V.A System Analysis

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

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Objectives

- Analyze the viability (i.e. cost, safety, and performance) of ammonia-based chemical hydrides as hydrogen (H₂) storage compounds for fuel cell applications.
- Identify the pros and cons of using ammonia (NH₃) as a chemical carrier for H₂.
- Evaluate the viability of autothermal NH₃ reformation on-board fuel cell vehicles.
- Analyze the viability (cost and performance) of using ammonia-borane complex (H₃BNH₃) 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 H₃BNH₃, 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 H₂ 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 H₃BNH₃ as a hydrogen storage media to that of sodium borohydride (NaBH₄) and ionic hydrides such as lithium hydride (LiH) and calcium hydride (CaH₂).
- 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 NH₃ gas to hydrogen.

Evaluated a number of ammonia adducts, including H₃BNH₃, 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 H₃BNH₃ as a H₂ 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 H₃BNH₃.

Introduction

The aim of this project is to assess the issues of cost, safety, performance, and environmental impact associated with the production of hydrogen (H₂) 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 (CH₄) and hydrogen sulfide (H₂S) gas with and without using solar energy; 2) ammonia (NH₃) 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 CH₄/H₂S has been submitted previously. This second report is concerned with the prospects of NH₃ 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 NH₃. Anhydrous ammonia costs about $150 per short ton (f.o.b. U.S. Gulf Coast) or less than $6.25 per million BTU of H₂ contained. Besides the large volume of production and use, and relatively low cost, NH₃ 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 NH₃ transportation, distribution, storage and use already exists.
- Simplicity - its use requires no shift converter, selective oxidizer or co-reactants.
- No purification is needed for NH₃ use with alkaline fuel cells (AFCs).
- Only 16% of the energy stored in NH₃ is needed for its conversion to N₂ and H₂.
- There are good NH₃ 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 % NH₃ vs. 18.3-59 volume % H₂).
• Using ammonia in fuel cell power plants does not generate carbon dioxide (CO₂) or nitrogen oxides (NO₂) emissions.

There are several drawbacks to ammonia as a fuel and chemical carrier for H₂, 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 H₂. 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 NH₃ 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 [BₓNₓHᵧ]) known as amine-boranes that contain H₂ at gravimetric and volumetric densities comparable to that of anhydrous ammonia. The simplest known stable compound in this class is ammonia-borane, H₃BNH₃ (or borazane). Borazane is a white crystalline solid that when heated releases hydrogen in a sequence of reactions that occur at distinct temperature ranges. H₃BNH₃ 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 H₂ forming per mol of BH₃NH₃ reacted. Reaction products, in addition to hydrogen, have included monomeric aminoborane (BH₂NH₂) and a small amount of volatile borazine (B₃N₃H₆). The monomeric aminoborane is unstable at room temperature, oligomerizing to form a non-volatile white solid residue of poly (aminoboranes) (BH₂NH₂)ₓ. The inorganic analog of polyethylene, polymeric (NH₂BH₂)ₓ, is still not fully characterized. Crystalline cyclic oligomers, (NH₂BH₂)ₓ (where, n = 2, 3, 4, 5) have been prepared, and an amorphous (NH₂BH₂)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 BH₃NH₃ (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 H₃BNH₃ and its intermediate compounds, nonetheless the following sequence of events occur (BN = boron nitride, g = gas phase, [HBNH]ₓ = polyborazine, [HBNH]₁ = borazine, H₂BNHₓ = monomeric aminoborane, [HₓBNHₓ]ₓ = polymeric aminoborane, kJ/mol = kilo Joule per mole, s = solid phase, ΔHₚ = heat of reaction, β = heating rate):

\[
\begin{align*}
H₃BNH₃ (l) & \rightarrow H₂BNH₂ (s) + H₂ (g) \quad ΔH_r = -21.7 \pm 1.2 \text{ kJ/mol} \\
& \text{at } \beta = 5-10°C/\text{min, } \Delta H_r = -21.7 \pm 1.2 \text{ kJ/mol} \\
\text{or} & \text{at } \beta = 10°C/\text{min}
\end{align*}
\]

Due to the large amount of evolved H₂ and the exothermicity of the process, ammonia-borane appears to be a more effective chemical carrier for H₂ than anhydrous NH₃. Other physicochemical
properties of ammonia-borane complex are given in Table 1 below.

