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A reactor model for hydrogen generation from sodium borohydride and water vapor

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ABSTRACT

This paper reports new data on the production of hydrogen from water vapor plus NaBH_4 , or $\text{NaBH}_4 + 10\% \text{CoCl}_2$. Data were collected with the aid of an isothermal semi-batch reactor with in-situ H_2 rate measurement. The reaction of NaBH_4 to generate H_2 proceeds via three steps: deliquescence, dissolution and reaction. The deliquescence regime of NaBH_4 in the presence of 10 weight percent CoCl_2 is defined. The H_2 yield is quantified at various reaction conditions (reaction temperature 70–120 °C, relative humidity 31–69%). CoCl_2 significantly accelerates the rate of H_2 production compared to deliquescence + reaction of pure NaBH_4 . It is also found that a combination of high temperature and high relative humidity contributes to high H_2 rate and yield, and either of the two factors dominates the reaction at different conditions. A two-part reactor model accounting for the mechanism of the steam hydrolysis by NaBH_4 is developed. The model captures the dissolution + reaction step as well as reaction-only step and was validated by experimental data.

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1. Introduction

Practical means of hydrogen production and storage are essential to enable the goal of using hydrogen as an energy carrier to address the public concern of the depletion of fossil fuel and environmental pollution [1–3]. The specific means of hydrogen storage will depend on the application, and so a variety of approaches are being considered for both niche and large-scale applications. Many investigations are aimed at discovering and evaluating the most effective hydrogen storage materials. Use of compressed gaseous or liquefied H_2 [4], carbon nanotubes [5], metal organic frameworks [6] and chemical methods [7] have been actively studied. For portable applications, the first three methods have disadvantages such as low volumetric and gravimetric density, high energy

consumption, and rigorous operating conditions [4–6]. However, chemical storage with complex hydrides, for example, NaBH_4 , LiBH_4 , and $\text{Mg}(\text{BH}_4)_2$ etc., have been found to be promising candidates for portable applications because of their high gravimetric hydrogen storage capacity (over 10 wt.%) and near ambient operating conditions [8,9]. Among them, NaBH_4 is one of the most promising because of its stability, low cost, non-flammability, non-toxicity, and high theoretical storage density [10]. The Department of Energy keeps the recommendation for NaBH_4 as one of the best candidates for application in portable devices, though it has been down selected for on-board use [11].

Most work on hydrolysis of NaBH_4 [12–16] has been done in aqueous solutions, and most recent work has focused on supported metal or metal salt catalysts. Meanwhile, there has been only limited study on another reaction pathway, so-

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called “steam hydrolysis”, i.e. reacting NaBH_4 with water vapor. One advantage of this reaction pathway is that high H_2 production rates and yield can be achieved by controlling temperature and humidity [17]. Another advantage is that one can potentially reduce the excess water that present in aqueous reaction by using water vapor, which has the potential to improve the storage density for the whole system. Previously, Aiello [17] and Beaird [21] have focused on experimental screening and Marrero [18–20] focused on physical characterization of the borate products. Aiello found that a H_2 yields up to 90% can be achieved even without catalyst at 110°C [17]. Marrero found that reactant physical form, such as a thin film, can improve the H_2 production rate [19] and different metaborate products are obtained at different reaction temperatures [18]. Beaird [21] determined the deliquescence regime under which reaction temperature and relative humidity were favored for pure NaBH_4 hydrolysis.

Despite the previous efforts on the steam hydrolysis, no detailed quantitative reports have been published on the kinetics of the steam hydrolysis reaction. Because knowledge of the H_2 release rate and yield is essential for application in a fuel cell system, we have investigated the apparent H_2 generation kinetics in the vapor deliquescence pathway, using both pure NaBH_4 and NaBH_4 mixed with a metal salt catalyst, anhydrous cobalt(II) chloride. Herein we report a greatly improved hydrogen production rate and yield when CoCl_2 is added in the steam reaction. The deliquescence behavior of the mixture and its effect on the H_2 rate are discussed. Quantification of the effect of temperature and relative humidity on the H_2 yield is reported. Finally, we propose a reaction rate model incorporating deliquescence, dissolution and reaction as observed in the steam hydrolysis pathway.

