SYNTHESIS OF SODIUM BOROHYDRIDE FOR ENERGY APPLICATIONS

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Introduction

Sodium borohydride (NaBH₄) has been demonstrated as an effective hydrogen storage material. Its hydrolysis generates high purity humidified hydrogen suitable for use in PEM fuel cells. Although the technology can be scaled and tailored for many different applications from very small portable power to fuel cell vehicles, the current high cost of NaBH₄ is limiting early adoption of the technology to premium power applications. The utilization of NaBH₄ in high demand, continuous power generation and fuel cell vehicles will not be economically feasible until the production cost of NaBH₄ can be significantly reduced.

Discussion

Sodium borohydride is a structurally simple, yet complex chemical. It does not occur in nature; therefore it has to be synthesized from sodium and boron containing raw materials. The production of NaBH₄ requires the combination of three elements, Na, B, H, and a large amount of energy input. Intrinsically, the level of complexity is derived from significant enthalpic and entropic barriers associated with the strength of the boron-oxygen bond. Low cost NaBH₄ will depend on the availability of a production process that combines the necessary raw materials (borates, hydrogen, and sodium) in a pathway of optimum overall energy efficiency.

The current state-of-the-art NaBH₄ production process is based on the reduction of the trialkylborate, B(OR)₃, with NaH, known as the Schlesinger Process [1]. The following chemical equations describe the synthetic pathway to NaBH₄:

\[
\text{Na}_2\text{B}_2\text{O}_3 + \text{H}_2\text{SO}_4 + 5 \text{H}_2\text{O} \rightarrow 4 \text{H}_2\text{BO}_3 + \text{Na}_2\text{SO}_4 \quad (1.1)
\]

\[
\text{H}_2\text{BO}_3 + 3 \text{CH}_3\text{OH} \rightarrow \text{B(CH}_3)_3 + 13 \text{H}_2\text{O} \quad (1.2)
\]

\[
\text{NaCl} \rightarrow \text{Na} + \frac{1}{2} \text{Cl}_2, \text{by electrolysis.} \quad (1.3)
\]

\[
4 \text{Na} + 2 \text{H}_2 \rightarrow 4 \text{NaH} \quad (1.4)
\]

\[
\text{B(CH}_3)_3 + 4 \text{NaH} \rightarrow \text{NaBH}_4 + 3 \text{NaOCH}_3 \quad (1.5)
\]

\[
3 \text{NaOCH}_3 + 3 \text{H}_2\text{O} \rightarrow 3 \text{CH}_3\text{OH} + 3 \text{NaOH} \quad (1.6)
\]

**Overall Reaction:**

\[
\text{Na}_2\text{B}_2\text{O}_3 + 16 \text{Na} + 8 \text{H}_2 + \text{H}_2\text{SO}_4 + 5 \text{H}_2\text{O} \rightarrow 4 \text{NaBH}_4 + 12\text{NaOH} + \text{Na}_2\text{SO}_4 \quad (1.7)
\]

The various steps of the Schlesinger Process are fragmented among various chemical producers, lacking integration and producing undesirable by-products. Although the process provides high purity NaBH₄, the individual reaction steps are not optimized for energy efficiency. An examination of the primary energy input for the process versus the eventual chemical energy stored in NaBH₄ will be provided to identify areas for energy efficiency improvements. For example, the process uses large amounts of Na metal. This subjects the overall energy efficiency to the limitations in energy efficiency of the Na process. The current NaCl electrolysis process for Na metal is less than 50% energy efficient. Additionally, reactions (1.4) and (1.5) are both exothermic, losing a significant portion of the original energy input to reaction heat. Compounded together, the overall reaction of (1.7) is less than 20% energy efficient. Clearly, for NaBH₄ to become an effective energy carrier, the energy efficiency of its production process has to be significantly improved.

In light of the multi-step nature of the synthetic process, it is important to improve the energy efficiency of each step. The single most costly raw material is Na metal. It follows that major improvements in Na production will have a significant impact on the NaBH₄ production efficiency. Alternatively, an intermediate other than NaH may be considered to avoid the large enthalpic loses associated with reactions 1.4 and 1.5.

