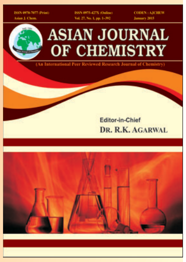
Asian Journal of Chemistry; Vol. 27, No. 3 (2015), 1040-1044

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18097



Chemical Reactor Design for Hydrogen Generation from Solid Sodium Borohydride by Ferric(III) Sulfate

CHANG-FENG YAN[1,2,3,*], ZHAOJUN FANG[2], SHILIN HUANG[1], CHANGQING GUO[1], RONGRONG HU[1] and WEIMIN LUO[1]

[1]Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P.R. China
[2]University of Chinese Academy of Sciences, Beijing 100039, China
[3]Key Lab of Renewable Energy, Chinese Academy of Sciences, Guangzhou 510640, P.R. China

*Corresponding author: E-mail: yancf@ms.giec.ac.cn

Received: 19 May 2014; *Accepted*: 21 August 2014; *Published online*: 19 January 2015; AJC-16720

Catalytic generation of hydrogen from the hydrolysis of sodium borohydride over ferric(III) sulfate has been studied in a new reactor. The system $NaBH_4$- ferric(III) sulfate (both in solid state) is an attractive storage way for portable application. 1) ferric(III) sulfate was cost-effective, 2) the solid state of $NaBH_4$ do not need the stabilizer regent, 3) A toroidal tube distributor helps to disperse water uniformly in order to constant generation of hydrogen and 4) no pretreatment step was needed. The effects of catalyst to sodium borohydride ratio, water flow rate and initial temperature on hydrogen generation were investigated. Hydrogen yield of > 90 % can be achieved with pure water and an active non-noble intermediate, Fe_2B, produced during the reaction. A burst of hydrogen flow rate accompanied with the appearance of the highest reaction temperature caused by exothermic effect. The rate of hydrolysis reaction was sensitive to temperature.

Keywords: Sodium borohydride, Hydrogen generator, Hydrogen generation, Ferric(III) sulfate.

INTRODUCTION

Fuel cells that can provide power for stationary and portable applications are regarded as a green solution for solving energy and environmental problems in that they are energy-efficient, zero emission and fuel-flexible. High density storage and high-efficiency production of hydrogen for power portable and niche applications *via* polymer electrolyte membrane fuel cells (PEMFC) are two important aims to current research and development[1,2]. However, hydrogen fuel safely supply, continuously and spontaneously to PEMFCs are the unsolved problems up to now. Sodium borohydride ($NaBH_4$) is a good candidate for hydrogen storage and production for fuel cells[3]. Hydrolysis of sodium borohydride can take place at relatively low temperatures with promising hydrogen storage efficiency. Hydrogen is generated according to the following reaction, where the factor "x" in eqn. 1 was termed as "excess hydration factor"[4].

$$NaBH_4 + (2 + x)\,H_2O \longrightarrow NaBO_2{\cdot}xH_2O + 4H_2\uparrow \quad (1)$$

The hydrogen yield from $NaBH_4$ compound is defined as the ratio of the experimentally hydrogen-generated volume to the theoretical one, which is usually calculated on the basis of the reaction (1) without considering the excess hydration factor. The reaction is very fast in the presence of a catalyst and there is no need to supply external heat for the reaction to occur. There are three possible routes of hydrogen generation from $NaBH_4$. 1) The concentrations of the aqueous $NaBH_4$ should be as high as possible to improve the energy density of the system. However, when the concentration is high, the by-product sodium metaborate precipitates from the sodium, which block the active sites of the catalyst and thus reduces the life of the catalyst. Precipitation of the byproduct would also bring about problems in solution transportation, such as blockage of the piping system. 2) To increase hydrogen generation capacity for the borohydride system, solid $NaBH_4$ as hydrogen source for the PEMFC seems to be a good solution. One way is to use catalyst solution with solid $NaBH_4$. 3) The last solution envisage solid $NaBH_4$ mixed a solid state catalyst. Water was added in controlled amount, which corresponds to the desired amount of hydrogen to be generated[5,6]. From the point of view of safety and portable application, the route 3 is better than others[7]. Kojima and co-workers[8] have developed a 10 kW-scale hydrogen generator, but the maximum gravimetric and the volumetric H_2 densities of the system were 2 wt. %. Zhang[9] has designed a 1 kW hydrogen generation system by hydrolysis of $NaBH_4$ which maximum gravimetric density reached 3.1 wt. %. Because there was a limitation of $NaBH_4$ concentration mainly related to temperature and reaction products of $NaBO_2$ hydrates. When the concentration of sodium borohydride solution was more than 20 wt. %, H_2 flow increased quickly with a burst of temperature. It is a phenomenon called thermal runaway which caused safety problem.