2. Experimental method

An isothermal semi-batch reactor combined with a visualization device was used for the study of sodium borohydride reacting with water vapor. Fig. 1 shows the schematic of the reactor assembly, originally designed by Beaird [21], modified

for this study. The reactor is a 1 inch diameter quartz tube, which was filled with 0.2 ± 0.03 g of anhydrous NaBH_4 powder (98%, Alfa Aesar) for each run. In experiments with mixtures, 10 wt.% anhydrous CoCl_2 powder was added. These two powders were mixed together in a mortar prior to loading in the reactor. To prevent loss of the powder and unwanted interactions with moisture in air, glass wool was placed in both ends of the tube. All solid mixing and loading was performed in a controlled atmosphere glove box. A Hawkeye classic precision borescope with video camera was positioned above the reactor through an opening in the top oven wall. A fiber optic illuminator (Fiber-Lite Model 3100 by Dolan Jenner Industries Inc.) was introduced through a 1 cm diameter opening on the right side of the oven wall. The use of the illuminator coupled with video camera ensured an enhanced continuous in-situ visualization of the reaction.

To prevent pre-absorption of water during startup, the reaction system was purged with ultrahigh purity nitrogen (National Welders) while the oven was heated to the reaction temperature. The desired mole fraction of water was achieved by flowing the nitrogen carrier gas at 0.1 SLPM (standard liter per minute) through a heated 500 mL saturator (refer to Fig. 1) containing deionized water ($17 \text{ M}\Omega \text{ cm}$ resistivity) from a Barnstead system. The nitrogen flow rate was controlled with a Teledyne mass flow meter. The saturated nitrogen was directed through a pre-heating coil inside the oven to equilibrate to the reaction temperature. The relative humidity of the humid nitrogen stream entering the reactor was determined from the mole fraction of water exiting the saturator and the pressure (1 atm) and temperature of reactor. Blank tests were performed to demonstrate water balance closure within 5%.

The hydrolysis experiments were carried out over a range of temperatures between 40 and 120°C . We allowed 5–15 min per experiment to observe the onset of deliquescence and H_2 evolution. If no water uptake was observed during this interval, the reaction temperature was decreased, i.e. the relative humidity in the reactor was increased, and the system was again allowed to equilibrate. This process was continued until water sorption on the $\text{NaBH}_4 + \text{CoCl}_2$ mixture was visually observed. Hydrogen evolution began shortly after

Fig. 1 – Isothermal semi-batch reactor with in-situ H_2 rate measurement.

observation of water sorption. Humid gas ($\text{N}_2 + \text{H}_2\text{O} + \text{H}_2$) from the reactor passed through a condenser, then a desiccant tube. The hydrogen generation rate was quantified by measuring the total mass flow rate after the desiccant, and subtracting the inlet N_2 flow rate. The inlet and outlet flow meters were controlled by Labview.

3. Hydrogen production from steam hydrolysis

Fig. 2 shows the effect of adding CoCl_2 to NaBH_4 for the steam hydrolysis for H_2 . It is known that CoCl_2 is a catalyst for aqueous hydrolysis of NaBH_4 [16]. In the present work, water first deliquesces on the surface of the solid mixture, followed by dissolution. Therefore, CoCl_2 is still a liquid phase catalyst. It is seen in Fig. 2 that the hydrolysis for 0.20 g NaBH_4 without CoCl_2 takes 110 min to reach 0.4 L of H_2 , near 80% the yield. By contrast, it takes only 45 min to reach 100% yield in the presence of 10% by weight CoCl_2 . Therefore, CoCl_2 significantly increases the H_2 production yield and rate in steam hydrolysis.

To further elucidate the pathway of steam hydrolysis, the deliquescence relative humidity for water vapor on pure NaBH_4 , and on a mixture of NaBH_4 with 10% CoCl_2 was measured. Table 1 shows the deliquescence relative humidity (DRH). The right column represents the DRH for pure NaBH_4 taken from Beard's work [21] and the left column represents DRH for the mixture measured in this work. It is seen that over the range of $y_{\text{H}_2\text{O}}$ (water mole fraction), the deliquescence temperature decreases for the mixture compared to that for pure NaBH_4 . That is to say, adding CoCl_2 increases the DRH (the humidity required for the onset of deliquescence).

The increase in deliquescence relative humidity for the solid electrolyte mixture merits some explanation. The theory of so-called “deliquescence lowering” in binary electrolytes has been presented in detail by Wexler and Seinfeld [24]. This

Fig. 2 – H_2 production from pure NaBH_4 and $\text{NaBH}_4 + 10 \text{ wt.\% CoCl}_2$ ($T_{\text{reaction}} = 90^\circ\text{C}$, Relative humidity = 69%).

Table 1 – Deliquescence relative humidity at ambient pressure for NaBH_4 and $\text{NaBH}_4 + 10\% \text{ CoCl}_2$.

