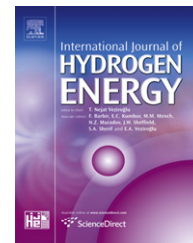


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Vapor phase batch hydrolysis of NaBH₄ at elevated temperature and pressure

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ABSTRACT

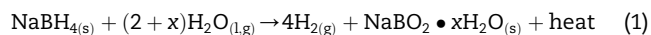
Complex chemical hydrides are a means to store hydrogen in the solid state near ambient temperatures and pressures. Hydrolysis of hydrides has the potential to provide high gravimetric and volumetric energy densities if water consumption can be minimized. At low temperatures (110–140 °C), the product of NaBH₄ hydrolysis is NaBO₂·2H₂O (dihydrate), consuming 2 mol of unutilized water. The objective of this work was to conduct water vapor hydrolysis of NaBH₄ at elevated pressure and temperature above 150 °C. It was hypothesized that this would yield a solid borate with decreased water bound in the crystal structure. A series of batch reactions were conducted to verify the hypothesis. Experimental characterization of the sodium metaborate byproducts indicated that the primary product of water vapor hydrolysis was NaBO₂·1/3H₂O (hemihydrate) under a variety of reaction conditions. For the most cases, the conversion of NaBH₄ approached 100%.

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1. Introduction

Hydrolysis of complex hydrides (NaBH₄, LiBH₄, LiAlH₄ etc.) has been investigated for hydrogen storage applications [1–9]. Borohydrides are attractive because, on a materials only basis, they can theoretically generate over 10 wt % hydrogen. NaBH₄ is of interest by virtue of its 10.8 wt % theoretical hydrogen capacity [10]. It is also stable under ordinary, dry storage conditions and does not undergo violent reactions with water [11].

NaBH₄ reacts with water vapor to generate hydrogen and sodium metaborate according to the reaction shown in Eq. (1):



Ideally, the hydrolysis reaction would proceed to completion with $x = 0$, meaning only 2 mol of water would be required to release 4 mol of hydrogen. In practice, there are two primary factors leading to excess water utilization when

NaBH₄ hydrolysis is conducted in the liquid phase. The first is linked to NaBO₂ solubility in water. Hydrolysis is typically conducted in the aqueous phase at room temperature, and if it is desired to keep reactants and products in solution then substantial excess water is required because of the low solubility of the chemical hydride (55 g NaBH₄/100 g H₂O at 25 °C) [12]. The metaborate byproducts are even less soluble in water (28 g NaBO₂/100 g H₂O at 25 °C) [3] and the NaBH₄ concentration at 25 °C should be below 16 g NaBH₄/100 g H₂O to maintain dissolved NaBO₂ [12].

The second factor is that the solid byproduct (NaBO₂·xH₂O) exists in varying degrees of hydration with a generic stoichiometry x , where $x = 1/3, 2$, and 4 are well known. The hydrates differ in stability, and the hydrated form that persists after hydrolysis is a function of the reaction conditions and the pathway of the reaction. Thus at typical reaction conditions (temperatures below 120 °C and with excess water provided for solution) the product is a hydrate, typically $x = 2$ or 4, that

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binds excess water in the crystal structure. Table 1 [13] shows how the theoretical gravimetric efficiency decreases with increasing x for several complex chemical hydrides (based on materials only). For $x = 0$ and assuming 100% conversion of the hydride, NaBH_4 has a gravimetric H_2 capacity of 10.83 wt %. As x increases, the mass efficiency decreases rapidly. Thus, it is desired to identify a reaction pathway and conditions that decrease x , the amount of structural water bound to the metaborate product. There are two primary reaction pathways for device designers to minimize both the mass and volume of a hydrogen storage system and improve the hydrogen gravimetric storage on a material basis.

The best known hydrolysis pathway is contacting solid NaBH_4 with liquid water and a catalyst to produce hydrogen. Catalysts are useful in controlling the rate of reaction, but do not affect the hydration state. For example, Kojima et al. [14] reported an effective gravimetric hydrogen storage capacity of 9.0 wt % based on materials only. However, this work utilized a Pt–LiCoO₂ catalyst and the reported pressures were up to 25 MPa. Clearly, the mass of such a pressure vessel would decrease the system volumetric efficiency. Recently, Liu et al. [15] obtained a final hydrogen capacity of 6.7 wt % based on materials only with over 90% conversion of NaBH_4 , when the reactants were contacted with a 4:1 M ratio of $\text{H}_2\text{O} : \text{NaBH}_4$ using CoCl_2 as catalyst. Hua et al. [4] utilized the aqueous solution pathway with a nickel boride catalyst (Ni_xB) and obtained the same hydrogen capacity of 6.7 wt % at 45 °C. Both Liu et al. [15] and Hua et al. [4] were inherently limited by feeding two extra moles of water. Later, Liu et al. [16] provided uniform dispersion of resin-supported Ru^{3+} catalysts among pulverized NaBH_4 (SBH) for hydrogen generation with controlled addition of water into NaBH_4/Ru composites. Consequently, complete conversion and a gravimetric H_2 storage capacity of 7.3 wt % were achieved for a molar ratio of $\text{SBH}/\text{H}_2\text{O} = 1/4$. Nevertheless, from the viewpoint of the products of reaction, the SBH/ H_2O system is not favored and its products are found to most likely $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ (tetrahydrate). As Table 1 [13] suggests, the hydrolysis products strongly influence the gravimetric hydrogen storage capacity. The theoretical gravimetric efficiency of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ would be as low as 5.48 wt % H_2 . Previous work with catalysts still does not approach the theoretical gravimetric efficiency of 10.83 wt %.

