

IV.B.5 Development of Regenerable High Capacity Boron Nitrogen Hydrides as Hydrogen Storage Materials

Ashok Damle
RTI International
3040 Cornwallis Road
P.O. Box 12194
Research Triangle Park, NC 27709
Phone: (919) 541-6146; Fax: (919) 541-8002
E-mail: adamle@rti.org

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire
Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-FG36-05GO15005

Subcontractors:
State Scientific Research Institute for Chemistry
and Technology of Organoelement Compounds
(GNIChTEOS), Moscow, Russian Federation
Intematix Inc., Fremont, California

Start Date: March 15, 2005
Projected End Date: November 30, 2008

Objectives

- Evaluate approaches for complete and fast release of pure hydrogen from ammonia-borane.
- Develop an on-board hydrogen extraction process.
- Design an on-board hydrogen storage and extraction system.
- Demonstrate individual steps involved in ammonia-borane synthesis starting from the ammonia-borane decomposition products for their recycle.
- Scale-up the ammonia-borane synthesis process.
- Develop an integrated process design for ammonia-borane production.
- Design, develop, and demonstrate prototype (1 kg hydrogen capacity) hydrogen extraction system with >9 wt% hydrogen capacity.
- Determine technical and economic feasibility of utilizing ammonia-borane as an on-board hydrogen storage medium.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal
- (J) Thermal Management

Technical Targets

This project is evaluating the feasibility of using ammonia-borane (NH_3BH_3) as an on-board hydrogen storage medium. With 19.6% by weight of hydrogen in its molecular formula, ammonia-borane has potential to meet DOE's year 2015 targets of gravimetric (0.09 kg H_2 /kg of system weight) as well as volumetric (0.081 kg H_2 /L of system volume) energy densities. Evaluation of approaches to regenerate ammonia-borane decomposition products will determine the feasibility of approaching DOE's fuel cost (\$2 to \$3/GGE ~ kg H_2) target. Development of an efficient hydrogen extraction system will allow approaching the storage system cost (\$67/kg H_2) target.

Accomplishments

- Studies involving slow heating of ammonia-borane indicated three distinct stages of hydrogen release occurring at 85-100°C, 105-150°C, and beyond 200°C respectively. About 2/3 or 67% of the available hydrogen was released during the first two stages with a material based hydrogen density of 13 wt%.
- Studies involving rapid heating of ammonia-borane indicated release of ~85% of the available hydrogen in ammonia-borane at 500°C in less than 30 seconds with a material-based hydrogen storage density of 16.5 wt%.
- The commercial boron nitride (BN) was found to be non-reactive to chlorination with no

- observed formation of boron tri-chloride, BCl_3 , at temperatures up to $1,120^\circ\text{C}$.
- The products of thermal decomposition of ammonia-borane were, however, found to be reactive to chlorine beginning at 500°C with complete conversion of the decomposition products to boron tri-chloride by 900°C .
 - Components for an on-board hydrogen extraction system based on short-time, fast heating of ammonia-borane were identified.

Introduction

The objective of this two-phase project is to develop synthesis and hydrogen extraction processes for nitrogen/boron hydride compounds that will permit exploitation of the high hydrogen content of these materials. The primary compound of interest in this project is ammonia-borane (NH_3BH_3), a white solid, stable at ambient conditions, containing 19.6% of its weight as hydrogen. With a low-pressure on-board storage and an efficient heating system to release hydrogen, ammonia-borane has potential to meet DOE's year 2015 specific energy and energy density targets. If the ammonia-borane synthesis process could use the ammonia-borane decomposition products as the starting raw material, an efficient recycle loop could be set up for converting the decomposition products back into the starting boron-nitrogen hydride. With production at a large scale typical of a commodity chemical (as may be expected from a potential gasoline substitute), the cost of ammonia-borane regeneration has potential to meet DOE's fuel cost targets based on the cost of hydrogen and raw materials used for regeneration. By designing an efficient heating system for aminoborane decomposition, a net high energy density will be realized and the system cost will be minimized approaching DOE's goals.

Approach

This project is addressing two key challenges facing the exploitation of the boron/nitrogen hydrides (ammonia-borane), as hydrogen storage material:

- Development of a simple, efficient, and controllable system for extracting most of the available hydrogen, realizing the high hydrogen density on a system weight/volume basis, and
- Development of a large-capacity, inexpensive, ammonia-borane regeneration process starting from its decomposition products (BNH_x) for recycle.

