Journal of Alloys and Compounds 468 (2009) 493–498

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Solid sodium borohydride as a hydrogen source for fuel cells

Bin Hong Liu [a,*], Zhou Peng Li [a], S. Suda [b]

[a] *College of Materials and Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China*
[b] *Materials & Energy Research Institute Tokyo, Ltd., 1-1 Sawarabi-Daira, Tateshina-Chuokogen, Kitayama, Chino-shi, Nagano 391-0301, Japan*

Received 15 December 2007; received in revised form 5 January 2008; accepted 7 January 2008

Abstract

Hydrolysis of sodium borohydride $NaBH_4$ is a promising method for on-board hydrogen supply for fuel cells. In this study, the hydrolysis reaction was studied by starting with solid $NaBH_4$ rather than aqueous borohydride solutions, and adding less amount of water in an attempt to explore the maximum hydrogen generation capacity. It was found that hydrogen could be liberated at very high rates and over than 90% conversion rates were achieved when the mole ratio of water to sodium borohydride was not less than 4:1. The final hydrogen generation capacity was achieved as high as 6.7 wt%. Materials such as $CoCl_2$ or cobalt powder were found to be effective as the catalysts for the hydrolysis reaction at such reaction conditions. A large heat effect due to the exothermic reaction and a low melting point of $NaBO_2{\cdot}4H_2O$ led to the acceleration of hydrogen generation at the latter part of the hydrolysis process. It is thus promising to utilize these reaction conditions to achieve high hydrogen generation capacity by proper system design.

Keywords: Hydrogen generation; Borohydride; Hydrolysis; Catalyst; Kinetics; Capacity

1. Introduction

Fuel cells are regarded as one of solutions for solving energy and environmental problems by generating power with higher efficiency and zero emission. The proton exchange membrane fuel cell (PEMFC) is the most promising fuel cell type for commercialization due to its excellent performance at low temperatures. However, safe and efficient hydrogen supply to PEMFCs is still a problem to be solved. There are several options for hydrogen storage and supply: hydrogen can either be stored as compressed gas, as a liquid or in hydrogen storage materials. Hydrogen can also be supplied by reforming hydrocarbons. However, these methods are inadequate in terms of their volumetric or gravimetric storage densities. For example, hydrogen stored in pressurized vessels has low volumetric density and safety concern. Liquid hydrogen is energy-consuming for preparation and storage. Hydrogen storage in metal hydrides is advantageous in its volumetric density and safety but the gravimetric density needs to be improved. Reformation from hydrocarbons requires high temperature and produces hydrogen with CO impurities that will poison electrocatalysts in fuel cells. Recently, aqueous sodium borohydride solutions are attracting considerable attentions as hydrogen source for fuel cells due to high hydrogen contents and the ease of hydrogen generation by the catalyzed hydrolysis reaction according to the following equation:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 + 300\,kJ \quad (1)$$

There have been quite a lot of studies on hydrogen generation from hydrolysis of borohydrides [1–17]. It has been found that Pt [4], Ru [1,9,15], Co_2B [17,19], Ni_2B [5], Ni [8], Raney Ni [11,20], Mg_2Ni [3] are good catalysts for the hydrolysis reaction. Some prototype hydrogen generators were built up to power fuel cells [6,16,17]. On the other hand, it has also been found that the hydrolysis product sodium meta-borate $NaBO_2$ has a relatively small solubility in water. Although $NaBH_4$ shows a solubility of 55 g in 100 g water at 25 °C, $NaBO_2$ has only 28 g in 100 g water at 25 °C [6]. Correspondingly, it was reported that the optimum concentration of $NaBH_4$ in starting solution was about 15 wt% [4,9,12], otherwise $NaBO_2{\cdot}4H_2O$ would precipitate out from the solution and possibly damage the catalyst or clog tubes in the reaction system. As a result, hydrogen generation capacity in the system will be limited to 3.2 wt%, quite inadequate considering

---

* Corresponding author. Tel.: +86 571 87951770; fax: +86 571 87951770.
E-mail address: liubh@zju.edu.cn (B.H. Liu).

