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Hydrogen generation from hydrolysis of solid sodium borohydride promoted by a cobalt–molybdenum–boron catalyst and aluminum powder

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ABSTRACT

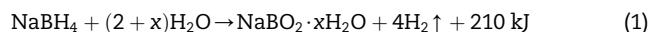
Direct use of solid sodium borohydride (NaBH_4) to react with minimized amount of water provides a straightforward means for increasing the hydrogen density of the system. But meanwhile, the resulting solid–liquid reaction system always suffers from serious kinetic problem. Our study found that the cobalt–molybdenum–boron (Co–Mo–B) catalyst prepared using an ethylene glycol solution of cobalt chloride is highly effective for promoting the hydrolysis reaction of solid NaBH_4 . Particularly, a combined usage of small amounts of Co–Mo–B catalyst, aluminum powder and sodium hydroxide enables a rapid and high-yield hydrogen generation from the hydrolysis reaction of solid NaBH_4 . A systematic study has been conducted to investigate the property dependence of the system on the components. In addition, the by-products of reaction were analyzed using powder X-ray diffraction and thermogravimetry/differential scanning calorimetry/mass spectroscopy techniques. Our study demonstrates that the multi-component system with an optimized composition can fulfill over 95% fuel conversion, yielding 6.43 wt% hydrogen within 3 min. The favorable combination of high hydrogen density, fast hydrogen generation kinetics and high fuel conversion makes the newly developed solid NaBH_4 -based system promising for portable hydrogen source applications.

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1. Introduction

Hydrogen storage is one of the major obstacles to the implementation of hydrogen fuel cell technology. The extensive studies for decades on interstitial metal hydrides, complex hydrides and physisorbents have led to no viable material that can reversibly store >6 wt% hydrogen at moderate temperatures with fast kinetics [1]. In a general view, the chemisorbent materials always contain strongly chemically bound hydrogen that is not readily retrievable, whereas the physisorbents show only weak binding of hydrogen, which

necessitates the use of cryogenic temperatures for a significant hydrogen uptake. Stimulated by this situation, many recent efforts have been directed toward the development of chemical hydrides as hydrogen storage media. Among the chemical hydrides of interest, sodium borohydride (NaBH_4) received the most extensive studies [2].



NaBH_4 can react with water at ambient temperature following Eq. (1), yielding H_2 and sodium metaborate (NaBO_2) by-product. As the hydrolysis reaction of NaBH_4 can be

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effectively accelerated/decelerated by employing catalyst/alkali, respectively, the combination of aqueous solution of NaBH_4 , alkali stabilizer and metal catalyst constitutes a safe, convenient and controllable source of high purity hydrogen [3]. In the past decade, a number of noble or non-noble metals/alloys/salts [2–8] have been identified to be catalytically active toward the hydrolysis reaction of NaBH_4 . A series of prototype systems [7,8] have been demonstrated that show favorable on-demand hydrogen generation (HG) performance. However, even with these encouraging advances, the NaBH_4 -based HG system is still limited in most practical applications owing to low effective hydrogen density and high cost [9]. The former originates from the solubility limitation of NaBO_2 in aqueous solution and the presence of “dead weight” water of hydration. The latter should be essentially ascribed to the lack of energy-efficient and cost-effective regeneration route.

Direct use of solid NaBH_4 to react with minimized amount of water provides a straightforward means for increasing the hydrogen density of the system. According to the literature reports, the catalyzed hydrolysis systems using solid NaBH_4 at atmospheric pressure can yield 6 ~ 7 wt% hydrogen [10–12], which is much higher than the hydrogen density (2 ~ 4 wt% hydrogen) achievable using conventional solution pathway [9]. But meanwhile, the dramatic reduction of water supply may cause serious mass transfer problem and thereby, poor HG kinetics and low fuel conversion of the system. In practice, the researchers always solve this problem via adding a large amount of catalyst, that is, to create a catalyst-rich environment to increase the reaction probability. But from a practical point of view, this strategy is far from ideal as increasing catalyst amount will not only negatively impact the hydrogen density of the system, but also cause increase of hydrogen cost.

