

IV.B.4g New Methods for Promoting Amineborane Dehydrogenation/Regeneration Reactions

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Objectives

- Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets.
- Develop high conversion off-board methods for chemical hydride regeneration.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Costs
- (D) Durability/Operability
- (R) Regeneration Processes

Technical Targets

Target Year	H ₂ Release (kg-H ₂ /kg)	H ₂ Release (kg-H ₂ /L)
2007	0.045	0.036
2010	0.06	0.045
2015	0.09	0.081

Accomplishments

- Chemical additives, ionic liquids and/or metal catalysts were shown to increase the rate and extent of thermolytic hydrogen release from ammonia borane and several systems have been identified that have potential to meet DOE targets.
- A system composed of a 90/10 mol% mixture of ammonia-borane/lithium-amide was found to liberate 6.85 wt% H₂ at 6 h and 9.28 wt% H₂ at 15 h and 85°C, making this system one of the best amineborane-based hydrogen release systems that has been reported.
- A convenient and safe method for the synthesis of ammonia triborane was developed and our studies of its hydrolytic reactions demonstrated that it is both soluble and stable in water, but that upon the addition of acid or an appropriate transition metal catalyst it rapidly releases hydrogen.
- The rhodium-catalyzed hydrolysis reaction of a highly concentrated (22.7 wt%) sample of aqueous ammonia triborane yielded 6.1 wt% H₂ (based on materials) suggesting that the DOE 2007 total-system target of 4.5 wt% for hydrogen release from a chemical hydrogen storage system might be attainable with this system.
- Studies of amineborane regeneration reactions demonstrated that trifluoroacetic acid can be used to digest the boron-nitrogen polymer that is produced by ammonia borane dehydrogenation and that amineboranes can then be regenerated by reaction of these solutions with alane amines.

Introduction

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The objectives of this project are both to develop new methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets and to develop high-conversion off-board methods for chemical hydride regeneration.

Approach

Because of their protonic amine-hydrogens and hydridic borane-hydrogens, amineboranes such as ammonia borane, NH₃BH₃ (19.6 wt% H₂) and ammonia triborane, NH₃B₃H₇ (17.7 wt% H₂) are unique when

compared to other chemical hydrides in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation and hydrolysis reactions. In collaboration with the other center partners Los Alamos National Laboratory, Pacific Northwest National Laboratory, the Universities of Washington, Alabama, and Northern Arizona, Intematix, and Rohm and Haas, our approach is to develop new methods for amineborane hydrogen-release and regeneration reactions that will enable their use for chemical hydrogen storage.

Results

Enhanced Hydrogen Release from Ammonia Borane. Partial dehydrogenation of neat ammonia borane can be thermally induced in the solid-state, but to be useful for hydrogen storage, milder conditions and more controllable reactions still need to be developed. Our recent work has shown that chemical additives, ionic liquids and metal catalysts can be used to significantly increase the rate and extent of hydrogen release from ammonia borane.

The results of the dehydrogenation of neat ammonia borane at 85°C versus a reaction having added lithium amide are summarized in Figure 1. For the neat ammonia borane reactions there was negligible hydrogen production after 3 h, and after 15 h, only 0.89 equivalents of H₂ were obtained. Even with prolonged heating (67 h) at this temperature only a minor amount of additional H₂ release was observed. In contrast, ammonia borane mixtures containing 10 mol% of LiNH₂ showed both faster rates and more extensive hydrogen release giving 1.12 and 1.52 equivalents after only 6 and 15 h. The high weight percent of hydrogen release achieved (6.85 wt% at 6 h and 9.28 wt% at 15 h) make these systems particularly attractive for hydrogen storage applications.

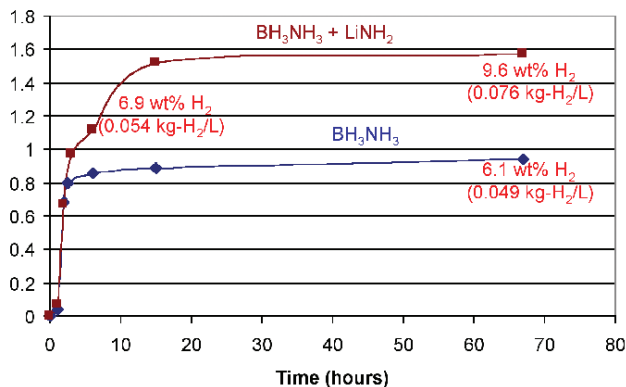


FIGURE 1. Summary of H₂ Release at 85°C for Samples of: (bottom curve) Neat Ammonia Borane; and (top curve) Ammonia Borane Containing 10 mol% of LiNH₂

Unlike the reactions of neat ammonia borane, the reactions of ammonia borane dissolved in the 1-butyl-3-methyl-imidazolium chloride (bmimCl) ionic liquid at 85°C showed no induction period for hydrogen release producing 0.5, 0.91 and 1.10 equivalents of hydrogen after only 1, 3 and 6 h, respectively (Figure 2). As indicated in the figure, the degree of dehydrogenation could also be significantly increased by raising the temperature of the ammonia-borane/bmimCl solution to only 95°C.