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.01.023

the theoretical 10.8 wt% in Eq. (1) and a target of 6.0 wt% set by Department of Energy (DOE), USA, for hydrogen storage systems [18].

To make the system more attractive and competitive, it is highly desirable to increase hydrogen generation capacity for the borohydride system. However, few investigation results were reported about hydrogen generation at very high borohydride concentrations or using solid sodium borohydride as a hydrogen source for the PEMFC. The reaction kinetics and hydrogen yield remain unclear when water is not abundantly supplied. In this work, we studied characteristics of the hydrolysis reaction by using solid $NaBH_4$ and adding less amount of water. Hydrogen generation rates and conversion rates were investigated by examining the effects of water amounts as well as catalyst additions. Reaction mechanisms were discussed on the basis of the experimental results.

2. Experimental

2.1. Reaction mode

In this research, sodium borohydride was not dissolved in water to prepare a solution prior to the reaction. As shown in Fig. 1, 1 g of sodium borohydride powder was put at the bottom of a 200 ml three-neck flask. The hydrated cobalt chloride $CoCl_2·6H_2O$ was dissolved in a portion of water. Then the solution of the catalyst was injected into the flask using a syringe to initiate the hydrolysis reaction. A thermocouple was embedded in borohydride powder to monitor the temperature during the reaction. No stirring was applied and no water bath was used during the reaction. The volume of generated hydrogen was measured as a function of time by passing it through a wet drum gas meter and the volume was transformed to the standard temperature and pressure (S.T.P) before calculating hydrogen generation rates. When cobalt powder was used as the catalyst, it was premixed with sodium borohydride powder in a mortar and put into the flask before water was injected.

2.2. Materials

Two materials in different forms were tested as the catalysts for the hydrolysis reaction: $CoCl_2·6H_2O$ and fine cobalt powder. In the case of $CoCl_2·6H_2O$, a certain amount of $CoCl_2·6H_2O$ was dissolved in different volumes of water and then the solutions were injected into the flask. A fine cobalt power from Johnson Mathey Company with a powder size of 1.6 μm was also tested as the catalyst. It was premixed with sodium borohydride powder before the test. No stabilizer reagent such as sodium hydroxide was employed in this research.

Sodium borohydride used in the experiments was commercially available with a purity of 96%. De-ionized water was used in this research.

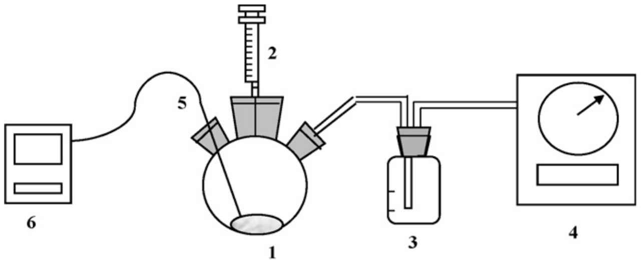

Fig. 1. The experiment setup: 1: three-neck flask, 2: syringe, 3: bottle for gas washing, 4: gas meter, 5: thermal couple, 6: temperature measurement unit.

2.3. Instrumental analyses

The hydrolysis products after the reaction were analyzed by X-ray diffraction (XRD) on a Rigaku D/MAX-RA using Cu Kα radiation. Also a commercial product of $NaBO_2·4H_2O$ was analyzed by differential scanning calorimetry (DSC) on Shimadzu DSC60. Alumina crucibles were used in the DSC measurement and α-Al_2O_3 powder was used as the reference. The DSC sample was heated at a rate of 4.5 °C/min.

3. Results and discussion

When the initial concentration of sodium borohydride was more than 10 wt%, it has been found that crystals of the hydrolysis product sodium meta-borate $NaBO_2·4H_2O$ would appear after the reaction finished. The presence of hydrated meta-borate crystals inevitably affects the subsequent reaction, especially when crystals appear on the surface of the catalyst. In case the hydrogen generation system is clogged or damaged by crystals, it was well reported that the optimum initial concentration of sodium borohydride is about 15 wt% [4,9,12]. It inevitably results in a maximum hydrogen generation capacity of 3.2 wt%, a value far less than the theoretical 10.8 wt% in Eq. (1). To explore the possibility of achieving larger hydrogen generation capacity, it is essential to investigate characteristics of the hydrolysis reaction when water is not very abundant. It is expected that solids will be formed during the reaction. We were interested in studying how hydrogen generation kinetics and the final conversion rate would become under this kind of reaction condition.