During Phase I, two different approaches of heating ammonia-borane are being investigated: a) "heat to

material approach" in which a fixed compartmentalized ammonia-borane cartridge will be heated by directing the heating medium to progressive zones with a carefully controlled heating pattern, and b) "material to heat approach" in which a small amount of ammonia-borane will be dispensed at a time in a fixed hot zone. In the first approach the ammonia-borane heating rate as well as the rate of hydrogen release from the storage system will be regulated by a controlled heating pattern, whereas, in the second approach the hydrogen release rate will be controlled by the rate of ammonia-borane dispensing in the hot zone. Utilization of solid phase catalysts mixed with ammonia-borane will be explored to assist in thermal decomposition of ammonia-borane to lower the decomposition temperature, to increase the rate of hydrogen release, and to lead to decomposition products that may easily be regenerated by direct hydrogenation of the decomposition products in the presence of catalysts.

The complete decomposition of the ammonia-borane is overall exothermic which would allow the small "hot zone" used in the second approach to be self-sustaining. Careful heat management both to supply the heat during the initial heating and removal of heat, if necessary to maintain a desired temperature, will be needed in the first approach. Two possible modes of supplying heat will be considered in the on-board storage system design: direct hydrogen combustion, and resistive heating using fuel cell power.

The ammonia-borane decomposition products can be regenerated into ammonia borane through a series of chemical process steps involving chlorination of decomposition products to produce boron trichloride (BCl_3), hydrogenation of BCl_3 to form diborane (B_2H_6), and ammoniation of diborane to form ammonia-borane. Each of these steps will be investigated and demonstrated during the Phase I effort, on a laboratory scale, leading to optimized process conditions for each of the reaction steps. Phase I effort will also investigate direct catalytic hydrogenation of the decomposition products to identify promising catalysts and process conditions necessary for direct hydrogenation.

Based on the results of the ammonia-borane decomposition studies, a conceptual design will be prepared for an on-board hydrogen storage system using the most promising approach for maximum and high purity hydrogen yield. Techno-economic feasibility analysis will then be conducted to estimate the storage system as well as regeneration (fuel) costs to provide a go/no go decision for Phase II.

Upon successful completion of Phase I, the individual ammonia-borane synthesis process steps will be integrated and scaled up in Phase II to be able to synthesize sufficient quantities of ammonia-borane for testing, demonstration, and delivery to DOE. A prototype on-board hydrogen storage system with 1 kg

hydrogen capacity will be designed and fabricated for demonstration of this concept. An integrated process design will be developed for large-scale synthesis of ammonia-borane and an economic analysis will be conducted to determine the minimum production volume necessary to be able to meet DOE's fuel cost targets.

Results

- Thermal decomposition of ammonia-borane was studied using two different approaches for heating ammonia-borane material: a) slow heating with controlled heating program to identify stages of ammonia-borane decomposition, and b) fast heating of ammonia-borane in a high temperature reactor to determine hydrogen release as a function of temperature and exposure time.
- Slow heating studies were conducted using a thermogravimetric analyzer (TGA) as well as temperature programmed desorption (TPD) techniques in an inert atmosphere. Gas species released during heating were monitored by an on-line mass spectrometer and the total amount of hydrogen released was quantified by an on-line thermal conductivity detector analysis. Three distinct stages of hydrogen release were observed occurring at 85-100°C, 105-150°C, and beyond 200°C respectively. The three observed hydrogen release stages are seen clearly in the thermal conductivity detector (TCD) trace of the gas produced during the heating of the ammonia-borane sample as shown in Figure 1. About 2/3 or 67% of the available hydrogen was released during the first two stages with a material based hydrogen density of 13 wt%.