The 6 h weight release data for the lithium amide and several ionic-liquid based systems are compared in Figure 3 where it can be seen that several of these systems have the potential to meet the DOE total-system targets.

Ammonia Triborane: A Promising New Candidate for Chemical Hydrogen Storage. The high hydrogen release capacities that could potentially be achieved from ammonia triborane by either hydrolytic or thermolytic

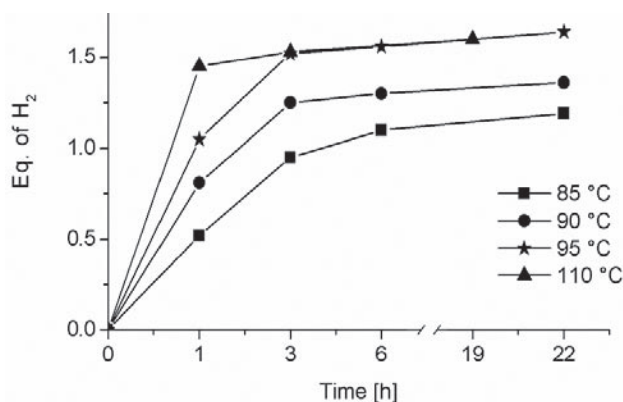


FIGURE 2. Summary of H₂ Release at Different Temperatures from Equal Weight Mixtures of BmimCl and Ammonia Borane

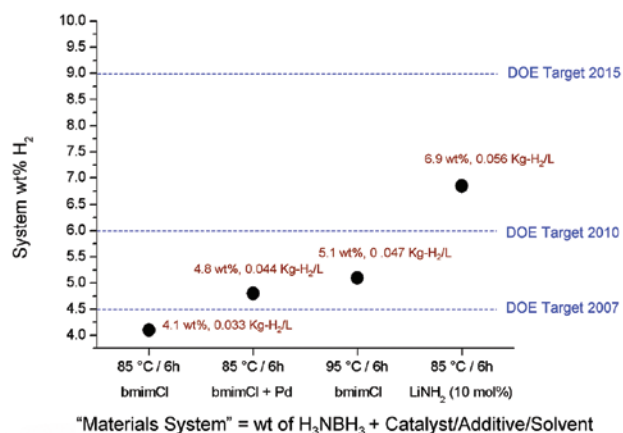
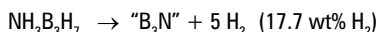
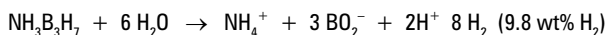


FIGURE 3. Comparisons of the 6 h Hydrogen-Release Results of the NH₃BH₃/ionic-liquid and NH₃BH₃/LiNH₂ Storage Systems with the DOE Total-System Targets

processes make it an attractive candidate for chemical hydrogen storage.



Our work has now led to a convenient and safe method for the synthesis of ammonia triborane that is allowing for the first time a systematic evaluation of its hydrogen storage potential. Initial studies of the hydrolytic process have demonstrated that ammonia triborane is both soluble and stable in water, but that upon addition of an appropriate transition metal catalyst it rapidly releases hydrogen by the hydrolytic process in the equation above.

As illustrated in Figure 4, the hydrolysis reaction of a highly concentrated 22.7 wt% sample of aqueous ammonia triborane containing 0.30 g of H_2O , 0.10 g of $\text{NH}_3\text{B}_3\text{H}_7$ (1.8 mmol) and 0.04 g of 5 wt% $\text{Rh}/\text{Al}_2\text{O}_3$ (0.02 mmol of Rh) produced 0.027 g (13.5 mmol, 7.5 equivalents) of H_2 (measured by gas buret) over 3 h at 21°C. This result corresponds to a production of 6.1 wt% H_2 based on materials [wt% = $\text{H}_2 \text{ wt}/(\text{NH}_3\text{B}_3\text{H}_7 + \text{H}_2\text{O} + \text{Rh}/\text{Al}_2\text{O}_3 \text{ - wts)}$] and suggests that the DOE 2007 total-system target of 4.5 wt% for hydrogen release from a chemical hydrogen storage system may be attainable with this system. Under these concentrated conditions, ^{11}B nuclear magnetic resonance studies showed that the hydrolysis reaction yielded condensed polyborates, which upon addition of water form mixtures of $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$. Thus, the real utility of this process as a chemical hydrogen storage system will ultimately require the