Several metals such as Ru, Co and Ni which were usually deposited in supports have been shown active effect on the hydrolysis reaction. Nickel acetate catalyzed $NaBH_4$ cartridges have been prepared and hydrolyzed with water for hydrogen generation[10]. A porous water diffuser and a hydrophobic membrane have been tested to increase the overall hydrogen yield. The cartridge hydrogen density based on water and sodium borohydride weight was as high as 4.64 wt. %. Kim[11] investigated hydrogen generation from solid $NaBH_4$ with hydrogen peroxide decomposition reaction for a fuel cell. Cobalt nitrate solution was investigated to accelerate the hydrolysis reaction. Pure hydrogen could be generated by catalytic hydrolysis reaction which the water was obtained from the hydrogen peroxide decomposition. Liu and co-workers[12] studied the hydrolysis reaction by starting with solid $NaBH_4$ rather than aqueous sodium borohydride solutions. Materials such as $CoCl_2$ or cobalt powder were found to be effective as the catalysts. Compared with cobalt powder, the $CoCl_2$ solution showed much more effective catalytic effect due to the initial acidic catalysis and cobalt boride formed. The sudden acceleration of hydrogen flow usually took place around 60 °C, which was highly related with the melting of $NaBO_2·4H_2O$, probably due to alternations in water activity or thermal property. Some patent applications concerning the solid state hydrolysis of $NaBH_4$ have also been published[13,14]. Ferric salts were reported as an inexpensive accelerator for hydrogen production. Wu and co-workers[15] reported ferric catalysts as accelerators for fast hydrogen generation from $NaBH_4$ solution. The hydrogen generation route using $FeCl_3$ as the pre-infused ferric salt shows excellent activity, resulting in a high H_2 generation efficiency (over 94 %) and an average H_2 generation rate of 1.08 L/min. Fe was also added to Co-B catalyst by chemical reduction of the corresponding its salts. Patel and co-workers[16] reported that only metallic Co acts as a main active site in the Co-Fe-B alloy and that Fe-dopant behaves as a promoter. A simple system in our work was built for continuous H_2 generation from the solid mixture of $NaBH_4$ and catalyst at room temperature. The effects of the ratio of ferric sulfate catalyst to $NaBH_4$, water flow rate and reaction temperature on hydrogen generation were discussed.

EXPERIMENTAL

Sodium borohydride ($NaBH_4$, reagent grade = 98 %, AR, Tianjin Damao Chemical reagent Factory) was used as received. Ferric sulfate, Fe of 21-23 %, Sinopharm Chemical Reagent Co., Ltd) in solid forms was tested as catalysts for this hydrolysis reaction. Pure water (18.25 MΩ cm@ 25 ºC) was obtained from EPED's water purification system (GREEN-10T).The catalyst of solid $NaBH_4$ and $Fe_2(SO_4)_3$ was prepare by a physical mixed method.

General procedure: Fig. 1(a) shows the prototype of hydrogen generator which was made of a hydrogen generation chamber, a buffer chamber and a water distributor that helps disperse active water homogeneously. The buffer chamber was made of organic glass, while the others were made of stainless steel (316) and a seal ring was used to prevent hydrogen leakage. The hydrogen generation system was show in the Fig. 1(b).