To make the hydrolysis reaction as deep as possible even after crystals emerge, it is important to select an active catalyst that is able to be finely distributed in the reactants. Among possible catalysts for the borohydride hydrolysis reaction [20], we found that cobalt chloride $CoCl_2$ could serve the purposes. It has been reported that the catalytic mechanism for cobalt chloride is first an acidic catalysis and then a subsequent catalysis from a reduction product cobalt boride Co_2B [20]. The reduction reaction can be written as follows [21].

$$CoCl_2 + 2NaBH_4 + 3H_2O = 6.25H_2 + 0.5Co_2B + 2NaCl + 1.5HBO_2 \qquad (2)$$

Co_2B produced from above reaction was reported as a very good catalyst for borohydride hydrolysis [19–21]. In this work, we expected that the formed fine Co_2B could be distributed in the reactants promptly and thoroughly to make the hydrolysis reaction fast and deep.

Fig. 2 shows hydrogen generation under the catalysis of 0.1 g $CoCl_2·6H_2O$ and at a 1:2 weight ratio of sodium borohydride to water. From Fig. 2, it can be seen that the hydrogen generation curve shows two steps. The measured temperature is also found to have the similar shape. During the experiment, it was observed that the reduction reaction took place very quickly as the slurry turned into black almost simultaneously when the $CoCl_2$ solution was injected into the flask. After the black cobalt boride was formed, it acted as the catalyst of the subsequent hydrolysis reaction. According to the reaction (2), 0.1 g $CoCl_2·6H_2O$ would only consume 0.033 g $NaBH_4$ and produce 59 ml H_2.

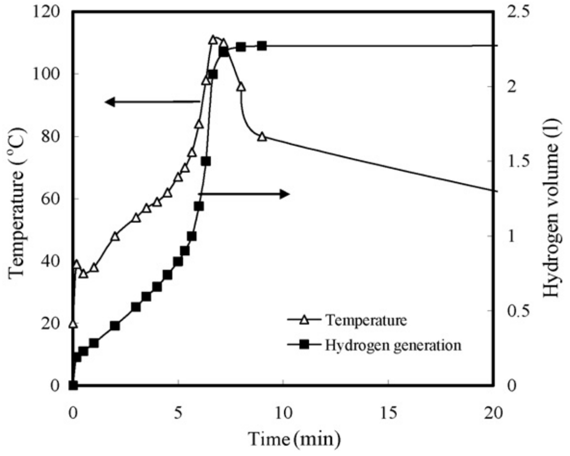

Fig. 2. Hydrogen generation volume and temperature as a function of time (NaBH$_4$: 1.0 g, H$_2$O: 2.0 g, CoCl$_2$·6H$_2$O: 0.1 g).

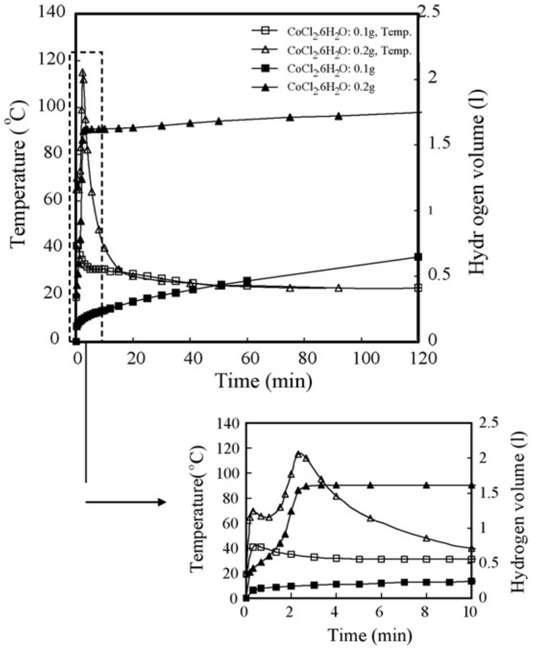

Fig. 3. Hydrogen generation at two different catalyst additions (NaBH$_4$: 1.0 g, H$_2$O: 1.5 g).

