V.A System Analysis

V.A.1 Analysis of Hydrogen Production Using Ammonia and Ammonia-Borane Complex for Fuel Cell Applications

Ali T-Raissi (Primary Contact)
University of Central Florida
Florida Solar Energy Center
Cocoa, FL 32922-5703
(321) 638-1446, fax: (321) 638-1010, e-mail: ali@fsec.ucf.edu

DOE Technology Development Manager: Roxanne Danz
(202) 586-7260, fax: (202) 586-4753, e-mail: Roxanne.Danz@ee.doe.gov

Objectives

- Analyze the viability (i.e. cost, safety, and performance) of ammonia-based chemical hydrides as hydrogen (H_2) storage compounds for fuel cell applications.
- Identify the pros and cons of using ammonia (NH_3) as a chemical carrier for H_2.
- Evaluate the viability of autothermal NH_3 reformation on-board fuel cell vehicles.
- Analyze the viability (cost and performance) of using ammonia-borane complex (H_3BNH_3) as a chemical hydrogen storage medium on-board fuel cell vehicles.
- Identify technoeconomic barriers to the implementation and use of amine borane complexes, in general, and H_3BNH_3, in particular, as prospective chemical hydrogen storage media on-board fuel cell vehicles.

Approach

- Review all published papers, reports, patents, etc. in the past 50 years related to the development of ammonia-based chemical hydrides as H_2 storage compounds.
- Develop contacts with and inquire about information from the researchers and/or companies involved with the development of ammonia-based chemical hydrides.
- Use FactSage Program to calculate and optimize the performance parameters for the autothermal reformation of ammonia to hydrogen gas.
- Compile information on the physiochemical properties and synthesis of ammonia-borane complex.
- Compare the characteristics and costs of H_3BNH_3 as a hydrogen storage media to that of sodium borohydride ($NaBH_4$) and ionic hydrides such as lithium hydride (LiH) and calcium hydride (CaH_2).
- Identify possible approaches that have potential to significantly reduce the cost of ammonia-borane synthesis.

Accomplishments

- Reviewed and evaluated more than 120 published papers, reports, patents and other archival records related to ammonia-based chemical hydrides, including amine borane complexes, as prospective chemical hydrogen storage compounds.
- Completed an assessment of the pros and cons of ammonia-based hydrogen storage compounds for vehicular fuel cell power applications.

- Used FactSage 5.1 Program for Computational Thermochemistry to determine the performance parameters for the autothermal reformation of NH_3 gas to hydrogen.
- Evaluated a number of ammonia adducts, including H_3BNH_3, as non-toxic, non-cryogenic alternatives to ammonia for use in vehicular fuel cell applications.
- Completed a tentative evaluation of the production costs of ammonia- and amine borane-based hydrogen storage compounds.
- Identified the current high costs of ammonia-borane complex production as the main drawback to the successful implementation of H_3BNH_3 as a H_2 storage compound for the vehicular fuel cell applications.

Future Directions

- Complete technoeconomic analysis of ammonia-borane complex as a hydrogen storage compound for fuel cell applications.
- Conduct a thorough literature search to identify and evaluate new, more advanced and potentially lower cost chemical processes for the synthesis of H_3BNH_3.

Introduction

The aim of this project is to assess the issues of cost, safety, performance, and environmental impact associated with the production of hydrogen (H_2) by several methods, not presently funded by the U.S. DOE Hydrogen, Fuel Cell and Infrastructure Program. Three technology areas being evaluated are: 1) thermochemical reformation of methane (CH_4) and hydrogen sulfide (H_2S) gas with and without using solar energy; 2) ammonia (NH_3) and ammonia adducts as hydrogen storing chemical hydrides for fuel cell applications; and 3) thermochemical water-splitting cycles suitable for solar power interface.

A report on the first topic involving an assessment of the thermochemical reformation of CH_4/H_2S has been submitted previously. This second report is concerned with the prospects of NH_3 and ammonia-borane as hydrogen storage media for fuel cell applications.