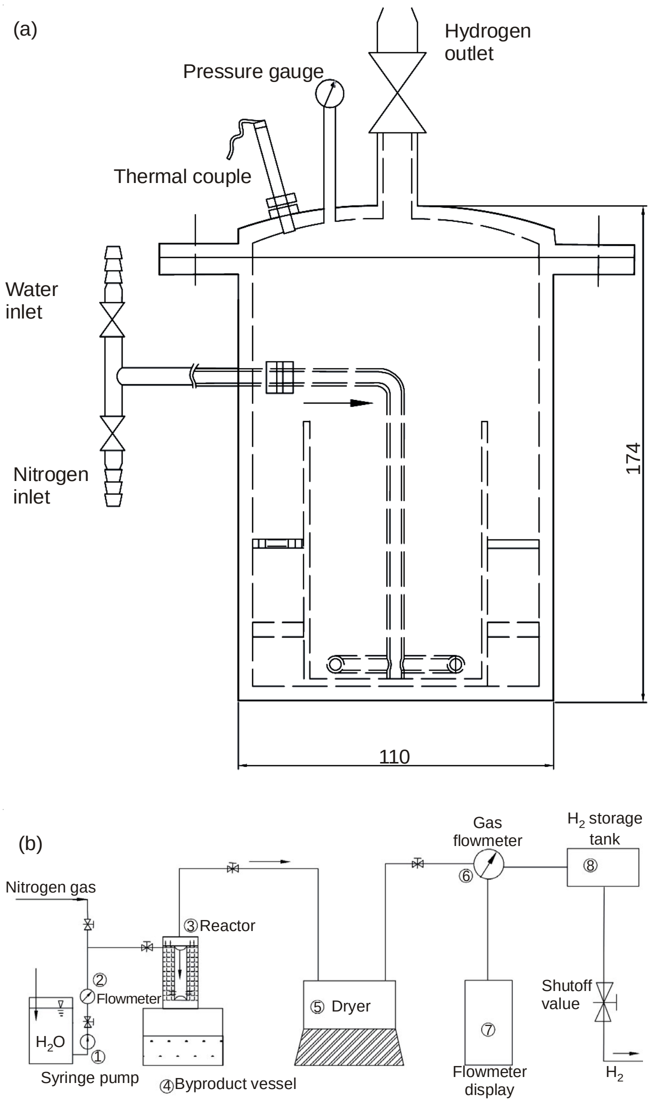


Fig. 1. (a) Overview of hydrogen generator; (b) schematic representation of the reactor test

The air in generator was purged by > 99 % N_2 gas (flow rate of 600 mL/min) before water flowed into the hydrogen generation chamber where the mixture of sodium borohydride and catalyst were pre-stored. When water contacts with the mixture powders, hydrogen produces quickly from the catalytic hydrolysis reaction of sodium borohydride. Hydrogen generated flows into the buffer chamber and has gone out of the reactor through the outlet. The gas was then filtered to remove residual solution drops. Hydrogen flow rate can be controlled by regulating the feed water flow rate. The initial temperature was controlled by a thermostatic water bath. Typically a total weight about 2.1 g mixed powder of sodium borohydride and ferric sulfate was placed in the hydrogen generation chamber.

The hydrogen was determined by a gas chromatographer (WUFENG GC522) equipped with a TCD detector and a FID detector.

The hydrolysis residue was cleaned then dried at 85 °C for 48 h. The sample was fully grinded then analyzed by X-ray diffraction (XRD, Multi-Purpose Diffractometer). The range of diffraction angle (2θ) is from 5-80° with CuK_{α} radiation (40 kV, 30 mA).

RESULTS AND DISCUSSION

Effect of initial temperature on hydrolysis reaction: In order to understand the influence of reaction temperature on the hydrogen yield, effect of initial temperature vary from 20 to 50 °C on the hydrolysis reaction as shown in Fig. 2 over the catalysis of $Fe_2(SO_4)_3$ of 2 mol % $NaBH_4$ and at feed water flow rate of 0.25 mL/min. The hydrogen yield was 79.2 % when the reaction temperature was 20 °C. When increasing the initial temperature from 20 to 50 °C, hydrogen yield improved to 93 %, decreased the time to reach the constant hydrogen output (48 to 17 min).