In the first approach, we propose an electrochemical reaction utilizing an anodic reducing agent to lower the operating voltage of the electrochemical cell, thereby achieving overall energy savings in the production of Na. In the second approach, we propose an alternative synthetic pathway that proceeds through diborane (B₂H₆), an energy-rich hydride intermediate that is closer in energy to NaBH₄. The interconversion of B₂H₆ and NaBH₄ can be manipulated by the appropriate selection of reagent. For example, the reaction of NaBH₄ with certain oxidizing agents generates B₂H₆[2], and B₂H₆ can be converted to NaBH₄ with a variety of Na containing salts [3]. In this approach, the overall process will include the following proposed reaction steps:

\[
4 \text{NaBO}_2 + 2\text{CO}_2 + 12\text{ROH} \rightarrow 2 \text{Na}_2\text{CO}_3 + 4 \text{B(OR)}_3 + 6\text{H}_2\text{O} \quad (2.1)
\]

\[
4 \text{B(OR)}_3 + 12 \text{H}_2 \rightarrow 2 \text{B}_2\text{H}_6 + 12\text{ROH} \quad (2.2)
\]

\[
2\text{B}_2\text{H}_6 + 2\text{Na}_2\text{CO}_3 \rightarrow 3\text{NaBH}_4 + \text{NaBO}_2 + 2\text{CO}_2 \quad (2.3)
\]

**Overall Reaction:**

\[
\text{NaBO}_2 + 4 \text{H}_2 \rightarrow \text{NaBH}_4 + 2\text{H}_2\text{O} \quad (2.4)
\]

Experimental

In the first step, Reaction 2.1, relatively inexpensive sodium borates was used as the starting material. Building upon existing knowledge of alkylborate synthesis, we have developed an improved reaction for the preparation of B(OR)_3, including trimethyl and tributyl borates, from the discharged product of the Hydrogen on Demand™ system. Other precursors investigated include borax and anhydrous sodium metaborate, and could be extended to any inexpensive borate salts. The reactions were carried out under reflux conditions in alcohol under a CO₂ atmosphere. The use of CO₂ produces Na₂CO₃ as a byproduct, which is used in Reaction 2.3 to form NaBH₄ from B₂H₆.

We also report here some preliminary results on Reaction 2.3, which was developed based on the knowledge that Na-containing Lewis bases can react with B₂H₆ to form NaBH₄. Initial experiments were modeled after those described by Davis and Gottbrath [4], who conducted the reaction of B₂H₆ with aqueous NaOH. In our experiments, Na₂CO₃ was used instead of NaOH. Yields ranged from 6% to 25%, with higher concentration Na₂CO₃ and greater ratio of Na₂CO₃ to B₂H₆ giving rise to higher yields. Product characterization carried out by infrared spectroscopy (IR), proton and boron nuclear magnetic resonance (¹H NMR and ¹¹B NMR), and by powder X-ray diffraction (XRD) confirmed that NaBH₄ was indeed synthesized.

The technique of ball-milling was then employed to study the direct interaction of the gaseous diborane and the solid Lewis bases. At the same time, the competing borane decomposition pathway with water was removed by avoiding the aqueous medium. Using this method, higher yields of NaBH₄ were achieved, from 15% to 65%. The yield was further increased by increasing B₂H₆ pressure within.

the reaction vessel. Additionally, diglyme was added to the ball mill to facilitate the dissolution of product NaBH₄, thereby exposing more Na₂CO₃ surfaces for further reaction. Pressures up to 40 psig were employed, and yields up to 72.8% were obtained at these increased pressures along with the utilization of diglyme.

Reaction 2.2 involves the hydrogenolysis of trialky borate, B(OR)₃, to give the intermediate HB(OR)₂, which subsequently disproportionate to generate B₂H₆. The details of this reaction is beyond the scope of this paper, and will be address in future publications.

Conclusions

We have successfully demonstrated the feasibility of converting diborane to borohydride, which represents an important step towards developing a new NaBH₄ synthesis process. Various reducing agents are being studied for the conversion of B-O bonds to B-H bonds.

Reference