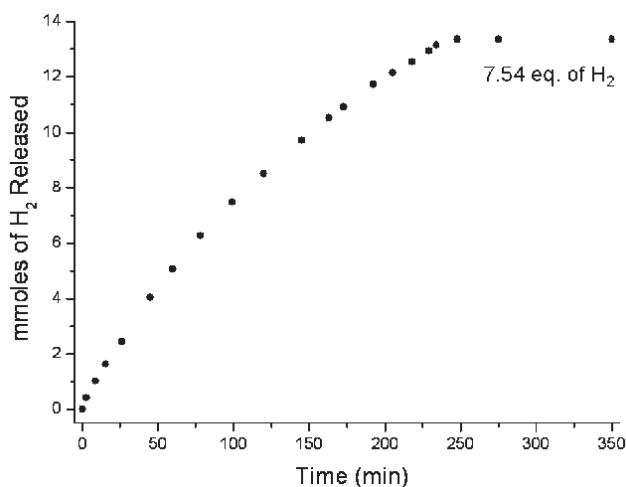


FIGURE 4. Rhodium (5wt% $\text{Rh}/\text{Al}_2\text{O}_3$, 1.0 mol% Rh) Catalyzed Hydrogen Release from a 22.7-wt% Aqueous Solution of Ammonia Triborane (1.8 mmol) Yielding 6.1 wt% H_2 [wt% = $\text{H}_2 \text{ wt}/(\text{NH}_3\text{B}_3\text{H}_7 + \text{H}_2\text{O} + \text{Rh}/\text{Al}_2\text{O}_3 \text{ wts)}$]

development of new methods to regenerate ammonia triborane from these borates.

The thermolytic decomposition of ammonia triborane has even greater potential than hydrolysis to meet the 2007 and future DOE targets (2010, 6.0 wt%; 2015, 9.0 wt%) and we are now taking advantage of the new availability of ammonia triborane to develop new methods for promoting both the rate and extent of hydrogen release by this process.

Conclusions and Future Directions

As discussed in the previous section, our studies during the last year have identified several promising hydrogen release systems based on ammonia borane and ammonia triborane. During the next year, we plan to:

- Develop new metal-catalyst and/or chemical-additive systems with improved hydrogen release rates for thermolytic hydrogen release from ammonia borane.
- Further optimize the catalyzed hydrolytic hydrogen release from ammonia triborane.
- Carry out systematic studies of the use of metal-catalysis and/or chemical-additives to promote thermolytic hydrogen release from ammonia triborane.
- Determine which of the ammonia borane and ammonia triborane dehydrogenation products have the highest regeneration activities.
- Develop new strategies for amineborane regeneration.

FY 2006 Publications/Presentations

Publications

1. M. E. Bluhm, M. G. Bradley, R. Butterick III, U. Kusari and L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids" *J. Am. Chem. Soc.* **2006**, *128*, 7748-7749.
2. M. E. Bluhm, M. G. Bradley and L. G. Sneddon "Promoted Hydrogen Release from Amineborane" *Prepr. Sym., Am. Chem. Soc. Div. Fuel Chem.* **2006**, submitted.
3. C. Y. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage" submitted.

Presentations

1. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" Tech Team Meeting, Houston, Texas, February 2006.

2. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Hydrogen Annual Merit Review Meeting, Washington, DC, May 2006.
3. M. G. Bradley, M. E. Bluhm and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" to be presented at the Boron Americas Meeting, San Juan, Puerto Rico, August 2006.
4. C. Y. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage" to be presented at the Boron Americas Meeting, San Juan, Puerto Rico, August 2006.
5. M. E. Bluhm, M. G. Bradley and L. G. Sneddon "Promoted Hydrogen Release from Ammonia Borane" to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.
6. M. E. Bluhm, M. G. Bradley, R. E. Butterick, U. Kusari and L. G. Sneddon "Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids" poster to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.
7. C. Y. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage" poster to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.
8. L. G. Sneddon, M. E. Bluhm and M. G. Bradley "Amineborane Chemical Hydrogen Storage" invited lecture in the symposium on Hydrogen Storage at the Materials Research Meeting, Boston, November 2006.