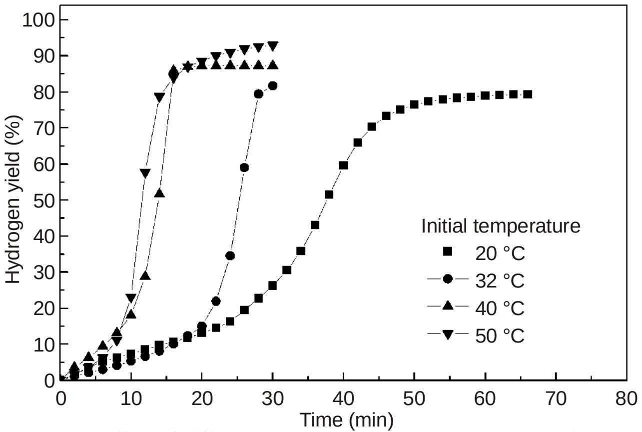


Fig. 2. Effect of different reaction temperature on hydrogen yield

Reaction temperature was plotted as a function of time in Fig. 3. It showed the reaction temperature varied with catalyst's ratios ranging from 1 to 6 mol %. When the feed water flow rate was kept at 0.20 mL min^{-1} and initial temperature was 19 ºC. The temperatures evolution showed a similar trend that a surge of temperature took place when the hydrogen yield nearly reached the maximum value in each run. The reaction temperature surged > 45 ºC than normal reaction temperature as mentioned above. This phenomenon was a threat to safety if the generator was in larger scale application. Two reasons may be responsible for the temperature surge. One reason is that the reaction is exothermic. It usually caused the reaction temperature to increasing as showed in Fig. 3. When the ratio was at 6 mol %, the reaction temperature increased to nearly 70 ºC in less than 20 min. When the molar ratio of catalyst was at 1 mol %, the reaction temperature changed slowly to maximum 25 ºC. It seems that if the initial reaction was not quick enough to trigger the heat effect, hydrogen generation would become rather slow. A heat management needs to pay attention in future design. It is necessary to continuously move the heat out of the reactor in time in that the heat is rather high (270 kJ/mol $NaBH_4$) and it could not be neglected in a reactor when high flow rate of H_2 was required. The hydrogen yield increased with the temperature increased. The other one is that the ratio of H_2O to $NaBH_4$ is lower[17].

Feed water flow rate on hydrolysis reaction: The flow rate of feed water is an important operating parameter in hydrolysis reaction. The quantity of water would affect the hydrogen yield and system storage density. Fig. 4 (a) shows hydrogen generation volume under $Fe_2(SO_4)_3$ of 2 mol % and $NaBH_4$ of 2 g at 32 °C with different feed water flow rates. When the water flow rate was at 0.05 mL/min, the hydrogen generation volume was 3070 mL. When the water flow rate was at 0.5 mL/min, the hydrogen generation volume increased to 4050 mL/min. The hydrogen volume increased with the increasing of feed water flow rate in that a larger feed water flow rate can provide with an excess water circumstance for $NaBH_4$ hydrolysis reaction, which was benefit for $NaBH_4$ hydrolysis and impeded the crystals formation of byproducts to wrap the un-reacted $NaBH_4$ powder. Fig. 4(b) shows the effect of water flow rate on the hydrogen generated rate. When the feed water flow rate was 0.05 mL/min, $NaBH_4$ hydrolysis reaction took a longer incubation time hydrogen generation rate was slow. Hydrogen yields of the $NaBH_4$ hydrolysis was performed at different feed flow rate ranging from 0.05 to 0.50 mL/min as showed in Fig. 4 (c). When the water flow rate increased to 0.2-0.5 mL/min, the hydrogen yields reached to more than 80 % in the Fig. 4 (c).

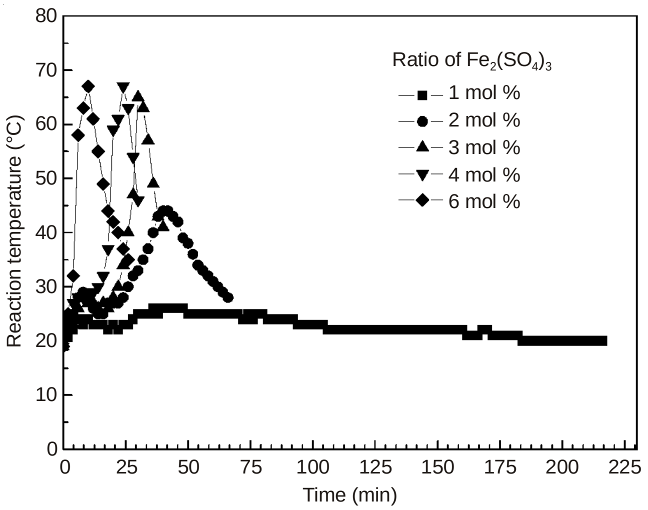


Fig. 3. Reaction temperature as a function of time under 2 g $NaBH_4$, feed water flow rate of 0.20 mL/min, initial temperature of 19 ºC