Advantages and Drawbacks to Ammonia Use

Ammonia is the second largest synthetic commodity product of the chemical industry, with world production capacity exceeding 140 million metric tons. In 2000, the U.S. consumed in excess of 20 million metric tons of NH_3. Anhydrous ammonia costs about $150 per short ton (f.o.b. U.S. Gulf Coast) or less than $6.25 per million BTU of H_2

contained. Besides the large volume of production and use, and relatively low cost, NH_3 has the following advantages as a hydrogen-rich fuel for fuel cell applications:

- Energy density - contains 17.8 weight % hydrogen (liquid ammonia stores 30% more energy per unit volume than liquid hydrogen).
- Infrastructure for NH_3 transportation, distribution, storage and use already exists.
- Simplicity - its use requires no shift converter, selective oxidizer or co-reactants.
- No purification is needed for NH_3 use with alkaline fuel cells (AFCs).
- Only 16% of the energy stored in NH_3 is needed for its conversion to N_2 and H_2.
- There are good NH_3 decomposition catalysts such as: ICI-47-1 (10 weight % nickel on alumina); Haldor Topsøe DNK-2R (triply promoted iron-cobalt); SÜD-Chemie 27-2 (nickel oxide on alumina); various supported nitrided catalysts (e.g. molybdenum nitride and nickel molybdenum nitride on - α alumina); and ruthenium modified nickel oxide on alumina.
- Flammability range for ammonia -air (at 0°C and 1 atm) is much narrower than that for hydrogen-air mixtures (i.e. 16-27 volume % NH_3 vs. 18.3-59 volume % H_2).

- Using ammonia in fuel cell power plants does not generate carbon dioxide (CO_2) or nitrogen oxides (NO_2) emissions.

There are several drawbacks to ammonia as a fuel and chemical carrier for H_2, especially in vehicular applications, including safety concerns with the widespread transportation, utilization and use of ammonia as a transportation fuel; storage requirements for sub-ambient temperatures and/or elevated pressures; and requirements for on-board reformation to liberate H_2. These limitations make the widespread ammonia use as a transportation fuel problematic. Furthermore, cost and energy efficiency considerations dictate that any chemical hydride employed as a vehicular hydrogen storage medium, including ammonia, not require complicated on-board reformation in order to generate hydrogen.
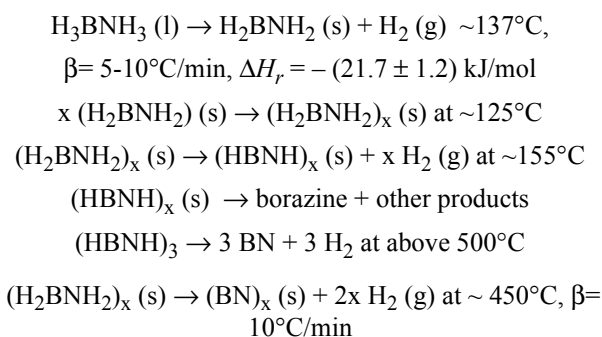
To mitigate ammonia's shortcomings, our approach involved complexing NH_3 with other hydrides to form compounds that are stable but not toxic or cryogenic. In particular, our approach considered a class of compounds (with generalized formula amine boranes [$B_xN_xH_y$]) known as amine-boranes that contain H_2 at gravimetric and volumetric densities comparable to that of anhydrous ammonia. The simplest known stable compound in this class is ammonia-borane, H_3BNH_3 (or borazane). Borazane is a white crystalline solid that when heated releases hydrogen in a sequence of reactions that occur at distinct temperature ranges. H_3BNH_3 contains about 20 weight % hydrogen and is stable in water and ambient air.

Physiochemical Properties and Synthesis of Ammonia-Borane Complex

Pyrolysis of ammonia-borane is a complex process, and the products of the decomposition reaction markedly depend on the conditions employed. Furthermore, the initial process is a solid-state reaction for which the onset of decomposition is a function of heating rate of the substrate (β). In thermogravimetric analyzer-Fourier transform infrared (TGA-FTIR) and thermogravimetric analyzer-differential scanning (TGA-DSC) analysis, heating a borazane sample to 90°C at a rate of 0.5°C/min and then holding it at that temperature for 200 min resulted in a loss of about 10.2% of initial

sample mass. FTIR analysis of the evolved gases has shown approximately one mol of H_2 forming per mol of BH_3NH_3 reacted. Reaction products, in addition to hydrogen, have included monomeric aminoborane (BH_2NH_2) and a small amount of volatile borazine ($B_3N_3H_6$). The monomeric aminoborane is unstable at room temperature, oligomerizing to form a non-volatile white solid residue of poly (aminoboranes) (BH_2NH_2)$_x$. The inorganic analog of polyethylene, polymeric (NH_2BH_2)$_x$, is still not fully characterized. Crystalline cyclic oligomers, (NH_2BH_2)$_n$ (where, n = 2, 3, 4, 5) have been prepared, and an amorphous (NH_2BH_2)$_x$ consisting of solvated linear chains with x= 3-5 has also been produced by gas-phase pyrolysis of ammonia-borane.

