IV.B.1b 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

TABLE 1. Progress toward DOE targets: Summary of AB H_2-release studies for 80:20 and 50:50-wt% AB:BmimCl mixtures and 50:50-wt% AB:BmimCl with 5 mol% PS at 120 and 110°C.

	AB and 20 wt% bmimCl		AB and 50 wt% bmimCl		AB and 50 wt% bmimCl 5 mol % PS
	120°C Two equiv. in 52 min	110°C Two equiv. in 157 min	120°C Two equiv. in 7 min	110°C Two equiv. in 22 min	110°C Two equiv. in 9 min
Initial Rate (mol/sec)	4.4×10^{-5}	1.8×10^{-5}	2.3×10^{-5}	8.3×10^{-6}	2.1×10^{-5}
Grav. density (Mat. wt%)	11.4 2.2 Equiv.	11.4 2.16 Equiv.	7.2 2.06 Equiv.	6.9 2.11 Equiv.	6.1 2.21 Equiv.
Vol. density (Kg-H_2/L Mat.)	0.089	0.095	0.067	0.063	0.057
H_2 Flow Rate (g/s) per kg Material	0.47	0.193	0.08	0.056	0.119
Kg of Mat. for 0.8 mol/sec	3.4	8.4	10	29	13

Accomplishments

- Significant rate enhancements along with high mat-wt% H_2-release (up to 11.4%) were demonstrated with 20 wt% ionic-liquid/ammonia borane (AB) mixtures at 110°C.
- Base-induced H_2-release in ionic liquids was extended to new bases and shown to increase the release rate of the second AB H_2-equivalent.
- A variety of metals were found to catalyze AB H_2-release in ionic liquids with significant increase for the rate of loss of the first AB H_2-equivalent.
- Completion of our work on ammonia triborane resulted in a new synthesis, its definitive structural determination and the optimization of its hydrolytic H_2-release properties.
- New solid-state and in situ nuclear magnetic resonance (NMR) studies confirmed that while there are different mechanistic pathways for AB H_2-release, the final spent fuels all contain trigonal sp^2 polyborazylene type structures.

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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 ammonia borane, NH_3BH_3 (AB), 19.6 wt% H_2, and ammonia triborane $NH_3B_3H_7$ (AT), 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 (PNNL), the Universities of Washington and Alabama and the Rohm & 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. In order for amine boranes to be useful for hydrogen storage, methods for more controllable H_2-release reactions must 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 both AB and AT.

During the past year our completed studies on AT were published demonstrating (1) a new, efficient preparation of AT that now makes this compound easily available; (2) new crystallographic and computational studies of the solid-state structure of AT, along with a structural determination of the AT-18-crown-6 adduct, that resolves the contradictions with previous computational structural predictions; and (3) a demonstration that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of AT rapidly release hydrogen, with 6.1 materials-wt% H_2-release being achieved from a 22.7-wt% aqueous solution of AT at room temperature in the presence of 5 wt%-Rh/Al_2O_3 (1.1 mol% Rh).

One the major objectives of last year's work was to collect detailed kinetic data, with the aid of a PNNL-designed automatic gas burette, for the H_2-release from a variety of ionic liquid-based systems in order to identify the optimal temperatures and compositions for these systems. Important findings resulting from these studies are summarized in Table 1 and Figures 1-3.

The H_2-release studies in Figure 1 of the temperature dependence of the reactions of 50:50-wt% AB:bmimCl mixtures demonstrated that dramatic rate enhancements for H_2-release are possible with only a modest increase in temperature. Thus, at 110°C, over 2 H_2-equivalents are released in only ~20 min.

Our studies (Figure 2) of 80:20-wt% AB:bmimCl mixtures at various temperatures showed that significant rate enhancements could still be achieved, with over 1.5 equiv of H_2 being released during the first 5 min at 110°C. This decrease in the amount of ionic-liquid then provides, as indicated in Figure 2, a significant increase in the materials-wt% H_2 that can be attained with these systems.