A somewhat newer reaction pathway is the ‘solid phase’ or ‘steam hydrolysis’ of NaBH_4 , which does not require the dissolution of reactants or products and thus may be a good way to minimize the water utilization. Aiello et al. [9] and Kong et al. [17] demonstrated that solid NaBH_4 can react with water

vapor to generate H_2 . Most recently, Marrero et al. [6] conducted pure steam hydrolysis of NaBH_4 producing up to 95% yield of hydrogen, with 1 mol % of a gas phase promoter (acetic acid) added at 110 °C. Marrero et al. [7] identified the solid byproduct at these conditions as $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ by thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Also, she observed that $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ dehydrated to the anhydrous form as the temperature was increased above 300 °C during TGA analysis. Similarly, Demirci et al. [18] pointed out that $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ is the favored product of hydrolysis at these temperatures. Thus, steam hydrolysis at these conditions does not provide a distinct advantage over liquid phase hydrolysis in terms of the hydration state of the borate product. It is therefore important to consider the individual steps in the steam hydrolysis pathway to search for means to improved performance.

The likely steps in the water vapor hydrolysis pathway are described by Beaird et al. [19]. The essential first step is that NaBH_4 absorbs water vapor at temperatures near the boiling of water. Subsequently, NaBH_4 deliquesces to produce a liquid phase, then hydrogen is released via an aqueous phase mechanism. In order for the reaction to occur, the vapor phase humidity must be above the deliquescence relative humidity at a given temperature and pressure. The solid product is a mixture of any unreacted NaBH_4 and hydrated sodium metaborates. Also, Beaird et al. [19] quantified how the reaction depends on the reaction temperature and relative humidity, but all the experiments reported were at about 1 bar pressure, and to maintain the requisite deliquescence phenomenon the reactor temperatures were at or below about 150 °C.

Based on the known stable temperature ranges of the various hydrates, we hypothesize that at high temperatures the stable hydrate product will have a hydration factor x of less than 2. However, it is necessary to maintain the deliquescence relative humidity (DRH) and high conversion, which requires operating at pressures above 1 bar. So, in this work we utilize pressurized batch apparatus, similar to the one used by Marrero et al. [6,7] to conduct the water vapor hydrolysis for obtaining the sodium metaborate products with a lower hydration factor ($x < 2$). Other experimental parameters including feed molar ratio ($\text{H}_2\text{O} : \text{NaBH}_4$) and temperature were explored.

2. Experimental

2.1. Apparatus

The water vapor hydrolysis of NaBH_4 was performed in a batch reactor in order to produce solid byproducts for subsequent characterization. The reactions were conducted at 150 °C, 180 °C and 200 °C. The experimental apparatus is shown in Fig. 1. The reactor was flushed and pressurized to 30 psi with N_2 before each trial. To charge the reactor, 0.25 g NaBH_4 powder (0.066 mol) with a purity of 99% was measured into a Teflon beaker. The beaker was then placed inside pressure vessel. Liquid water, ranging from 3 to 7 g (0.17–0.39 mol), was put in the reactor but outside the beaker. NaBH_4 powder thus did not contact or directly react with liquid water. Rather, upon heating the liquid water

Table 1 – Theoretical Hydrogen storage capacity (H_2 wt %) for hydrolysis of hydrides based on materials only.

| Hydration state of oxide products | NaBH | Materials-only H_2 wt % | | |
|-----------------------------------|-------|----------------------------------|-----------------|------------------|
| | | LiAlH_4 | LiBH_4 | NaAlH_4 |
| $x = 0$ | 10.83 | 10.81 | 13.83 | 8.88 |
| $x = 1/3$ | 10.01 | 10.0 | 12.53 | 8.33 |
| $x = 2$ | 7.28 | 7.27 | 8.52 | 6.34 |
| $x = 4$ | 5.48 | 5.47 | 6.16 | 4.93 |

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