Hydrogen production by sodium borohydride in NaOH aqueous solution

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Abstract. The kinetics of hydrolysis reaction of NaBH₄ in NaOH aqueous solution is studied. The influence of pH of the NaOH aqueous solution on the rate of hydrogen production and the hydrogen production efficiency are studied for the hydrolysis reaction of NaBH₄. The results show that the activation energy of hydrolysis reaction of NaBH₄ increased with the increase of the initial pH of NaOH aqueous solution. With the increasing of the initial pH of NaOH aqueous solution, the rate of hydrogen production and hydrogen production efficiency of NaBH₄ hydrolysis decrease.

1. Introduction
The intensive use of fossil fuels has caused great environmental problems [1]. As a promising energy, hydrogen energy is pollution free for its combustion only generating water without any byproduct [2-5]. At present, many countries around the world are studying hydrogen production both in large quantities and at low cost. People can produce hydrogen in different ways, for example, reforming, decomposition, and hydrolysis of compounds, water electrolysis or microbial fermentation or photosynthesis [6]. Boride hydride has high hydrogen storage density and it is solid state at room temperature and normal pressure. This makes it to be a good prospect as a miniaturized and mobile hydrogen source [7]. At present, hydrolysis and pyrolysis are two main ways to obtain hydrogen from boride hydride. Among the boride hydrides, NaBH₄ is the most studied used for hydrogen production by hydrolysis [8]. However, at room temperature, NaBH₄ reacts slowly in alkaline solution, and the hydrogen production efficiency is very low. Kreevoy proposed the following empirical equation [9]:

$$\log t_{1/2} = pH - (0.034T - 1.92)$$  \hspace{1cm} (1)

Where $t_{1/2}$ is the half-life time, the unit is minute. T is the absolute temperature.

Hydrogen production by NaBH₄ in NaOH aqueous solution is investigated in this paper.

2. Experimental
Five glasses of 200 ml NaOH aqueous solution were prepared, their pH were 7.07, 7.59, 8.01, 8.49 and 9.00. In the five glasses of 200 ml NaOH aqueous solution, each of them was added 3 g NaBH₄ at 293.16 K. The hydrogen-production rate and the total amount of produced hydrogen of the hydrolysis of NaBH₄ were measured. After an hour of reaction, pH of the solution was measured.
The reaction facility is shown in figure 1. In a airtight room, the beaker contains NaOH aqueous solution, and 3 g NaBH₄ powder is put into the beaker by a lifting rod. The hydrogen-production rate is measured by the gas pipe and a glass rotameter. Temperature-control system is used to control the temperature.

![Figure 1](image1.png)

**Figure 1.** Schematic representation of the self-designed reaction facility.

### 3. Results and discussion

The relation between the rate and the pH of NaOH aqueous solution is shown in figure 2. The total production of hydrogen is obtained by integral of the curve in figure 2. Then the relation between hydrogen production and the pH of the NaOH aqueous solution is obtained, as shown in figure 3. The efficiency of hydrogen production of five glasses of 200 ml NaOH-NaBH₄ aqueous solution is 10.5 %, 9.6 %, 8.9 %, 8.4 % and 7.0 %, respectively.

One can see from figure 2 and figure 3, both of the rate of hydrogen production and the efficiency of hydrogen production decrease with the increase of pH of the NaOH aqueous solution.

![Figure 2](image2.png) ![Figure 3](image3.png)

**Figure 2.** Dependence of hydrogen-production rate of NaBH₄ on the reaction time.

**Figure 3.** Dependence of the hydrogen-production of NaBH₄ on the reaction time.

The pH of the solution is measured with a pH meter 1 hours after the initiation of the reaction. It is found that the pH value of the final NaOH-NaBH₄ aqueous solution saturated at about 10.60.

The activation energy for hydrogenation is obtained by means of the Arrhenius equation:

$$E_a = -RT \ln \left( \frac{k}{k_0} \right)$$  \hspace{1cm} (2)

$E_a$ is the activation energy, $R$ is the gas constant, $T$ is the absolute temperature, $k_0$ is a pre-exponential factor, $k$ is the temperature dependent reaction-rate constant.