Accordingly, the first step found in the hydrogen generation and temperature curves in Fig. 2 (about 175 ml of hydrogen and a rise of temperature to 40 °C) was already the result of two catalysis effects. Therefore, it appears that the reaction (2) only showed effects at very initial stage of the experiment and the subsequent hydrolysis was only under the catalysis of the formed Co$_2$B. Although the mole ratio of H$_2$ to NaBH$_4$ is 3.125:1 in reaction (2), which is smaller than 4:1 in reaction (1), the decrease of hydrogen volume due to reaction (2) would be only 19 ml when 0.1 g CoCl$_2$·6H$_2$O was used. This amount is negligible compared with 2370 ml hydrogen generated from 1 g NaBH$_4$ in reaction (1). Therefore, the influence of CoCl$_2$ reduction on total released hydrogen volume would be negligible.

Under the catalysis of Co$_2$B, the reaction was then found to proceed at a constant rate though the temperature was gradually increased due to the exothermic reaction. However, a surge of hydrogen generation took place when the conversion reached about 35%. The burst of hydrogen generation was also accompanied by a quick rise of temperature. As can be seen in Fig. 2, the temperature was elevated to be as high as 110 °C. When the reaction proceeded further and water was almost consumed, hydrogen generation was found to slow down. The reaction finally reached a conversion of 92% after 24 h and a hydrogen weight percentage of 6.1 wt% was achieved on a mass basis of all reactants and the catalyst.

Fig. 3 shows that hydrogen generation was largely depressed by decreasing the amount of the catalyst. Although it is definite that the reaction slows down with the decrease of catalyst, the large difference in hydrolysis kinetics for two catalyst additions shown in Fig. 3 is supposed to be mainly caused by the heat effect. It seems that if the initial reaction was not quick enough to trigger the heat effect, hydrogen generation would become rather slow. It would take several hours rather than a few minutes to reach the same conversion.

Fig. 4(a and b) shows the effects of water amount on the hydrolysis reaction when the weight of sodium borohydride was kept at 1 g. As can be seen from Fig. 4(a), hydrogen generation rate was first decreased and then increased with decreasing water from 7 to 2 g. On the whole, hydrogen generation was very fast and finished within several minutes. The conversion could finally reach more than 90% as shown in Fig. 5. When water amount was further decreased to be less than 2 g, the conversion rate turned to be largely decreased. Also the kinetics slowed down with decreasing water addition. Based on above results, we suppose that hydrogen generation rates were mainly influenced by two counter effects: a decrease in water activity and an increase in heat effect due to a reduction of the total amounts of the reactants when water was less added.

The experiment results are summarized in Table 1. It shows that the final hydrogen generation capacity reached 6.7 wt% that is high enough as a viable hydrogen generation system. Table 1 also shows that there were no apparent decreases of released hydrogen volume due to the reduction of CoCl$_2$.

Fig. 6 shows the XRD analysis results of the final solid products after hydrogen was released. In these three samples, several solid phases were detected: NaBO$_2$·2H$_2$O or NaB(OH)$_4$, NaBO$_2$·4H$_2$O or NaB(OH)$_4$·2H$_2$O, Na$_2$B$_4$O$_7$·5H$_2$O and Na$_2$CO$_3$·H$_2$O. The presences of NaBO$_2$·2H$_2$O and NaBO$_2$·4H$_2$O were within expectation but the appearances of small amount of Na$_2$B$_4$O$_7$·5H$_2$O and Na$_2$CO$_3$·H$_2$O were unexpected. The formation mechanism of Na$_2$B$_4$O$_7$·5H$_2$O and Na$_2$CO$_3$·H$_2$O may be originated from the following reaction [22].

