IV.B.1g Amineborane-Based Chemical Hydrogen Storage

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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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

(A) System Weight and Volume
(B) System Costs
(E) Charging/Discharging Rates
(R) Regeneration Processes

Technical Targets

- Gravimetric Density: 0.045 (2007); 0.06 (2010); 0.09 (2015) kg-H_2/kg
- Volumetric Density: 0.036 (2007); 0.045 (2010); 0.081 (2015) kg-H_2/L
- H_2 Flow Rate

TABLE 1. Progress Toward DOE Targets: Summary of AB H_2-Release Studies for 50:50, 60:40 and 80:20 wt% AB:BmimCl mixtures at 120°C

Metrics	AB Thermolysis at 120°C		
	Solution-State (15 min, ~2 Eq. H_2)		
	50 wt% BmimCl	40 wt% BmimCl	20 wt% BmimCl
Grav. density (Mat. wt%)	7.2	8.7	10.2
Vol. density (kg-H_2/L Mat.)	0.067	0.078	0.086
H_2 Flow Rate (g/s) per kg Material	0.08	0.097	0.114
kg of Mat. for 0.8 mol/sec	20	17	14

Accomplishments

- A greatly increased rate of H_2-loss (~2.3 equivalent in 15 min) with 10.2 mat-wt% from ammonia borane (AB)/ionic-liquid mixtures was achieved at 120°C.
- A rhodium catalyzed AB H_2-release in an ionic liquid was demonstrated that increases the loss rate for the first H_2-equivalent.
- Proton sponge in ionic liquids was shown to both increase the release rate of the second AB H_2-equivalent and greatly reduce foaming.
- Nuclear magnetic resonance (NMR), differential scanning calorimetry and rate studies revealed that while there are different mechanistic pathways for AB H_2-release, the final spent fuels all contain trigonal sp^2 BNH_x structures thus enabling a common regeneration strategy.
- New high yield processes for the conversion of BX_3 to AB were developed that avoid the formation of hazardous diborane and allow complete separation and recovery of all products.

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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 AB, NH_3BH_3 (19.6 wt% H_2) and ammonia triborane, $NH_3B_3H_7$ (17.7 wt% H_2) 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 and Alabama and the Rohm and Haas Company, our approach is to develop new methods for amineborane hydrogen-release and regeneration reactions that will enable their use for chemical hydrogen storage.

Results

Hydrogen Release Studies. Partial dehydrogenation of AB 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. In the first years of this project, we demonstrated that chemical additives, ionic liquids and metal catalysts could each be used to significantly increase the rate and extent of hydrogen release from AB. These results have clearly shown that, while improvements are still necessary, many of these systems have the potential to achieve DOE hydrogen-storage goals. In the last year, we have continued to investigate new methods of enhancing both the extent and rate of AB H_2-release and to elucidate the fundamental nature of the release steps and products. Some important results relating to H_2-release from the last year are briefly summarized below.

Our past studies of AB H_2-release in ionic liquids were at 85°C, but we have now found that greatly increased rates and extent of H_2-release from AB can be achieved at 120°C. Thus, as can be seen in Figure 1, a 50:50 weight% mixture of AB:BmimCl at 120°C releases ~2.3 equivalents of H_2 in only 15 min, corresponding to 7.2 mat-wt% H, whereas at 85°C this mixture would have released less than 0.4 equivalent. As also shown on this graph, this value is significantly higher than the ~1.4 equivalents that can be obtained from solid AB at this temperature, clearly demonstrating the activating effect of the ionic liquid.

We also demonstrated that for reactions at 120°C, it is no longer necessary to use 50:50 weight% mixtures. There was little, if any, decrease in the amount and rate of H_2-release produced with either 60:40 or 80:20 wt% AB/BmimCl mixtures. As a result, the mat-weight% H values for these systems are significantly improved. For example, as can be seen in Figure 2 for the 80:20 mixture, 10.2 mat-wt% H was achieved in only 15 min!

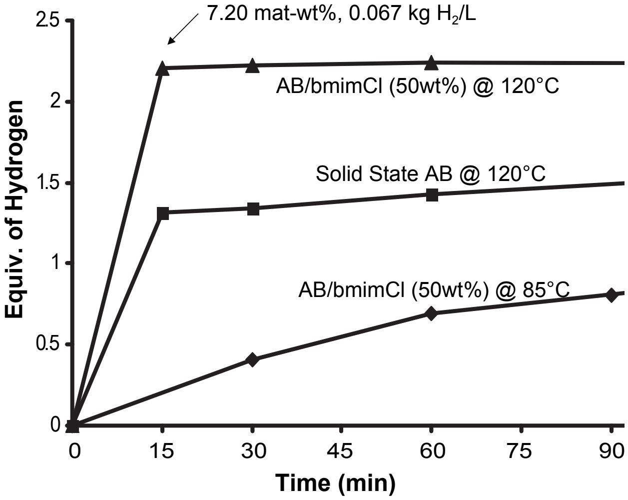


FIGURE 1. Summary of AB H_2-release studies in the bmimCl ionic liquid demonstrating that both the rate and extent of H_2-release are significantly increased at 120°C.