$\text{CoCl}_2 + \text{NaBH}_4$			Pure NaBH_4		
Temperature ($^\circ\text{C}$)	$y_{\text{H}_2\text{O}}$	RH %	Temperature ($^\circ\text{C}$)	$y_{\text{H}_2\text{O}}$	RH %
40	0.04	54.9	50	0.03	20.5
60	0.09	45.8	70	0.06	30.5
70	0.13	40.6	90	0.12	17.3
85	0.19	33.3	105	0.30	25.2
100	0.35	35.0	110	0.42	29.7
100	0.44	44.0	120	0.50	25.5
110	0.55	38.9	135	0.66	21.4
120	0.74	37.8	155	0.80	14.9

theory establishes that a binary mixture of deliquescing electrolytes will exhibit a minimum in the DRH at a certain composition, the “eutonic” composition (see Fig. 3). According to the theory, the DRH is a non-linear function of the composition of the two electrolytes, and the minimum DRH for the mixture must fall beneath the lowest DRH of the pure components [24]. However, in region 2 of Fig. 3, the mixture DRH may be between that of the single electrolytes. Indeed, the theory illustrated in Fig. 3 (which is modeled after the figure shown by Carroll et al. [25]) shows that the mixture DRH may lie above a straight line connecting the pure component DRH. In Fig. 3, curves 1 and 2 illustrate the deliquescence relative humidity of an electrolyte mixture on either side of the eutonic point. Pure CoCl_2 has a deliquescence relative humidity of 80% at 25°C [22] and pure NaBH_4 has a DRH of 26% [3]. We speculate that the eutonic composition for $\text{CoCl}_2 + \text{NaBH}_4$ is greater than 90% NaBH_4 , thus the 10% CoCl_2 mixture investigated in this work lies on curve 1, as suggested in Fig. 3. Additional measurements over the entire composition range would be warranted.

In all our experiments, we observed a lag time between the introduction of water vapor and the onset of hydrogen

Fig. 3 – Generic illustration of deliquescence lowering and the eutonic composition in a binary mixture of electrolytes. Taken after Carroll et al. [25].

production (see Fig. 4 as an example, where the lag time is about 5 min). When CoCl_2 is added as a catalyst, the lag time is consistently less. Because a higher relative humidity means higher water activity at a given reaction temperature and total pressure, this speeds up dissolution of the solid, which in turn decreases the lag time. In addition, because CoCl_2 is a catalyst [16], the combined effect of increased relative humidity and catalytic feature of CoCl_2 increases the observed rate of hydrogen release compared to hydrolysis of pure NaBH_4 .

Fig. 4 shows a typical curve for hydrogen production from $\text{NaBH}_4 + \text{CoCl}_2$ mixture. This particular data was obtained at 90 °C reactor temperature and 80 °C saturator temperature. The pathway of steam hydrolysis initiates with deliquescence, followed by dissolution and reaction steps [21]. In Fig. 4, the initial 5 min corresponds to the deliquescence process. After deliquescence completes, dissolution occurs and the H_2 is released. The hydrogen flow rate maximizes after nearly 10 min, reaching 0.026 L min^{-1} . After the maximum the rate decreases, indicating that NaBH_4 is completely dissolved and it is completely consumed after nearly 45 min of the reaction. Integrating the area under the curve gives the total hydrogen volume generated. For this run, 100% of the theoretical H_2 was achieved.

Fig. 5 shows the normalized H_2 yield as a function of various combinations of reactor temperature and saturator temperature. It is generally seen that the H_2 yield increases with saturator temperature (that is, with water mole fraction). However, the relative humidity is also a function of the reactor temperature (the temperature at which deliquescence takes place).

Comparing curves 1 and 2 in Fig. 5, where curve 1 is catalyzed by CoCl_2 and curve 2 is for pure NaBH_4 . It is seen that at the beginning of the reaction, curve 2 gives a higher yield than curve 1. This is because curve 2 has a high relative humidity (69%) which ensures a faster initiation of the reaction. However, as the reaction continues, curve 1 catches up with curve 2 and its yield and rate surpasses that of curve 2. Finally, the curve 1 achieve 100% yield earlier than curve 2. This is because

Fig. 4 – H_2 production rate for 0.2 g NaBH_4 with 10 wt% CoCl_2 .

Fig. 5 – H_2 yield at various reaction temperatures and relative humidities.

curve 1 is catalyzed by CoCl_2 and catalytic effect outplays the non-catalyzed reaction represented by curve 2.