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3 \tag{3}$$

Further investigation is needed to verify the above formation mechanism for Na$_2$B$_4$O$_7$. Although there existed unreacted NaBH$_4$ in the remaining samples when water amount was small, the peaks from NaBH$_4$ were not distinguishable. Also Co$_2$B was not well detected. The reason may situate in that they were covered by the products. For the samples produced from NaBH$_4$ and 2.0 g water or 0.8 g water, most NaBO$_2$·4H$_2$O turned into

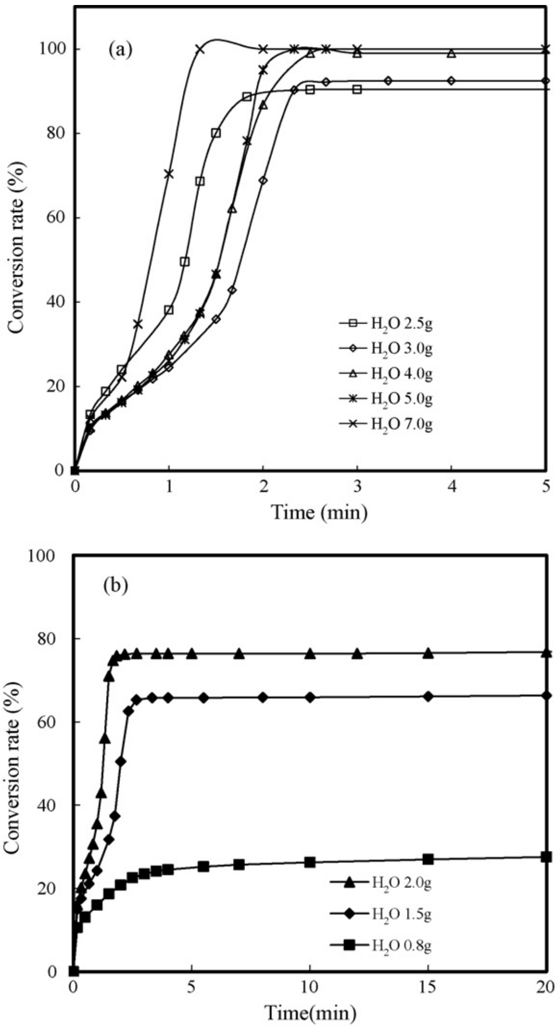

Fig. 4. Hydrogen generation characteristics at different water additions. (a) $NaBH_4$: 1.0 g; H_2O: 2.5–7.0 g; $CoCl_2{\cdot}6H_2O$: 0.2 g; (b) $NaBH_4$: 1.0 g; H_2O: 2.0–0.8 g; $CoCl_2{\cdot}6H_2O$: 0.2 g.

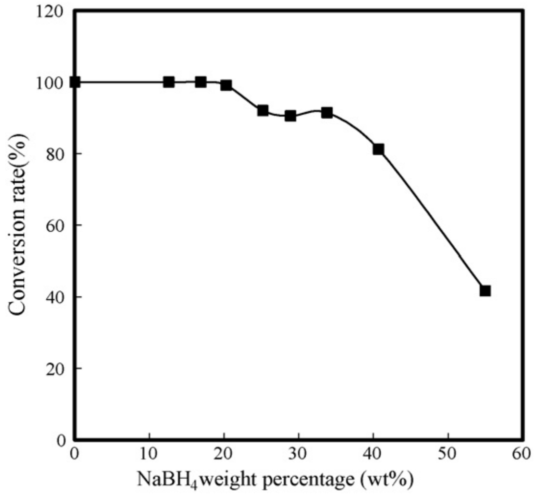

Fig. 5. Decrease of the final conversion rate with increasing of borohydride concentrations ($NaBH_4$: 1.0 g, $CoCl_2{\cdot}6H_2O$: 0.2 g).