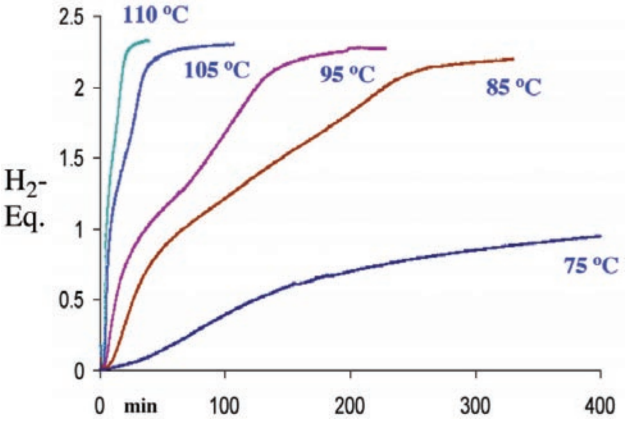

FIGURE 1. H_2-release data collected on the automated gas-burette for the reactions of 50:50-wt% AB:BmimCl at different temperatures.

As shown in Figure 3, our gas-burette studies also demonstrated that metal-catalyzed AB H_2-release can be attained with systems employing a variety of different ionic-liquids and metals.

Both solution and solid-state NMR studies during the last year 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 Figure 4, solid-state ^{11}B NMR studies by Penn students at the PNNL NMR facility characterized the steps and intermediates in the Proton Sponge promoted H_2-release from AB. The bottom spectrum shows the initial formation of both the diammoniate of diborane and sp^3-hybridized polyaminoborane polymers. However, as the reaction progresses, the low field peak near 30 ppm that is characteristic of sp^2-hybridized polyborazylene-type materials progressively grows until after the release of two equivalents of H_2 (top spectrum) only unsaturated B=N sp^2 products are present. These NMR studies thus strongly favor a dehydrogenation process involving H_2-elimination from adjacent polyaminoborane BH and NH groups to produce B=N unsaturated polyiminoboranes that further react to form cross-linked sp^2-bonded polyborazylene materials.

Ammonia Borane Regeneration. The efficient regeneration of ammonia borane 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/

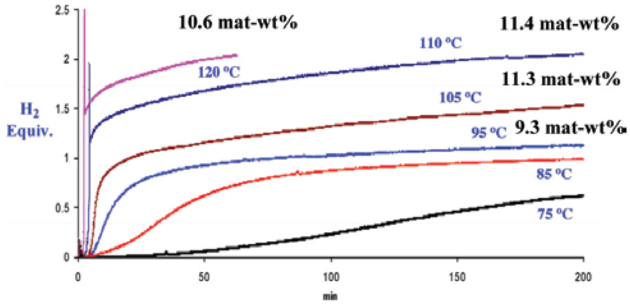

FIGURE 2. H_2-release data collected on the automated gas-burette for the H_2-release reactions of 80:20-wt% AB:bmimCl mixtures at different temperatures.

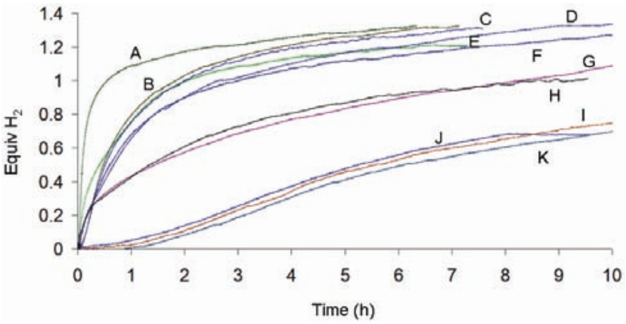

FIGURE 3. H_2-release data collected on the automated gas burette for metal-catalyzed AB H_2-release reactions with 5-mol% metals at 65°C with different ionic liquids (50wt%). A: $[Rh(COD)Cl]_2$ in bmimCl, B: $Ru(COD)Cl_2$ in bmimCl, C: $Ru(COD)Cl_2$ in bmimOTf, D: $RhCl_3$ in bmimCl, E: $[Rh(COD)Cl]_2$ in bmimOTf, F: $RuCl_3$ in bmimCl, G: $NiCl_2$ in bmimCl, H: $NiCl_2$ in bmimOTf, I: Rh powder in bmimCl, J: no catalyst in bmimCl, K: Ru powder in bmimCl.