**Table 1. Selected Physiochemical Properties of Ammonia-Borane Complex**

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>NH₃BH₃</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>30.86</td>
</tr>
<tr>
<td>X-ray structure</td>
<td>C₄ᵥ symmetry; unit cell is tetragonal</td>
</tr>
<tr>
<td>Odor</td>
<td>Ammonia-like</td>
</tr>
<tr>
<td>Density, kg/L</td>
<td>0.74</td>
</tr>
<tr>
<td>Melting point</td>
<td>112-114°C, slow decomposition at approx. 70°C</td>
</tr>
<tr>
<td>Heat of formation</td>
<td>ΔH_f° = -178 ± 6 kJ/mol</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>ΔH_c° = -1350 ± 3 kJ/mol</td>
</tr>
<tr>
<td>Water stability</td>
<td>10% solution stored at ambient temperatures:</td>
</tr>
<tr>
<td></td>
<td>Dormancy % hydrogen loss</td>
</tr>
<tr>
<td>4 days</td>
<td>1.8</td>
</tr>
<tr>
<td>11 days</td>
<td>3.6</td>
</tr>
<tr>
<td>1 month</td>
<td>4.8</td>
</tr>
<tr>
<td>2.5 months</td>
<td>9.3</td>
</tr>
<tr>
<td>18 months</td>
<td>45.0</td>
</tr>
</tbody>
</table>

Another important factor is interaction with water and other solvents. Unlike ionic hydrides, NH₃BH₃ 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, LiBH₄, in diethyl ether by either of the following two methods (LiCl = lithium chloride, Li₂SO₄ = lithium sulfate, NH₄Cl = ammonium chloride, [NH₄]₂SO₄ = ammonium sulfate):

LiBH₄ + NH₄Cl – in diethyl ether → LiCl + H₃BH₃ + H₂

2 LiBH₄ + (NH₄)₂SO₄ – in diethyl ether → Li₂SO₄ +
2 H₃BH₃ + 2 H₂

Alternatively, H₃BNH₃ is prepared directly from the gases by reacting diborane with ammonia in polar organic solvents (e.g. ether and dioxan) and in aqueous media:

(diborane) B₂H₆ + 2 NH₃ – in ether or dioxan → 2 H₃BNH₃

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Weight %</th>
<th>Temperature, ºC</th>
<th>Density of saturated solution, kg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>26</td>
<td>23</td>
<td>0.89</td>
</tr>
<tr>
<td>Methanol</td>
<td>23</td>
<td>23</td>
<td>0.78</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>0.80</td>
<td>24</td>
<td>0.71</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.003</td>
<td>25</td>
<td>0.56</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.03</td>
<td>25</td>
<td>0.87</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>0.08</td>
<td>21</td>
<td>1.32</td>
</tr>
</tbody>
</table>

For vehicular fuel cell applications, the main drawback to the use of amine-boranes, in general, and H₃BNH₃, 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 H₂ storage compounds for AFC applications has been analyzed. This application requires a hydrogen storage system capable of supplying H₂ 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 H₂.
(assuming 100% utilization). Table 3 depicts the cost of several H₂ storage media including H₃BNH₃.

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

<table>
<thead>
<tr>
<th>Storer</th>
<th>Mass, kg</th>
<th>Volume, Liters</th>
<th>Cost, US$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>1.7</td>
<td>3.7</td>
<td>109</td>
</tr>
<tr>
<td>CaH₂</td>
<td>4.5</td>
<td>4.0</td>
<td>104</td>
</tr>
<tr>
<td>NaBH₄ (35 Weight % aqueous)</td>
<td>6.21</td>
<td>6.21</td>
<td>102</td>
</tr>
<tr>
<td>H₃BNH₃</td>
<td>2.38</td>
<td>3.21</td>
<td>390-525</td>
</tr>
</tbody>
</table>

New chemical synthesis techniques and/or processes are needed to reduce the H₃BNH₃ 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 H₂ 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:

\[
\text{CH}_4 + 0.3035 \text{O}_2 + 1.131 \text{N}_2 + 1.393 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2.262 \text{NH}_3
\]

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 m³ per ton of NH₃ produced. Energetically, this corresponds to approximately 20.9 giga-joule (GJ) per ton of NH₃ (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) NH₃. This figure corresponds to a rather high efficiency of around 75% with respect to the theoretical minimum of 20.9 GJ/t NH₃, 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:

\[
\text{CH}_4 + 1.33 \text{BN} + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 1.33 \text{H}_3\text{BNH}_3
\]

Or,

\[
\text{CH}_4 + 0.667 (\text{HBNH})_3 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}_3\text{BNH}_3
\]

If similar processes could be developed at energy conversion efficiency levels that are comparable to the present day SMR-based NH₃ 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 NH₃. 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 NH₃ as hydrogen source for vehicular fuel cell vehicle applications. However, a major drawback is ammonia's extreme toxicity and adverse health effects. By complexing NH₃ with diborane, a stable, non-toxic and non-cryogenic material (H₃BNH₃) can be prepared. This ammonia-borane complex is stable in water and ambient air and when heated liberates H₂ in a sequence of reactions between 137°C and 400°C that reaches about 20% of the initial mass of H₃BNH₃. 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**


**Patent Applications**