Comparing curves 3 and 4, it is seen that curve 3 has a higher yield and rate initially than curve 4. That is because of a higher relative humidity for the reaction represented by curve 3. So a faster initiation of the deliquescence is seen which gives a higher apparent rate of hydrogen generation. As the reaction continues, the curve 4 catches up when the temperature plays a more important role. At the final stage, the curve 4 exceeds the curve 3 and achieves 100% yield earlier.

Notice that curve 5 gives faster H_2 generation rate than curve 3, while the reaction temperature is lower for curve 5 (90 °C) than curve 3 (100 °C). This is because the relative humidity of curve 5 is high (RH = 69%), almost twice the relative humidity of curve 3 (RH = 31%). This indicates that relative humidity is more important than temperature. In addition, by comparing curves 2 and 5, we find that by adding CoCl_2 the H_2 rate and yield are increased significantly.

Curve 6 (RH = 37%) gives higher rate and yield than curve 5 (RH = 69%), and curve 6 achieves complete yield earlier than curve 5. This indicates that high temperature can be more important than relative humidity for yield and rate in specific reaction condition range.

The above results all show how important it is to consider both reaction temperature and relative humidity (i.e. the water activity) as well as catalyst composition when designing a practical hydrogen generation reactor based on hydrolysis. The combined effect of high reaction temperature and high relative humidity ensures a faster H_2 rate and high yield.

4. Reactor model for NaBH_4 steam hydrolysis

The hydrolysis proceeds first by deliquescence and dissolution of the solids, followed by hydrolysis in the liquid phase [21]. Hydrogen release commences shortly upon deliquescence, but deliquescence continues until the water activity balances in gas and liquid phase and dissolution continues

Table 2 – Parameters and variables used in the dissolution + reaction model.

Estimated parameters	Value	Unit
k	2.7×10^{-2}	$\text{M}^{-1} \text{s}^{-1}$
k_{m1}	8.0×10^{-3}	s^{-1}
k_{m2}	6.0×10^{-5}	M s^{-1}

until all the solid is dissolved. Based on these physical processes, we propose a two-part model, where the first part deals with dissolution and reaction in parallel, and the second part deals with reaction-only step after the solids are fully dissolved. The model is validated by the experimental data on hydrogen production rate.

4.1. Two-part dissolution-reaction model

In order to simplify the processes, we made the following assumptions. We assume that NaBH_4 reacts with water only after the amount of condensed water is enough to initiate the dissolution in the deliquescence, i.e. no dissolution and reaction take place at $t = 0$; dissolution and reaction occur immediately at $t > 0$; NaBH_4 concentration is uniform in the liquid phase, i.e. no diffusion in the bulk solution. Considering the mass transfer and reaction, during the dissolution + reaction step, the mass balances of NaBH_4 and water and initial conditions are:

$$\frac{dC_{\text{NaBH}_4}}{dt} = k_{m1}(C_s - C_{\text{NaBH}_4}) - kC_{\text{NaBH}_4}C_{\text{H}_2\text{O}} \quad (1)$$

$$\frac{dC_{\text{H}_2\text{O}}}{dt} = k_{m2}(a_v - a_{\text{H}_2\text{O}}) - 4kC_{\text{NaBH}_4}C_{\text{H}_2\text{O}} \quad (2)$$

Initial condition: $t = 0$, $C_{\text{NaBH}_4} = 0$; $C_{\text{H}_2\text{O}} = 55.5 (\text{mol L}^{-1})$;

In Eqs. (1) and (2), the rate of change of NaBH_4 and water are affected by the rate of NaBH_4 and water transfer from solid and vapor phase, respectively, to solution as well as hydrolysis reaction rate. Because water has significant influence in the kinetics of steam hydrolysis, as will be proved later in the modeling result, we incorporated the water concentration in the reaction term. C_{NaBH_4} represents NaBH_4 concentration in solution and $C_{\text{H}_2\text{O}}$ represents water concentration in solution. C_s is solid NaBH_4 concentration (28.3 M) in solid phase and a_v is water vapor activity in gas phase. The $a_{\text{H}_2\text{O}}$ is water activity in liquid solution. Here, we use the experiment at 90 °C to model the H_2 evolution reaction. Table 2 lists parameters for the ordinary differential equations. According to the definition of activity, a pure species is used as reference. The water activity a_v is calculated as water partial pressure in gas phase divided by pure water saturated pressure at the same temperature; According to N_2 + steam gas mixture data from OLI database [2], water mole fraction is about 0.68 at 90 °C. The total gas pressure is 1 atm for our experiment. Hence, 0.69 atm is used for the partial pressure of steam. The saturated steam pressure in air at 90 °C is 0.69 atm. Because steam in air and steam in N_2 could be approximately considered to be same, we calculated that the water activity is nearly 1. Meanwhile, water concentration is converted to water activity $a_{\text{H}_2\text{O}}$ in terms of its concentration in solution divided by pure liquid water concentration of 55.5 mol L⁻¹.

