

IV.H.1 Purdue Hydrogen Systems Laboratory: Hydrogen Storage*

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Objectives

- Develop an energy efficient recycling protocol for ammonia borane (AB) from spent borate.
- Develop AB slurry-based subscale onboard hydrogen storage systems.
- Develop a new noncatalytic method for hydrogen generation from AB and water.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007):

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management
- (R) Regeneration Process
- (S) By-Product/Spent Material Removal

Technical Targets

On-board Storage	Units	2010/ Ultimate	Purdue 2009
System gravimetric capacity	H ₂ wt%	4.5/7.5	8.2-9.6 (material)
Overall efficiency of off-board regeneration	%	>60	Our process is being optimized

Note: the 2010/Ultimate system gravimetric densities are the revised DOE 2010 hydrogen storage targets.

Accomplishments

- Trimethyl borate was successfully converted to AB via reduction with diethylsilane in the presence of *N*¹,*N*¹,*N*²,*N*²-tetramethylethane-1,2-diamine (TMEDA), followed by the displacement of TMEDA with ammonia to obtain AB.
- Increased hydrogen storage capacity of the AB slurry hydrolysis approach from 7.5 wt% to 8.2 wt% by enhancing AB/water mixing.
- Implemented continuous measurements of AB/bminCl slurry dehydrogenation and observed extremely fast hydrogen release rate.
- Investigated noncatalytic AB hydrothermolysis for a wide range of AB concentration (5-65 wt%) and temperature (75-135°C) under modest pressure (~200 psia). It was found that while varying AB concentration in the investigated range, the total hydrogen yield remains in the narrow range of 2.25-2.75 equivalent per mole of AB.
- For noncatalytic hydrothermolysis of 40 and 65 wt% AB, hydrogen storage capacity of 6.0 and 9.6 wt% were achieved at temperature ~85°C, respectively.



Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus. This laboratory is engaged in basic research in hydrogen production and storage and has initiated engineering systems research with goals established as per the U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program. Hydrogen production research of this project is reported in report II.J.1.

The hydrogen storage research has been focused on improving the engineering performance of AB-based onboard hydrogen storage and finding energy

efficient ways to recycle the byproducts. The AB slurry dehydrogenation work has been focused on measuring engineering properties of onboard hydrogen discharge and fresh/spent fuel transfer and developing a subscale reactor module to provide a platform for the studies of AB and other potential off-board recyclable hydrogen storage materials. Slurries provide higher energy capacity than solutions and are easier to be transported onboard than solids. In addition, we have recently proposed and demonstrated a new approach to release hydrogen from heating dilute AB solutions under modest argon pressure. During the past year, AB hydrothermolysis was studied for rich-AB/water mixtures, over a wide temperature range. The use of D_2O , instead of H_2O , was continued to clarify the reaction mechanism. Since the release of hydrogen from AB via both thermolysis and hydrolysis is exothermic, it was expected that hydrogen could be released from rich-AB/water mixtures at temperatures lower than required for pure AB thermolysis.

Approach

We are developing methods for AB dehydrogenation and regeneration that will enable its use for onboard hydrogen storage. The AB regeneration scheme is illustrated in Figure 1. The spent fuel, ammonium borate were converted to triacyl- or trialkyl borates, which provided molecules with weaker B-O bond. The reduction of triacyl- or trialkyl borates in the presence of TMEDA, followed by the displacement of TMEDA using ammonia will eventually lead to efficient ammonia borane regeneration.

We investigated ultrasonic mixing techniques to improve ruthenium (Ru) catalyzed AB slurry hydrolysis approach to obtain high hydrogen yields near stoichiometry. Also, we are designing a benchmark continuous flow AB slurry reactor module to address various common engineering issues in on-board chemical hydrogen storage systems, such as slurry handling and thermal management. To facilitate the reactor design, we are investigating AB/ionic liquid slurry dehydrogenation kinetics characterizing flowability of AB slurries and spent fuels from various

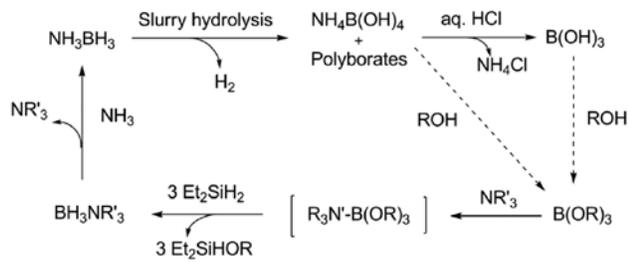


FIGURE 1. AB Recycling Scheme

reactions including hydrolysis, thermolysis and hydrothermolysis.