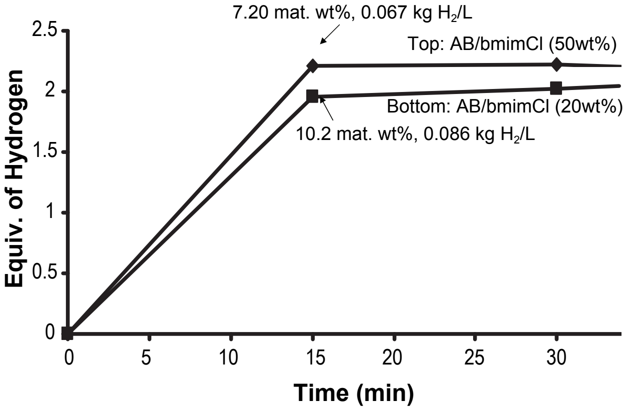
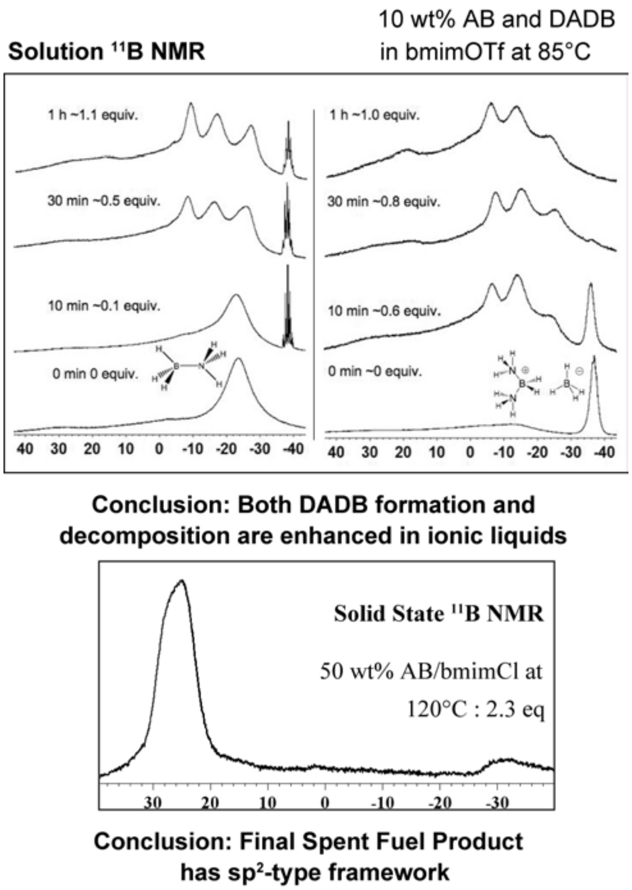


FIGURE 2. Summary of AB H_2-release studies of an 80:20 wt% AB:bmimCl mixture at 120°C showing the achievement of 10.2 mat-wt% H in only 15 min.

These results along with the other metric values for these systems are summarized in Table 1.

Both solution and solid-state NMR studies were also carried out during the last year that have revealed important details of both the mechanism of H_2-release in ionic liquids and the nature of the final spent fuel products. As shown in the example in Figure 3 (top), in situ NMR studies of H_2-release in the BmimOTf ionic liquid in conjunction with quantitative H_2-release measurements demonstrated that ionic liquids promote both the formation diammoniate of diborane (DADB) from AB and subsequent DADB decomposition. Furthermore, while the NMR studies showed that the initial H_2-release (i.e. ~1 equivalent of H_2) products of both AB and DADB were saturated polyaminoboranes, the solid state ^{11}B NMR studies Figure 3 (bottom)



Conclusion: Both DADB formation and decomposition are enhanced in ionic liquids

Conclusion: Final Spent Fuel Product has sp^2-type framework

FIGURE 3. Summary of in situ (top) and solid state (bottom) ^{11}B NMR studies for AB and DADB H_2-release in ionic liquids demonstrating that both DADB formation from AB and DADB H_2-release is promoted by ionic liquids.

of the spent fuels resulting from more extensive H_2-release (2.3 equivalents) demonstrated that the final products contain unsaturated polyborazylene-like structures. These studies strongly support a H_2-release process involving the stepwise formation of DADB, then a mixture of linear, cyclic and chain-branched polyamimoborane polymers and, finally, polyborazylene-like unsaturated materials.

Ammonia Borane Regeneration. The efficient regeneration of AB from spent fuel BNH_x is one of the most challenging problems that will have to be overcome in order to utilize AB-based hydrogen storage systems. The development of a general regeneration process is made complicated by the fact that, depending upon the conditions and extent of H_2-release, a variety of molecular, polymeric and/or solid state materials with very different chemical reactivities are formed. Thus, any viable process must both be capable of regenerating all of these spent-fuel materials and, in addition, avoid the formation of difficult to reduce intermediates (e.g. those containing boron-oxygen bonds).