Fig. 6 – NaBH_4 aqueous concentration profile for the dissolution + reaction step.

The rate constant is k , and mass transfer coefficient for solid to liquid phase is k_{m1} and for gas to liquid phase is k_{m2} . The estimated values for each variable are given in the table. The estimated rate constant k is $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. A typical value of k of hydrolysis in un-buffered or buffered water solution is 10^{-9} – $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C [23]. The estimated rate constant k is larger because the reaction is conducted at higher temperature and the rate constant also includes the catalytic effect of CoCl_2 . The mass transfer coefficients k_{m1} and k_{m2} are both estimated by fitting the model with experimental data. It is found that coefficients k_{m1} is $8.0 \times 10^{-3} \text{ s}^{-1}$ and k_{m2} is $6.0 \times 10^{-5} \text{ M s}^{-1}$.

When the solid NaBH_4 is dissolved, the process enters the reaction-only step. The governing equations become (3) and (4):

$$\frac{dC_{\text{NaBH}_4}}{dt} = -kC_{\text{NaBH}_4}C_{\text{H}_2\text{O}} \quad (3)$$

$$\frac{dC_{\text{H}_2\text{O}}}{dt} = k_{m2}(a_v - a_{\text{H}_2\text{O}}) - 4kC_{\text{NaBH}_4}C_{\text{H}_2\text{O}} \quad (4)$$

Eqs. (1)–(4) are solved numerically in Maple12.

4.2. Results and discussions

The computed NaBH_4 concentration during the dissolution + reaction step is shown in Fig. 6. It is seen that the

Fig. 7 – H_2O concentration profile for the dissolution + reaction step.

Fig. 9 – H₂O concentration profile for the reaction-only step.

concentration of NaBH₄ increases until dissolution is complete. At about 490 s, the NaBH₄ solid is completely dissolved. The maximum concentration is 9.78 mol L⁻¹. This confirms our assumption that steam hydrolysis is conducted in highly concentrated solution. Meanwhile, the corresponding water concentration decreases from 55.5 mol L⁻¹ to 47.6 mol L⁻¹, as shown in Fig. 7.

When the solids are completely dissolved, there remains only chemical reaction in the aqueous phase. This is the reaction-only step, shown in Figs. 8 and 9. It is seen that after another 3000 s, the concentration of NaBH₄ reaches zero, indicating complete reaction. Meanwhile, the concentration of water drops to 38.1 mol L⁻¹. The decrease of water concentration is because the consumption of water accelerates during the reaction-only step and water consumption continues for longer time than in the dissolution + reaction step.

A comparison between modeling data and experimental data is shown in Fig. 10. The left curve represents dissolution + reaction process and the right fitting curve represents reaction-only step. From $t = 0$, the solid starts to dissolve while the reaction initiates. Because dissolution dominates at this stage, the NaBH₄ concentration keeps increasing. After 490 s, the NaBH₄ completely dissolved, where a maximum is seen. Subsequently there is only NaBH₄ hydrolysis in liquid solution. The agreement of the model with experimental data validated our two-part dissolution + reaction model.

Fig. 8 – NaBH₄ concentration profile for the reaction-only step.

Fig. 10 – Model fitting for the experimental data of steam hydrolysis at 90 °C (0.2 g NaBH₄, 10 wt.% CoCl₂).

5. Conclusion

This study determines for the first time the region of temperature and relative humidity under which deliquescence of NaBH₄ and 10% CoCl₂ mixture is favored. Deliquescence is a necessary first step for release of hydrogen. CoCl₂ accelerates the reaction because of both as a catalyst and its effect on increasing DRH (compared to pure NaBH₄). The H₂ generation rate affected by both reaction temperature and relative humidity is revealed. Combining high reaction temperature and high relative humidity contributes to accelerated steam hydrolysis. A two-part reactor model accounting for deliquescence, solid dissolution, and hydrolysis to release H₂ is established for NaBH₄ steam hydrolysis, with reasonable estimated kinetic constant and mass transfer coefficients.

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