Unlike aminoborane oligomers, borazine (isoelectronic with benzene) is a volatile colorless liquid that boils at 55°C. Based on the TGA and DSC analysis, pyrolysis of ammonia-borane begins with a sharp endothermic peak that appears just above the melting point of BH_3NH_3 (112-114°C depending on the sample heating rate). Near 117°C, a steep exothermic peak occurs, reaching a maximum at about 130°C with rapid evolution of gas. A final broad exotherm appears near 150°C. Although processes other than step-wise decomposition and hydrogen loss are involved to some extent in H_3BNH_3 and its intermediate compounds, nonetheless the following sequence of events occur (BN = boron nitride, g = gas phase, [HBNH]$_x$ = polyborazine, [HBNH]$_3$ = borazine, H_2BNH_x = monomeric aminoborane, [H_2BNH_x]$_x$ = polymeric aminoborane, kJ/mol = kilo Joule per mole, s = solid phase, ΔH_r = heat of reaction, β = heating rate):

$$H_3BNH_3 \text{ (l)} \rightarrow H_2BNH_2 \text{ (s)} + H_2 \text{ (g)} \sim 137°C,$$

$$\beta = 5\text{-}10°C/min, \Delta H_r = -(21.7 \pm 1.2) \text{ kJ/mol}$$

$$x \, (H_2BNH_2) \text{ (s)} \rightarrow (H_2BNH_2)_x \text{ (s) at} \sim 125°C$$

$$(H_2BNH_2)_x \text{ (s)} \rightarrow (HBNH)_x \text{ (s)} + x \, H_2 \text{ (g) at} \sim 155°C$$

$$(HBNH)_x \text{ (s)} \rightarrow \text{borazine + other products}$$

$$(HBNH)_3 \rightarrow 3 \, BN + 3 \, H_2 \text{ at above } 500°C$$

$$(H_2BNH_2)_x \text{ (s)} \rightarrow (BN)_x \text{ (s)} + 2x \, H_2 \text{ (g) at} \sim 450°C, \beta = 10°C/min$$

Due to the large amount of evolved H_2 and the exothermicity of the process, ammonia-borane appears to be a more effective chemical carrier for H_2 than anhydrous NH_3. Other physicochemical
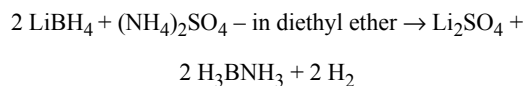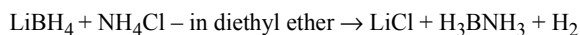
properties of ammonia-borane complex are given in Table 1 below.

Table 1. Selected Physiochemical Properties of Ammonia-Borane Complex

Property	Description
Formula	NH_3BH_3
Molecular weight	30.86
X-ray structure	C_{4V} symmetry; unit cell is tetragonal
Odor	Ammonia-like
Density, kg/L	0.74
Melting point	112-114°C, slow decomposition at approx. 70°C
Heat of formation	$\Delta H_f° = -178 \pm 6$ kJ/mol
Heat of combustion	$\Delta H_c° = -1350 \pm 3$ kJ/mol
Water stability	10% solution stored at ambient temperatures: Dormancy　　　% hydrogen loss 4 days　　　　　　1.8 11 days　　　　　　3.6 1 month　　　　　　4.8 2.5 months　　　　　9.3 18 months　　　　　45.0

Another important factor is interaction with water and other solvents. Unlike ionic hydrides, NH_3BH_3 does not react violently with water. Table 2 depicts the solubilities of borazane in water and a number of organic solvents.