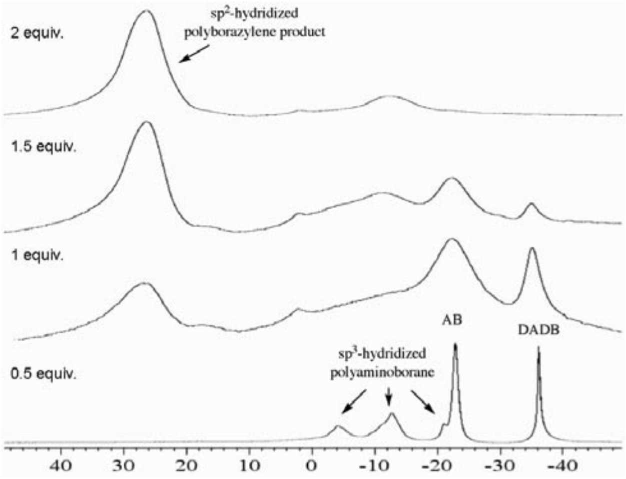

FIGURE 4. Solid-state ^{11}B NMR studies of the products of Proton Sponge induced H_2-release from AB leading to the formation of unsaturated sp^2-hybridized final products.

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). Studies were undertaken in the past year of new more efficient methods to convert spent fuel materials to boron trihalides. Since it has previously been reported that the $Na^+B(SO_3Cl)_4^-$ salt can be thermally decomposed to BCl_3 and SO_3, we investigated the digestion of several types of spent fuels with chlorosulfonic acid. We have found that spent-fuels and the polyborazylene polymer could be totally digested by chlorosulfonic acid to produce a single species with NMR data consistent with the formation of the $NH_4^+B(SO_3Cl)_4^-$ salt.

Conclusions and Future Directions

As discussed in the previous section, our past studies have led to both the discovery and continued improvements of promising H_2-release systems based on ammonia borane. These results have clearly shown that, while improvements are still necessary, many of these systems have the potential to achieve DOE hydrogen-storage goals. During the final year of the Center, we plan to:

- Complete H_2-release studies for: (1) ionic-liquid/AB mixtures at different temperatures, (2) base-initiated ionic-liquid/AB mixtures, and (3) metal-catalyzed ionic-liquid/AB.
- Complete the optimization of the temperature/weight-ratios for ionic liquid based H_2-release.
- Continue to develop and optimize new chemical-promoter systems with improved H_2-release rates.
- Explore the activities of non-precious metal catalysts in ionic liquids for improving the rate of AB H_2-release.
- Take advantage of synergistic mechanisms to improve H_2-release rates.
- Explore alternative methods for the formation of boron trihalides.
- Explore, with Center partners, the development of hybrid regeneration methods.

FY 2009 Publications/Presentations

Publications

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

3. C.W. Yoon, P.J. Carroll and L.G. Sneddon "Ammonia Triborane: A New Synthesis, Structural Determinations and Hydrolytic Hydrogen-Release Properties" *J. Am. Chem. Soc.* **2009**, *131*, 855-864.

4. D. W. Himmelberger, C.W. Yoon, M.E. Bluhm, P.J. Carroll and L.G. Sneddon "Base Promoted Ammonia Borane Hydrogen Release" submitted.

Presentations

1. 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.

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

3. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" invited lecture at the International Meeting on Boron Chemistry Barcelona, Spain, September 2008.

4. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Detroit, Michigan, March 2009.

5. L.G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Hydrogen Annual Merit Review Meeting, Washington DC, May 2009.

6. D. Himmelberger, L. Alden and L.G. Sneddon "Ionic Liquid Mediated Ammonia Borane H_2-Release" National American Chemical Society Meeting, Washington, DC, August, 2009.

7. E. Berkeley, L. Alden and L.G. Sneddon "Metal Catalyzed Ammonia Borane Dehydrogenations in Ionic Liquids" National American Chemical Society Meeting, Washington, DC, August, 2009.