed.* **2009**, *48*, 6812–6816.