Effect of $Fe_2(SO_4)_3$ on hydrolysis reaction: It was considered that the amount of solid $Fe_2(SO_4)_3$ catalyst would influence the hydrolysis of the solid $NaBH_4$. The investigations were conducted at 19 ºC at the $NaBH_4$ of 2 g and feed water flow rate of 0.20 mL/min are shown in Fig. 5. Hydrogen yield as a function of time for different molar ratio of $Fe_2(SO_4)_3$ is given in Fig. 5(a). A hydrogen yield higher than 90 % was obtained within 0.5 h with mixture of 6 mol % $Fe_2(SO_4)_3$. When the ratio of $Fe_2(SO_4)_3$ is 1 mol. %, $NaBH_4$ hydrolysis reaction took a longer incubation time and the conversion rate was slow. Hydrogen yield during the catalytic hydrolysis catalyzed by different molar ratios of $Fe_2(SO_4)_3$ was shown in Fig. 5(b). In order to get the relationship between $Fe_2(SO_4)_3$ loading and the hydrogen flow rate, the average H_2 flow rate *versus* mixture ratio of $Fe_2(SO_4)_3$ both in logarithmic scale, ln (v)-ln (mol %), was showed in Fig. 5(c). The slope of the line is found to be 0.53 that indicates a half pseudo reaction order with respect to the catalyst[18]. Hydrolysis kinetics is not only dependent on catalyst, but also on other factors[19]. It is beyond this study that a much deeper analysis would be required to explore the surface structure of the catalyst and the influence of $Fe(BO_2)_2$.