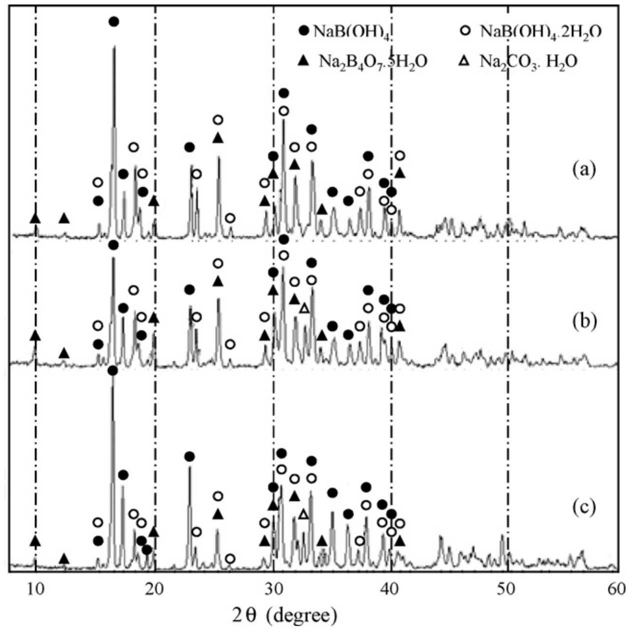

Fig. 6. XRD patterns of three hydrolysis product samples. (a) H_2O 2.0 g, $CoCl_2{\cdot}6H_2O$ 0.2 g; (b) H_2O 1.5 g, $CoCl_2{\cdot}6H_2O$ 0.1 g; (c) H_2O 0.8 g, $CoCl_2{\cdot}6H_2O$ 0.2 g.

$NaBO_2{\cdot}2H_2O$. But for the sample produced from $NaBH_4$ and 1.5 g water under the catalysis of 0.1 g $CoCl_2{\cdot}6H_2O$, a considerable portion of $NaBO_2{\cdot}4H_2O$ remained. As this sample underwent a slow kinetics as shown in Fig. 3, it is supposed that the low reaction temperature resulted in a difficulty in diffusion when $NaBO_2{\cdot}4H_2O$ crystals were formed and thus the reaction was impeded.

Fig. 7 shows the DSC analysis result of $NaBO_2{\cdot}4H_2O$. The first peak represents the melting of $NaBO_2{\cdot}4H_2O$ and dehydration to $NaBO_2{\cdot}2H_2O$. Further dehydration from $NaBO_2{\cdot}2H_2O$ needs to be higher than 110 °C. Combining hydrogen generation curves with the XRD and DSC analysis results, we suppose that due to a quick initial kinetics and a large heat effect, the temperature was elevated over the melting point of $NaBO_2{\cdot}4H_2O$ and then water reacted easily with borohydride to achieve a high conversion rate. If the temperature cannot be raised to the melting point, reaction kinetics will be much slower due to diffusion difficulty in solid, and also the conversion rate would be decreased as a result of slow kinetics. Therefore, it can be concluded that three factors were responsible for the quick and full conversion of borohydride to hydrogen with small amounts of water: (1) an effective catalyst, (2) large heat effect and (3) the low melting point for $NaBO_2{\cdot}4H_2O$.

To investigate effects of catalyst on the reaction characteristics, catalysts other than $CoCl_2$ were also tested. Fig. 8 demonstrates hydrogen generation behavior under the catalysis of cobalt powder. Compared with cobalt chloride, the cobalt powder has only one catalysis mechanism: a heterogeneous catalysis. As can be seen from Fig. 8, there show no initial steps in both the hydrogen generation curve and the temperature curve. At the initial stage, hydrogen was generated very slowly. But after several minutes of incubation time, there also showed a burst in hydrogen generation, similar to that under the catal-