Borazane can be prepared through several indirect procedures including the reaction with lithium borohydride, $LiBH_4$, in diethyl ether by either of the following two methods (LiCl = lithium chloride, Li_2SO_4 = lithium sulfate, NH_4Cl = ammonium chloride, $[NH_4]_2SO_4$ = ammonium sulfate :

$$LiBH_4 + NH_4Cl - \text{in diethyl ether} \rightarrow LiCl + H_3BNH_3 + H_2$$

$$2\ LiBH_4 + (NH_4)_2SO_4 - \text{in diethyl ether} \rightarrow Li_2SO_4 +$$

$$2\ H_3BNH_3 + 2\ H_2$$

Alternatively, H_3BNH_3 is prepared directly from the gases by reacting diborane with ammonia in polar organic solvents (e.g. ether and dioxan) and in aqueous media:
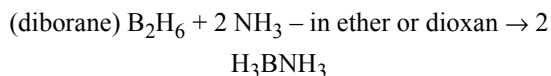
$$\text{(diborane) } B_2H_6 + 2\ NH_3 - \text{in ether or dioxan} \rightarrow 2$$

$$H_3BNH_3$$

Table 2. Solubilities of Ammonia-Borane Complex in Various Solvents

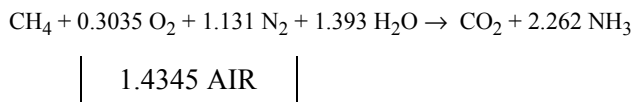| Solvent	Weight %	Temperature, °C	Density of saturated solution, kg/L
Water	26	23	0.89
Methanol	23	23	0.78
Ethyl Ether	0.80	24	0.71
Hexane	0.003	25	0.56
Benzene	0.03	25	0.87
Methylene Chloride	0.08	21	1.32

For vehicular fuel cell applications, the main drawback to the use of amine-boranes, in general, and H_3BNH_3, in particular, is the present high cost of these compounds and lack of a suitable reformer design for the on demand generation of hydrogen. No data could be found for the large-scale production costs of ammonia-borane. However, the Callery Chemical Co manufactures large quantities of dimethylamine borane (DMAB), which has significant use in the electroless plating industry. Depending on the volume, the price of DMAB is in the range of about $75-100/lb. It can be expected that the large volume price of ammonia-borane would also be in this range. The issue of the cost of ammonia-borane can be highlighted by comparing its price to the bulk material prices for other chemical hydrides under consideration as hydrogen storage compounds. The feasibility of using various ionic hydrides as potential H_2 storage compounds for AFC applications has been analyzed. This application requires a hydrogen storage system capable of supplying H_2 to an AFC producing 1 kW of electrical power for 8 h. The fuel cell is assumed to operate at 57% efficiency (at 0.7 volt), requiring 231 mol of H_2

(assuming 100% utilization). Table 3 depicts the cost of several H_2 storage media including H_3BNH_3.

Table 3. Required Mass, Volume and Cost of Chemical Hydrides for 8 hours/1 kW Duty

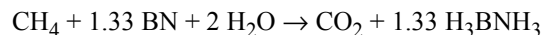| Storer	Mass, kg	Volume, Liters	Cost, US$
LiH	1.7	3.7	109
CaH_2	4.5	4.0	104
$NaBH_4$ (35 Weight % aqueous)	6.21	6.21	102
H_3BNH_3	2.38	3.21	390-525

New chemical synthesis techniques and/or processes are needed to reduce the H_3BNH_3 production costs. In addition to the cost issues, new processes must be developed to allow recycling of the by-products of ammonia-borane decomposition on-board fuel cell powered vehicles. For example, if an on-board ammonia-borane based hydrogen storage system is to be developed for maximum H_2 delivery, then it will be desirable, if not necessary, to be able to retrieve and recycle the boron nitride residue. Here, the challenge is to develop a chemical route for activating the boron-nitrogen bond in a manner analogous to dinitrogen bond activation in the Haber-Bosch process for ammonia synthesis. In a modern ammonia plant, steam reformation of natural gas is used as the primary source of hydrogen. A simple stoichiometric equation for ammonia production by steam methane reformation (SMR) is as follows:

$$CH_4 + 0.3035\ O_2 + 1.131\ N_2 + 1.393\ H_2O \rightarrow CO_2 + 2.262\ NH_3$$
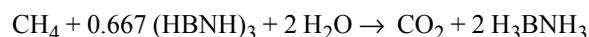
$$\underbrace{\qquad\qquad\qquad}_{1.4345\ AIR}$$

In practical processes, a high degree of irreversibility exists, and a considerable amount of energy is needed to produce ammonia from methane, air and water. The stoichiometric quantity of methane required in the equation above is about 583 m^3 per ton of NH_3 produced. Energetically, this corresponds to approximately 20.9 giga-joule (GJ) per ton of NH_3 (lower heating value). This is the minimum amount of energy needed per ton of ammonia produced using the SMR process. It is interesting to note that the best

energy figure reported for commercial ammonia production is about 27 giga Joule per metric ton (GJ/t) NH_3. This figure corresponds to a rather high efficiency of around 75% with respect to the theoretical minimum of 20.9 GJ/t NH_3, calculated as stoichiometric methane demand discussed above.