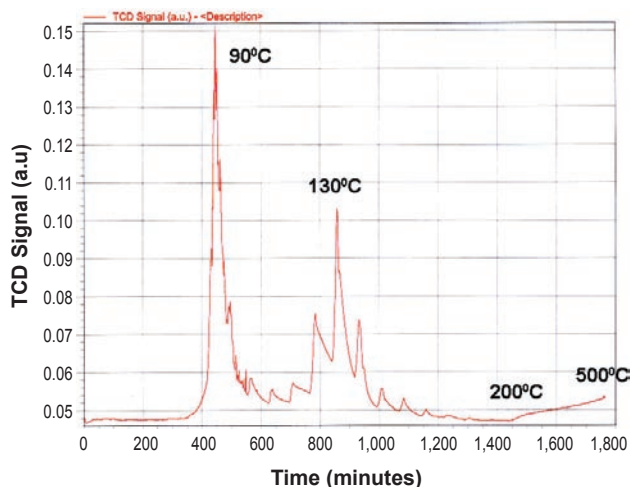


FIGURE 1. Release of Hydrogen in Three Distinct Stages during Heating of Ammonia-Borane as Detected by Continuous TCD Analysis of the Gas Produced

- Borazine ($B_3N_3H_6$) was found to be the primary minor impurity in the hydrogen gas released during heating of ammonia-borane. In general, greater release of borazine ($B_3N_3H_6$) is observed with sample heating at a greater rate (greater ramp rate, shorter hold time and/or larger temperature steps between holds).
- Fast heating studies were conducted using a high temperature tubing reactor for quantitative determination of the amount of hydrogen released as a function of the reactor temperature and the sample hold time. Gas species released during the fast heating were determined by the gas chromatographic and mass spectrometer analysis of the gas generated. About 85% of the available hydrogen in ammonia-borane was observed to be released at 500°C in less than 30 seconds with a material-based hydrogen storage density of 16.5 wt%. The elemental analysis of the decomposition product indicated a composition of an empirical formula $BN_{0.9}H$ consistent with the observed release of 85% of the available hydrogen in ammonia borane. Gas chromatographic analysis of the gas produced indicated hydrogen purity of over 98.5%. Mass spectrometer analysis of the gas produced indicated borazine to be the primary minor impurity in the gas produced.
- Information available in literature was reviewed for determining process conditions for chlorination of boron nitride as a first step in its regeneration into ammonia-borane.
- Chlorination of commercially available BN was investigated at temperatures up to 1,120°C without any catalyst and at temperatures up to 980°C in the presence of catalysts. The commercial BN was found to be non-reactive to chlorination with no observed formation of boron tri-chloride, BCl_3 .
- The products of thermal decomposition of ammonia-borane were, however, found to be reactive to chlorine beginning at 500°C with complete conversion of the decomposition products to boron tri-chloride by 900°C.
- Components for an on-board hydrogen extraction system based on short-time, fast heating of ammonia-borane were identified.

Conclusions and Future Directions

The hydrogen release studies have confirmed the potential of ammonia-borane for meeting U.S. DOE's 2015 hydrogen storage density targets. The ammonia-borane decomposition studies will be continued to evaluate non-catalytic as well as catalytic decomposition approaches and to optimize process conditions for maximizing hydrogen yield. Suitable catalysts will be identified using combinatorial synthesis technology to efficiently generate hundreds of different

catalyst compositions. The nature and concentration of impurities in the hydrogen gas produced will be determined and approaches will be evaluated to produce high purity hydrogen suitable for proton exchange membrane fuel cells.

Investigation of each chemical reaction step necessary for regeneration of ammonia-borane decomposition products will be continued. Process conditions for chlorination of ammonia-borane decomposition products as well as for diborane and ammonia-borane synthesis will be optimized for maximizing respective product yields. Direct catalytic hydrogenation of ammonia-borane decomposition products will be evaluated using the catalysts discovered for hydrogen release.

A conceptual design will be developed for an on-board hydrogen storage and delivery system with >9 wt% hydrogen storage capacity using the most promising approach for heating ammonia-borane. All of the components of the conceptual storage system will be

identified and preliminary component requirements will be developed to facilitate estimating the cost of the storage system. The cost of the regeneration of decomposition products will be assessed to determine the cost of the stored hydrogen. Realistic estimates of the system-based hydrogen capacity will be made and compared with DOE targets. The overall techno-economic feasibility of using ammonia-borane as a hydrogen storage medium will be determined to provide input for the go/no go decision for Phase II.

FY 2006 Publications/Presentations

1. Damle, A.S., "Development of Regenerable High Capacity Boron Nitrogen Hydrides as Hydrogen Storage Materials," FreedomCAR Hydrogen Storage Technical Team Review Meeting, June 22, 2006.
2. Damle, A.S., "Development of Regenerable High Capacity Boron Nitrogen Hydrides as Hydrogen Storage Materials," U.S. DOE/EERE Hydrogen Program Review Meeting, May 18, 2006.