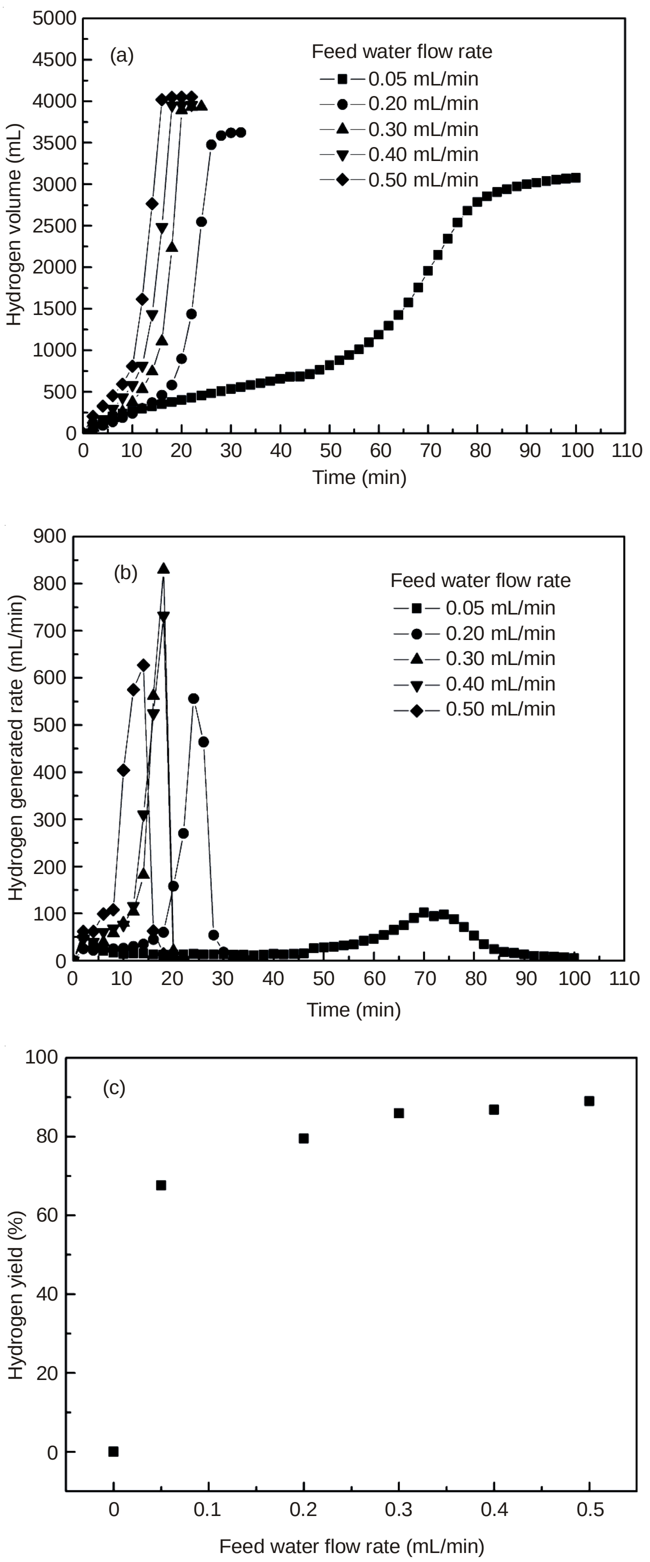


Fig. 4. (a) Hydrogen generation evolution; (b) Hydrogen generated rate varies with time; (c) Hydrogen yield varies with different water flow at initial temperature 32 ºC. (2 g $NaBH_4$)

Precipitates after hydrolysis reaction: Ferric boride was found in the XRD patterns of the precipitate in Fig. 6. The Fe_2B is accepted as the active species that catalyze $NaBH_4$ hydrolysis reaction and accelerate the subsequent H_2 generation[16]. The formation of ferric catalyst may follow reaction,