In a like manner, an idealized process for ammonia-borane synthesis from recycled BN (or borazine) may be written as:

$$CH_4 + 1.33\ BN + 2\ H_2O \rightarrow CO_2 + 1.33\ H_3BNH_3$$

Or,

$$CH_4 + 0.667\ (HBNH)_3 + 2\ H_2O \rightarrow CO_2 + 2\ H_3BNH_3$$

If similar processes could be developed at energy conversion efficiency levels that are comparable to the present day SMR-based NH_3 synthesis plants, then it would be possible to realize a major reduction in the production costs of ammonia-borane complex. We note that a concept similar to that discussed above has already been developed for nitric acid synthesis process based on boron nitride analogous to the Haber-Bosch route for nitric acid production from NH_3. Finally, recent results have shown that unusual parallel behavior exists between hydrocarbons and their corresponding B-N analogues. Thus, hydrogenation of benzene to cyclohexane may also provide a model for the reformation of borazine to other amine-boranes.

Conclusions

There are many advantages to the use of NH_3 as hydrogen source for vehicular fuel cell vehicle applications. However, a major drawback is ammonia's extreme toxicity and adverse health effects. By complexing NH_3 with diborane, a stable, non-toxic and non-cryogenic material (H_3BNH_3) can be prepared. This ammonia-borane complex is stable in water and ambient air and when heated liberates H_2 in a sequence of reactions between 137°C and 400°C that reaches about 20% of the initial mass of H_3BNH_3. Successful implementation of ammonia-borane as a potential future transportation fuel, however, requires new chemical techniques and/or processes for its synthesis that promise substantial reduction in its production costs.

FY 2002 Publications/Presentations

1. A. T-Raissi, "Ammonia and Ammonia Adducts as Hydrogen Energy Storers for Fuel Cell Applications," Proceedings of the 14th WHEC, Montreal, Canada, June 9-13 (2002).

2. C.A. Linkous, C. Huang, J. Fowler, G. Scott, A. T-Raissi, and N.Z. Muradov, "Closed Cycle Photochemical Methods for Deriving Hydrogen from Hydrogen Sulfide," Proceedings of the 14th WHEC, Montreal, Canada, June 9-13 (2002).

3. A. T-Raissi, "Technoeconomic Analysis of Area II Hydrogen Production, Part II - Hydrogen from Ammonia and Ammonia-Borane Complex for Fuel Cell Applications," Proceedings of the U.S. DOE Hydrogen Program Annual Review, Golden, CO, May 7 (2002), URL: http://erendev.nrel.gov/hydrogen/pdfs/ 32405b15.pdf.

4. A. T-Raissi, "Ammonia and Ammonia-Borane Complexes as Hydrogen Energy Storers for Fuel Cell Applications," at Session A2.8: Hydrides II, 14th WHEC, Montreal, Canada, June 10 (2002).

5. A. T-Raissi, "Technical Analysis of Hydrogen Production," Hydrogen Program Annual Review, Session B: Storage, Utilization, Analysis, Golden, CO, May 7 (2002).

Patent Applications

1. A. T-Raissi, N.Z. Muradov and E.D. Martin, "Method and Apparatus for Low Flux Photocatalytic Pollution Control," Serial No. 09/ 782,427, Feb. 12 (2001).

2. A. T-Raissi, N.Z. Muradov and E.D. Martin, "Apparatus and Method for Decoupled Thermo-Photocatalytic Pollution Control," U.S. Pat. No. 6,342,128 B1, Jan. 29 (2002).

3. A. T-Raissi, N.Z. Muradov and E.D. Martin, "Apparatus and Method for Decoupled Thermocatalytic Pollution Control," U.S. Pat. No. 6,334,936 B1, Jan. 1 (2002).

4. A. T-Raissi, N.Z. Muradov and E.D. Martin, "Method for High Flux Photocatalytic Pollution Control," U.S. Pat. No. 6,315,870 B1, Nov. 13 (2001).

5. A. T-Raissi, N.Z. Muradov and E.D. Martin, "Apparatus for Low Flux Photocatalytic Pollution Control," U.S. Pat. No. 6,309,611 B1, October 30 (2001).