The AB hydrothermolysis method for H_2 generation was studied over a wide range of AB concentrations (5-65 wt%), pressure (~200 psia) and temperature (75-135°C). To clarify the reaction mechanisms, isotopic labeling (D) was used, where measurements of H_2 and deuterium hydride (HD) concentrations in gaseous products allowed us to differentiate between the sources of the released hydrogen, i.e. AB vs. water.

Results

We computed the energetics of the steps involved in the recycling of spent borate to AB using B3LYP/aug-cc-pVDZ level of theory. We have recycled ammonia borate to AB via conversion to trimethyl borate followed by the reduction using diethylsilane. We developed novel protocol for the reduction of trimethyl borate. The reduction of trimethylborate in the presence of TMEDA using diethylsilane resulted in the formation of bisamine borane complex in quantitative yield (90%). The bisamine borane complex could be readily separated by filtration. The displacement of amine from the amine borane complex was readily achieved using ammonia in 80% yield. We have initiated energy efficient schemes to convert $NH_4B(OH)_4$ to AB via triacylborates. The advantage of conversion to such acylborate esters over simple alkylborate esters is that the B-O bond will be weakened enough to be reduced with mild hydride sources.

We studied catalytic AB water (1:2) slurry hydrolysis using ultrasonic mixing. The hydrogen yields of the four tests were 70%, 80%, 88% and 92%, respectively while the yields of tests with conventional mechanical mixing were around 75%. With 92% hydrogen yield of (1:2) AB/water slurry, the material based hydrogen storage capacity is 8.2 wt%. We also measured rheology properties of AB and sodium borohydride (SBH) spent fuels. This test, for the first time, quantitatively revealed that AB spent fuel has lower elastic stiffness (softer) and smaller viscous damping than those of SBH spent fuels. We also conducted a series of AB/ionic liquid thermolysis tests using an apparatus that allows continuous observation of hydrogen release. The AB/bmimCl mass ratio and reaction temperature were same as the tests described in the literature (Sneddon, 2008). It was observed that the reaction occurred very fast and a lot of hydrogen was released in the first minute. As illustrated in Figure 2, the hydrogen yield at 15 minutes after the beginning of reaction is same as what reported in the literature while the hydrogen release rate in the first five minutes is much faster than what indicated before (the dotted lines). This observation significantly complements the literature data and provides insightful information for system design.

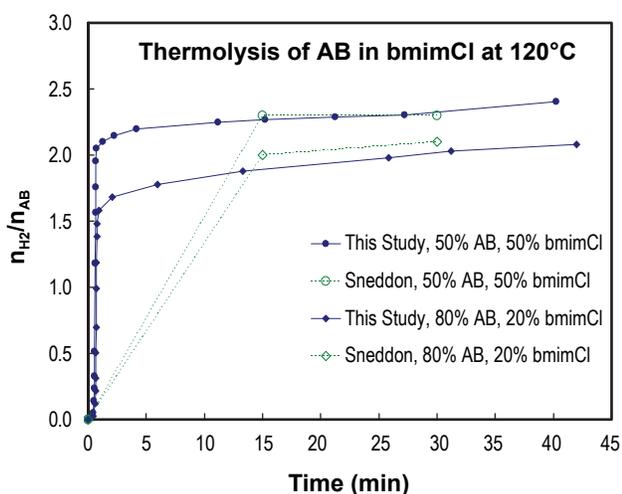


FIGURE 2. Continuous Measurements of Hydrogen Release of AB/bmimCl Slurry Dehydrogenation