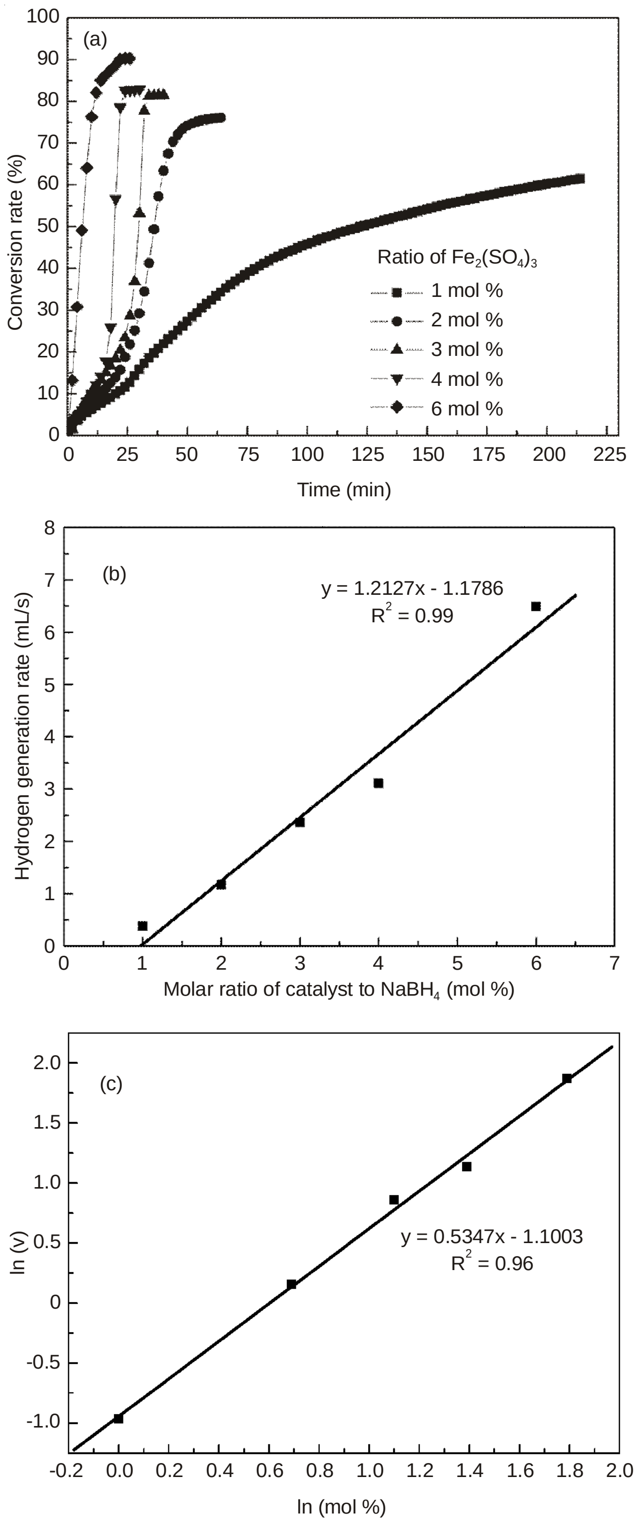


Fig. 5. (a) Hydrogen generation evolution; (b) Effect of mixture ratio of catalyst on hydrogen generation rate (v); (c) H_2-generated flow rate versus mixture ratio of $Fe_2(SO_4)_3$ both in logarithmic scale. (2 g $NaBH_4$, feed water flow rate of 0.20 mL/min, at 19 ºC)

$$Fe^{3+} + 3\ BH_4^- + 5\ H_2O = 9.75\ H_2\uparrow + 0.5\ Fe_2B + 2.5\ HBO_2 \quad (2)$$

Then the formation of fine Fe_2B could accelerate the hydrolysis reaction. It may be one reason leasing to the delay that the intermediate, catalyst Fe_2B formation depends on the chemical reduction process among $Fe_2(SO_4)_3$, $NaBH_4$ and water except that a physical process of the powder resolving into the water.

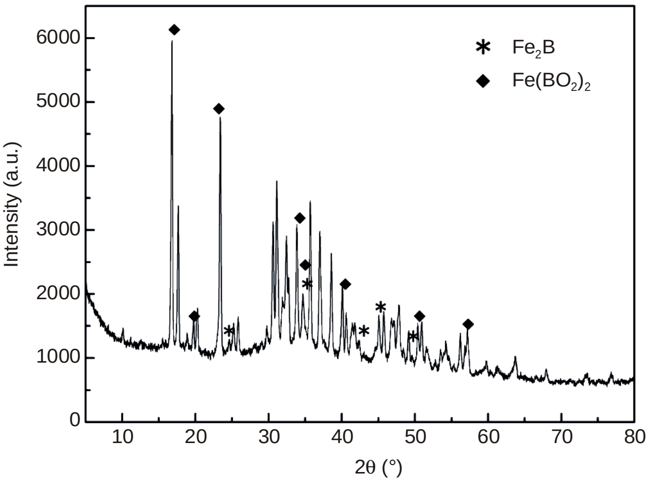


Fig. 6. XRD patterns of NaBH$_4$ powder after hydrolysis reaction

The dark brown borates solidified and clogged on the external surface of the water distributor when at a low feed water flow rate. A similar state has been reported by Gislon and co-workers[5]. There was less solidified products at the high feed water flow rate. Fe(BO$_2$)$_2$ was formed by a side reaction at the same time as observed several diffraction peaks in Fig. 6. Fe(BO$_2$)$_2$ formation decreased the BO$_2^-$ concentration which move the eqn. 2 to the right, which may accelerate the hydrogen generation. A small amount of un-reacted NaBH$_4$ was found in the samples[12]. The precipitation of byproducts may have made the hydrolysis rate of NaBH$_4$ and the energy density of the system decrease, because NaBH$_4$ and curbs the mass transfer of NaBH$_4$ to contact with Fe$_2$B.

From the whole process of hydrogen generation, there are several successive processes when water is introduced: 1) the dissolution being exothermic; 2) generates electrophilic Fe^{3+}; 3) reduces to ferric boride; 4) generates hydrogen and the formation. It is not easy to evaluate the limiting reaction step as the whole process involves heterogeneous phases[20]. Reaction mechanism of this work was similar to the one proposed by Andrieux and co-workers[21]. The difference was the formation of the catalytic phase mainly Fe$_2$B through reduction reaction. The hydrogen is released from this NaBH$_4$(s)/catalyst(s)-H$_2$O system only when the mixture powder resolved into the active water and the process of BH$_4^-$ ions diffusing to the ferric ions of the solution. The hydrogen generation rate can be controlled by the active water flow rate.