Table 1
Hydrogen generation characteristics via hydrolysis of sodium borohydride

Reactants			Catalyst (g)	Theoretical hydrogen volume[a] (l)	Released hydrogen volume (l)	Conversion rate (%)	Hydrogen generation capacity (wt%)
$NaBH_4$ (g)	H_2O[b] (g)	$NaBH_4$ (wt%)					
1.02	7.05	12.6	0.20[c]	2.32	2.32	100	2.57
1.02	5.03	16.9	0.20[c]	2.32	2.32	100	3.42
1.02	4.00	20.3	0.20[c]	2.32	2.30	99.1	4.09
1.02	3.03	25.2	0.20[c]	2.32	2.14	92.2	4.72
1.02	2.51	28.9	0.20[c]	2.32	2.10	90.5	5.31
1.02	2.00	33.8	0.10[c]	2.32	2.13	91.8	6.30
1.02	2.00	33.8	0.20[c]	2.32	2.12	91.4	6.27
1.01	1.50	40.2	0.10[c]	2.30	1.58	68.7	5.62
1.03	1.50	40.7	0.20[c]	2.34	1.90	81.2	6.70
1.04	0.80	56.5	0.20[c]	2.37	0.99	41.8	4.80
1.03	1.98	34.2	0.5[d]	2.34	2.21	94.4	6.56
1.03	2.07	33.2	1.0[d]	2.34	2.17	92.7	6.25

[a] According to the hydrolysis reaction (1) and the 96% purity of $NaBH_4$.
[b] Hydrates in $CoCl_2{\cdot}6H_2O$ were not included.
[c] $CoCl_2{\cdot}6H_2O$.
[d] Co powder.

ysis of $CoCl_2{\cdot}6H_2O$. When the cobalt powder was decreased to 0.5 g, hydrogen generation showed some interesting behaviors. Within the initial 40 min, hydrogen was liberated at almost a constant rate though the system temperature was increased gradually. But there was also a sudden rise in hydrogen release and system temperature. Combined with the results shown in Figs. 3 and 4, it was found that the sudden acceleration of the reaction usually took place around 60 °C. It is thus more evident that this kinetic behavior is highly related with the melting of $NaBO_2{\cdot}4H_2O$, probably due to alternations in water activity or thermal property.

Compared with cobalt powder, the cobalt chloride solutions showed much more effective catalytic effects due to the initial acidic catalysis and the very fine cobalt boride formed.

From above results, it can be concluded that the following equation shows the largest hydrogen generation capacity for the hydrolysis of sodium borohydride, in which water and sodium borohydride is in a mole ratio of 4:1 or a weight ratio of 2:1:

$$NaBH_4 + 4H_2O = NaBO_2{\cdot}2H_2O + 4H_2 \quad (4)$$

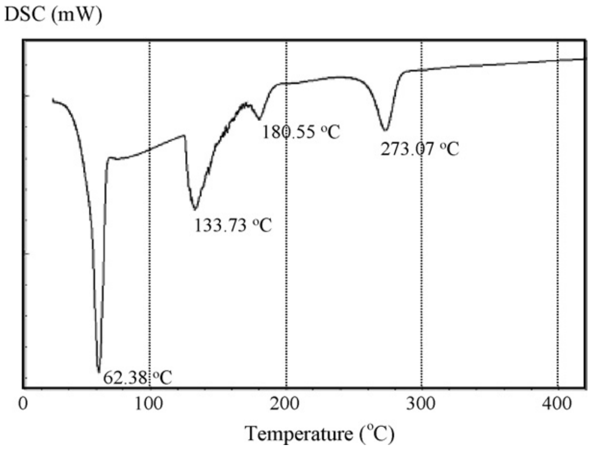

Fig. 7. DSC analysis result of $NaBO_2{\cdot}4H_2O$.

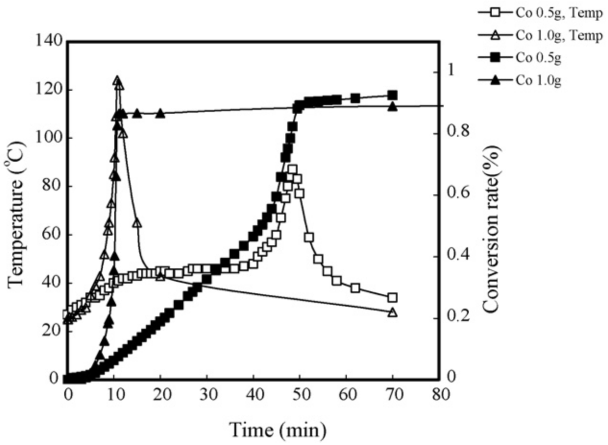

Fig. 8. Hydrogen generation characteristics under the catalysis of the cobalt powder ($NaBH_4$: 1.0 g, H_2O: 2.0 g).