In addition, hydrothermolysis of AB/D₂O solutions and slurries were studied in a 300-mL stainless steel Parr reactor over the temperature range 75-135°C under Ar pressure (initial) 200 psia. Mass spectral analysis of the reactor atmosphere after all experiments showed H₂ and HD as the main gaseous products. Apart from H₂ and HD, some NH₃ was also detected in the mass spectrometry analysis. It was found that for AB concentration >40 wt%, temperature (T_{reactor}) ~85°C is sufficient to release the same amount of hydrogen as at T ~135°C (Figure 3). For AB <30 wt%, however, T_{reactor} ~135°C was required instead of 85°C. As the AB concentration increased from 5 to 65 wt%, the H₂ yield increased from 0.75 to 1.75 equivalent, while HD yield decreased from 2 to 0.5 equivalent. However, the total hydrogen yield (H₂+HD) remained in the relatively narrow range of 2.25-2.75 equivalent. Thus, the role of thermolysis, as compared to hydrolysis, increases with AB concentration. As shown in Figure 2, hydrogen yield increased with AB concentration. For 40 and 65 wt% AB, hydrogen yields of 6.0 and 9.6 wt% respectively, were achieved. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at below proton exchange membrane (PEM) fuel cell operating temperatures.

Conclusions and Future Directions

We investigated fundamental chemistry of AB recycling and achieved conversion of trimethyl borate to AB. Using ultrasonic mixing, we observed 92% hydrogen yield in catalytic AB/water (1:2) slurry hydrolysis, which provides a hydrogen storage capacity of 8.2 wt%. Also, through continuous measurements, we observed extremely fast hydrogen release rate in AB/bmimCl slurry dehydrogenation process at 120°C.

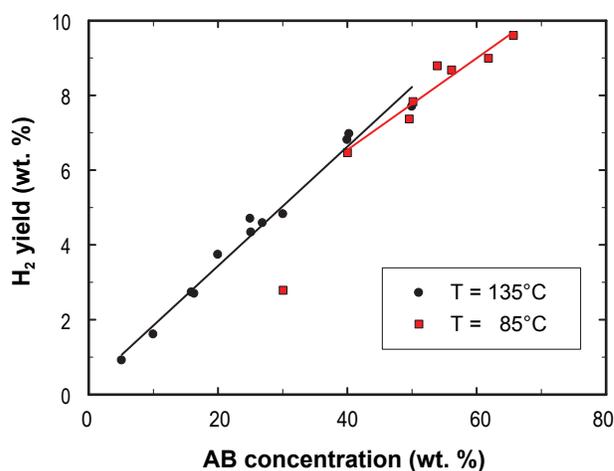


FIGURE 3. Hydrogen Yield vs. AB Concentration at P=200 psia

In addition, it was demonstrated that noncatalytic AB hydrothermolysis is a promising method for hydrogen storage. We have achieved hydrogen capacity up to 9.6 wt% using this approach, at temperature <85°C, along with rapid kinetics. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at below PEM fuel cell operating temperatures. Further, for the same temperature range, these yield values are higher than previously reported in the literature by either AB hydrolysis or thermolysis alone.

In the near future, we will work towards maximum AB recycling yield via a novel recycling pathway. The reduction of trimethyl borate using diethylsilane will be optimized with respect to temperature and pressure, silane and amines. The displacement of TMEDA from the corresponding bisborane adduct using ammonia will be standardized for the quantitative isolation of AB. Computations of the recycling of energy efficiency will be completed. We will continue to measure engineering properties of AB aqueous and non-aqueous slurries and develop a subscale reactor module and system to address various common engineering issues in on-board chemical hydrogen storage systems. Further, the reaction mechanisms and yield of hydrogen generation from AB hydrothermolysis in aqueous solutions and slurries (>65 wt%) will be determined. The reaction by-products will also be quantified. To better understand the temperature effects (heat evolution), a smaller size reactor (~50 ml) will be developed.

FY 2009 Publications/Presentations

- Basu, S., Brockman, A., Gagare, P., Zheng, Y., Ramachandran, P.V., Delgass, W.N., and Gore, J., 2009, "Kinetics of Ru-catalyzed Ammonia Borane Hydrolysis," *Journal of Power Sources*, 188: 238-243.

2. Diwan, M., Al-Kukhun, A., Hwang, H. and Varma, A., “Hydrogen Generation for Fuel Cell Applications,” *4th Annual Purdue Energy Center Hydrogen Initiative Symposium*, April 23, 2009, West Lafayette, IN.
3. Gagare, P., Brockman, A., Basu, S., Diwan, M., Al-Kukhun, A., Hwang, H., Zheng, Y., Ramachandran, P., Varma, A., Gore, J., “Purdue Hydrogen Systems Laboratory Part II: Hydrogen Storage,” *2009 Annual Merit Review & Peer Evaluation*, Washington, D.C.