Our latest study found that using a small amount of highly active catalyst can remarkably improve the HG performance of the solid NaBH_4 hydrolysis system. In addition, the reaction coupling between the hydrolysis reaction of NaBH_4 and the $\text{Al}/\text{H}_2\text{O}$ reaction can be utilized to improve the startup kinetics of the hydrolysis reaction of solid NaBH_4 . In the present study, we employed a combination of these two strategies to constitute a new HG system, which is composed of $\text{NaBH}_4/\text{Al}/\text{NaOH}/\text{catalyst}$ solid mixture and water. In comparison with the conventional NaBH_4 -based solution system, the newly developed system exhibits remarkable property advantages on hydrogen density and HG kinetics, which makes it promising for portable hydrogen source applications.

2. Experimental

2.1. Preparation of the catalysts and pretreatment of solid fuel

The catalysts were prepared by a facile chemical reduction method, as reported in our previous study [5], which involved using two solutions: the aqueous or ethylene glycol (EG) solution (A) containing 0.25 M CoCl_2 ; the aqueous solution (B) containing 1 M NaBH_4 , 0.25 M NaOH and 0.034 M Na_2MoO_4 . For comparison, a $\text{Co}-\text{B}$ catalyst was also prepared in aqueous solution. To ensure a homogenous mixing of the solid fuel and

catalyst, the $\text{NaBH}_4/\text{catalyst}$ and $\text{NaBH}_4/\text{Al}/\text{NaOH}/\text{catalyst}$ powder mixtures were mechanically milled under an Ar (99.999%) atmosphere.

2.2. Hydrogen generation performance testing

The catalyzed hydrolysis reaction was carried out in a 250 ml three-neck flask, wherein a certain amount of water was quickly injected to contact with the preloaded solid fuel powder. During the hydrolysis reaction, no mechanical or magnetic stirring was applied. The generated H_2 first went through a water trap to cool down to room temperature, and then through a drying column filled with silica gel to eliminate residual moisture. The HG rate was measured by an online mass flow meter (Sevenstar Huachang, MFM D07–7BM, accuracy within $\pm 2\%$) equipped with a computer. In the whole testing process, no attempt was made to control the temperature of the reaction system. The reaction temperature was monitored using a thermocouple embedded in the solid fuel powder and recorded using an online recorder. Each experiment was repeated twice. The determined relative error including the HG rate and reaction temperature was no more than 3%.

2.3. Characterization of by-products of reaction

The by-products of reaction were collected and characterized by powder X-ray diffraction (XRD, Rigaku D/MAX–2500, $\text{Cu K}\alpha$ radiation) and synchronous thermogravimetry/differential scanning calorimetry/mass spectroscopy analyzes (TG/DSC/MS, Netzsch 449C Jupiter/QMS 403C). In the thermal analyzes, the sample with a typical amount of about 4 mg was heated up to 450 °C at a ramping rate of 1 °C min^{-1} under a flowing argon (99.999% purity) atmosphere.

3. Results and discussion

3.1. Constructing solid NaBH_4 -based hydrogen generation system

Our previous study found that the $\text{Co}-\text{Mo}-\text{B}$ catalysts show higher catalytic activity than the $\text{Co}-\text{B}$ catalyst toward the hydrolysis reaction of NaBH_4 solution [5]. Particularly, the $\text{Co}-\text{Mo}-\text{B}$ catalyst that was prepared using an ethylene glycol solution of CoCl_2 (denoted as $\text{Co}-\text{Mo}-\text{B}$ (EG)) exhibits remarkably higher activity than the catalyst prepared in aqueous solution (denoted as $\text{Co}-\text{Mo}-\text{B}$ (AQ)). In the present work, we first examined and compared the three catalysts in terms of their catalytic activity toward the hydrolysis reaction of solid NaBH_4 . For comparison, the amount of the catalysts was fixed at 15 mg. As seen in the top of Fig. 1, the three systems with different catalysts showed remarkably different HG property. The system with the presence of $\text{Co}-\text{Mo}-\text{B}$ (EG) catalyst fulfilled 87% fuel conversion within 8 min, whereas the systems containing $\text{Co}-\text{Mo}-\text{B}$ (AQ) and $\text{Co}-\text{B}$ (AQ) catalysts showed the yields of only 21% and 2.5%, respectively, even after prolongation of reaction time over 70 min. According to the designed experiments (the inset of Fig. 1), the poor HG performance of the latter two systems should be

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