At the May 2007 program review, we presented a new potentially general scheme for the regeneration of AB from spent BNH_x fuels. The key steps in the process are: (1) digestion of the spent fuel with superacidic HX/AlX_3 solutions, (2) coordination of the BX_3 product to a base, (3) reduction of the boron-halide bonds by silanes or stannanes, and finally (4) exchange of the base by ammonia to regenerate NH_3BH_3. During the last year we developed improved reduction methods for the second step that uses sulfide bases in conjunction with either silane or silane reducing agents. As shown in the example in Figure 4, these new reduction methods give higher yields, lower temperature reactions and much faster rates than our previous methods and, most significantly, allow the quantitative separation of all reactants and products.

Conclusions and Future Directions

As discussed in the previous section, our past studies have let to the discovery and continued improvements of both several promising H_2-release systems based on AB that have the potential to meet DOE targets, and the demonstration of a super-acid/halide-reduction process for ammonia borane regeneration. During the next year, we plan to:

- Optimize the higher-temperature/weight-ratios for ionic liquid based H_2-release system.
- Continue to optimize and explore the activities of new metal-catalyst and/or ionic liquids for improving the rates of thermolytic hydrogen release from AB and ammonia triborane.
- Carry out extensive NMR studies focused on learning how to control H_2-release mechanisms to achieve the most regenerable spent fuels.
- Further improve and optimize the conditions and procedures for the super acid digestion step needed for ammonia borane regeneration.
- In collaboration with other center partners, carry out new investigations of the use of the super-acid/halide-reduction process for the regeneration of other fuels such as $LiNH_2BH_3$.

Special Recognitions & Awards/Patents Issued

1. Larry G. Sneddon: 2007 DOE Hydrogen Program R&D Award in Recognition of Outstanding Achievement in Storage R&D.

FY 2008 Publications/Presentations

Publications

1. L.R. Alden, C.P. Griffin and L.G. Sneddon " Metal-Catalyzed Hydrogen Release from Ammonia Borane in

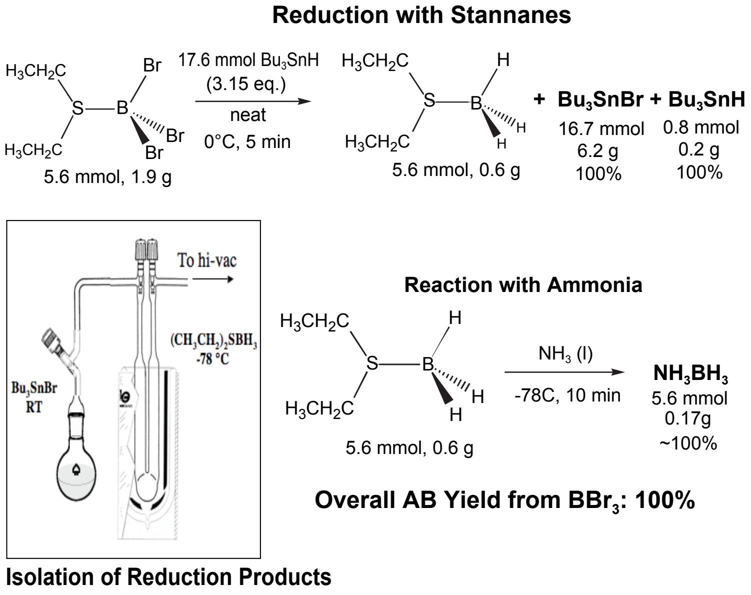


FIGURE 4. Newly improved method for the BX_3 reduction step in AB-regeneration that employs sulfide bases in conjunction with a tributylstannane reducing agent.

ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, 53, 670-671.

2. D. Himmelberger, M. Bluhm and L.G. Sneddon " Proton Sponge Induced Release from Ammonia Borane in ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, 53, 666-667.

Presentations

1. L.G. Sneddon, M.E. Bluhm, L. Alden, D. Himmelberger and M.G. Bradley "Amineborane Based Chemical Hydrogen Storage" invited lecture at the Symposium on Hydrogen Storage at the Materials Science and Technology Conference, Detroit, September, 2007.

2. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Detroit, Michigan, January, 2008.

3. L.R. Alden, M. E. Bluhm, C.P. Griffin, L.G. Sneddon "Improved Hydrogen Release from Ammonia Borane in Ionic Liquids" Materials Research Meeting, San Francisco, March, 2008.

4. B. Ewing and L.G. Sneddon "Progress Towards Ammonia Borane Regeneration" Materials Research Meeting, San Francisco, March, 2008.

5. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Hydrogen Annual Merit Review Meeting, Washington, D.C., June, 2008.

6. L. Alden, C.P. Griffin, and L.G. Sneddon "Metal Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August, 2008.

7. D. Himmelberger, M. Bluhm and L.G. Sneddon "Proton Sponge Induced Hydrogen Release in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August, 2008.

8. L.G. Sneddon, L. Alden, D. Himmelberger, C.W. Yoon, W. C. Ewing and M. E. Bluhm "Amineborane Based Chemical hydrogen Storage" invited lecture at the International Meeting on Boron Chemistry Barcelona, Spain, September, 2008.