Conclusion

The solid system NaBH$_4^-$ ferric (III) sulfate is an attractive storage way for portable application. 1) ferric (III) sulfate was cost-effective, 2) no stabilizer regent for NaBH$_4$, 3) A toroidal tube distributor helps to disperse water uniformly in order to stably generate hydrogen and 4) no pretreatment step was needed. Hydrogen yield of > 90 % can be achieved with a non-noble and active catalyst, Fe-B. The hydrogen generation volume increased with the increasing of feed water flow rate. Finally, the precipitation of byproducts such as NaBO$_2$·4H$_2$O have decreased the hydrolysis rate of NaBH$_4$ and the energy density of the system.

The burst of hydrogen generation is benefited for reaching higher hydrogen yield, but it is seriously threat to security of the reactor and the stability of hydrogen flow. Heat released is a problem in practical reactor when large-scale reactor would be designed. Active non-noble ferric catalyst and the NaBH$_4$(s)/catalyst(s)-H$_2$O route are relatively safe and probable for portable applications by optimized design and control.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 21276254) and Guangzhou Science and Technology Project (No. 2013J4500027, No. 2012J4300142)

REFERENCES

1. U.B. Demirci, O. Akdim and P. Miele, *Int. J. Hydrogen Energy*, **34**, 2638 (2009).
2. L. Schlapbach, *Nature*, **460**, 809 (2009).
3. Ç. Çakanyildirim and M. Gürü, *Int. J. Hydrogen Energy*, **33**, 4634 (2008).
4. E.Y. Marrero-Alfonso, Water Utilization in the Hydrolysis of Sodium Borohydride, College of Engineering and Information Technology University of South Carolina, Columbia (2008).
5. P. Gislon, G. Monteleone and P.P. Prosini, *Int. J. Hydrogen Energy*, **34**, 929 (2009).
6. Y. Kojima, Y. Kawai, H. Nakanishi and S. Matsumoto, *J. Power Sources*, **135**, 36 (2004).
7. Y.P. Wang, Y.J. Wang, Q.L. Ren, L. Li, L.F. Jiao, D.W. Song, G. Liu, Y. Han and H.T. Yuan, *Fuel Cells*, **10**, 132 (2010).
8. Y. Kojima, K. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbara, H. Nakanishi and S. Matsumoto, *J. Power Sources*, **125**, 22 (2004).
9. J.S. Zhang, Thermal Processes in Sodium Borohydride Hydrogen Storage Systems, Purdue University, Indiana (2006).
10. P.P. Prosini and P. Gislon, *Int. J. Hydrogen Energy*, **35**, 12234 (2010).
11. T. Kim, *Int. J. Hydrogen Energy*, **35**, 12870 (2010).
12. B.H. Liu, Z.P. Li and S. Suda, *J. Alloys Comp.*, **468**, 493 (2009).
13. G.H. Zhu, X.D. Xiang and J. Melman, Hydrogen Generator Solid Fuel Cartridge, US Patent 2007/0243431 (2007).
14. R.M. Mohring, R. Cantave, K.A. Fennimore and K.W. McNamara, Methods and Devices for Hydrogen Generation, US Patent 2009/0104481 (2009).
15. N. Patel, R. Fernandes and A. Miotello, *J. Catal.*, **271**, 315 (2010).
16. C. Wu, Y. Bai and F. Wu, *Mater. Lett.*, **62**, 4242 (2008).
17. J. Zhao, H. Ma and J. Chen, *Int. J. Hydrogen Energy*, **32**, 4711 (2007).
18. J. Andrieux, D. Swierczynski, L. Laversenne, A. Garron, S. Bennici, C. Goutaudier, P. Miele, A. Auroux and B. Bonnetot, *Int. J. Hydrogen Energy*, **34**, 938 (2009).
19. D.Y. Xu, P. Dai, X.M. Liu, C.Q. Cao and Q. Guo, *J. Power Sources*, **182**, 616 (2008).
20. S. Murugesan and V. Subramanian, *J. Power Sources*, **187**, 216 (2009).
21. Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai and H. Hayashi, *Int. J. Hydrogen Energy*, **27**, 1029 (2002).
22. C. Cento, P. Gislon and P.P. Prosini, *Int. J. Hydrogen Energy*, **34**, 4551 (2009).