By the Avrami equation, one can obtain the constant $k$ [10]:

$$f = 1 - \exp(-kt^n)$$  \hspace{1cm} (3)
f is the reaction function (here it is the volume fraction of theoretical hydrogen production of 3 g NaBH₄), n is the order of reaction and t is the reaction time. People can get the following equation from equation (2) and (3) [11]:

\[
\ln[-\ln(1-f)] = n \ln t + \ln k \tag{4}
\]

\[
Ea = -RT \ln k + RT \ln k_0 \tag{5}
\]

From the data in the figure 3, people can get the relation between ln[t] and ln[-ln(1-f)], as shown in figure 4.

**Figure 4.** Relation between ln[t] and ln[-ln(1-f)].

People can get lnk and n of the NaBH₄ hydrolysis reaction in the different NaOH aqueous solution by figure 4, as shown in table 1:

**Table 1.** n and lnk for hydrogen production from NaBH₄ hydrolysis at different pH.

| pH of NaOH(aq) | n  | lnk  |
|----------------|----|------|
| 7.07           | 0.99 | -9.19 |
| 7.59           | 0.87 | -9.36 |
| 8.01           | 0.88 | -9.48 |
| 8.49           | 0.88 | -9.59 |
| 9.00           | 0.99 | -10.62 |

In equation (5), k₀ is pre-exponential factor, it is a constant determined only by the nature of the reaction and independent of the temperature of the reaction and the concentration of matter in the system. So, the relation between the pH of NaOH aqueous solution and activation energy of NaBH₄ hydrolysis is similar to the relation between the pH of NaOH aqueous solution and -lnk, as shown in figure 5.

**Figure 5.** Relation between the pH of NaOH aqueous solution and -lnk.

One can see from figure 5, the activation energy of NaBH₄ hydrolysis increases with the increase of the pH of NaOH aqueous solution.

4. Conclusions

With the increase of the pH of NaOH aqueous solution, both of the rate of hydrogen production and the efficiency of hydrogen production decreases. Increasing the pH of NaOH aqueous solution increases the activation energy of NaBH₄ hydrolysis.

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References
[1] Sinha P, Roy S & Das D 2016 Genomic and proteomic approaches for dark fermentative biohydrogen production. Renewable & Sustainable Energy Reviews 56 1308-21
[2] Rosales-Colunga L M, Rodriguez A D L 2015 Escherichia coli, and its application to biohydrogen production Reviews in Environmental Science & Bio/technology 14(1) 123-35
[3] Steele B C, Heinzel A 2001 Materials for fuel-cell technologies Nature 414(6861) 345-52
[4] Gorte R J 2015 Cooling down ceramic fuel cells Science 349(6254) 1290-1290
[5] Costamagna P, Srinivasan S 2001 Srinivasan, s.: quantum jumps in the pemfc science and technology from the 1960s to the year 2000: part i. fundamental scientific aspects Journal of Power Sources 102(s 1–2) 242–52
[6] Holladay J D, Hu J, King D L & Wang Y 2009 An overview of hydrogen production technologies Catalysis Today 139(4) 244-60
[7] Satyapal S 2007 Annual Progress Report Department of Energy
[8] And Y S, Chen R 2006 Semiempirical hydrogen generation model using concentrated sodium borohydride solution Energy & fuels 20(5) 2149-54
[9] Kreevoy M M, Jacobson R W 1979 The rate of decomposition of NaBH₄ in basic aqueous solutions Ventron Alembic 15(2) 2-3
[10] Avrami M 1939 Kinetics of phase change. i general theory Journal of Chemical Physics 7(12) 1103-12
[11] Xu E, Li H, You X, Bu C, Zhang L & Wang Q et al. 2017 Influence of micro-amount O₂ or N₂ on the hydrogenation/dehydrogenation kinetics of hydrogen-storage material MgH₂ International Journal of Hydrogen Energy 42(12) 8057-62