Considering the possibility of achieving hydrogen generation capacity as high as 7.3 wt% in above reaction and very fast hydrogen generation kinetics, it is of interest to develop practical hydrogen generation systems with such high hydrogen capacity.

4. Conclusions

In this study, the hydrolysis reaction of sodium borohydride was studied when solid $NaBH_4$ was used and water was not abundantly supplied. It was found that the reaction could achieve very quick kinetics and more than 90% conversion rates if the mole ratio of water to borohydride was more than 4:1. Three factors were found to account for this reaction characteristic: the first was fast initial reaction kinetics under effective catalysis, then it induced a large heat effect to raise the temperature to higher than the melting point of $NaBO_2{\cdot}4H_2O$, and finally the melting of $NaBO_2{\cdot}4H_2O$ made the further reaction fast and deep. In this study, cobalt chloride was found to be more effective than the cobalt powder due to the initial acidic catalysis mechanism and fine structure of produced Co_2B. In account of the fast kinetics and high conversion rate, it is of interest to develop this reaction regime into a practical hydrogen generation system.

Acknowledgment

This work is supported by Hi-tech Research and Development Program of China (863), under the contract Nos. 2006AA05Z120 and 2007AA05Z144.

References

[1] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, J. Power Sources 85 (2000) 186.
[2] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969.
[3] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z.P. Li, J. Appl. Phys. A 72 (2001) 209.
[4] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy 27 (2002) 1029.
[5] H. Dong, H. Yang, X. Ai, C. Cha, Int. J. Hydrogen Energy 28 (2003) 1095.
[6] Y. Kojima, K. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbara, H. NaKanishi, S. Matsumoto, J. Power Sources 125 (2004) 22.
[7] Y. Kojima, Y. Kawai, H. Nakanishi, S. Matsumoto, J. Power Sources 135 (2004) 36.
[8] J.H. Kim, K.T. Kim, Y.M. Kang, H.S. Kim, M.S. Song, Y.J. Lee, P.S. Lee, J.Y. Lee, J. Alloys Compd. 379 (2004) 222.
[9] Z.T. Xia, S.H. Chan, J. Power Sources 152 (2005) 46.
[10] B.S. Richardson, J.F. Birdwell, F.G. Pin, J.F. Jansen, R.F. Lind, J. Power Sources 145 (2005) 21.
[11] B.H. Liu, Z.P. Li, S. Suda, J. Alloys Compd. 415 (2006) 288.
[12] Q. Zhang, G. Smith, Y. Wu, R. Mohring, Int. J. Hydrogen Energy 31 (2006) 961.
[13] A.M.F.R. Pinto, D.S. Falcao, R.A. Silva, C.M. Rangel, Int. J. Hydrogen Energy 31 (2006) 1341.
[14] R. Pena-Alonso, A. Sicurelli, E. Callone, G. Carturan, R. Raj, J. Power Sources 165 (2007) 315.
[15] J.S. Zhang, W.N. Delgass, T.S. Fisher, J.P. Gore, J Power Sources 164 (2007) 772.
[16] J. Zhang, Y. Zheng, J.P. Gore, T.S. Fisher, J. Power Sources 165 (2007) 844.
[17] S.J. Kim, J.Y. Lee, K.Y. Kong, C.R. Jung, I.G. Min, S.Y. Lee, H.J. Kim, S.W. Nam, T.H. Lim, J. Power Sources 170 (2007) 412.
[18] S.G. Chalk, J.F. Miller, J. Power Sources 159 (2006) 73.
[19] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra, E.K. Hyde, J. Am. Chem. Soc. 75 (1953) 215.
[20] C.M. Kaufman, B. Sen, J. Chem. Soc. Dalton Trans. (1985) 307.
[21] A. Levy, J.B. Brown, C.J. Lyons, Ind. Eng. Chem. 52 (1960) 211.
[22] Encyclopedia of Inorganic Chemistry X-2 (in Japanese), Maruzen Co. Ltd., 1965, p. 157.