Combined Usage of Sodium Borohydride and Aluminum Powder for High-performance Hydrogen Generation

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Abstract

The sodium borohydride (NaBH₄)-based hydrolysis system has received considerable interest as a potential hydrogen source for vehicular application. But its practical application was greatly restricted by the low hydrogen density and high material cost. In the present study, we reported that addition of aluminum (Al) powder is an easy but highly effective way for addressing the problems of the NaBH₄-based hydrolysis system. The system was composed of alkaline aqueous solution of NaBH₄ and solid powder mixture of Al and Co₂B catalyst. The effects of alkaline concentration, NaBH₄ concentration and Al amount on the hydrogen generation (HG) performance of the system were investigated. Our study showed that there exist a mutual-promoting mechanism between the hydrolysis reaction of NaBH₄ and the Al/H₂O reaction. As a consequence, this system exhibited distinct advantages over the conventional NaBH₄-based system in terms of HG rate, fuel conversion, hydrogen density and H₂ production cost. These favourable attributes make the (NaBH₄+Al)/H₂O system attractive for mobile/portable hydrogen source applications.

Keywords: Aluminum Powder, Co₂B Catalyst, Hydrolysis, Hydrogen Generation, Sodium Borohydride

1 Introduction

Hydrogen storage is a major technological barrier to the development of hydrogen-powered vehicles [1]. In comparison with pressurized tank and cryogenic liquid hydrogen, solid state hydrogen storage materials hold greater promise to provide safe and efficient on-board hydrogen source. However, the extensive studies for decades have led to no viable system that can reversibly store > 6 wt.-% hydrogen at practical conditions. Since the end of the 1990s, chemical hydrogen storage emerged as a new promising approach for developing on-board hydrogen source [2–4]. In great contrast to the reversible dehydrogenation/rehydrogenation in metal hydrides, chemical hydrogen storage involves well-separated hydrogen generation (HG) and spent fuel regeneration processes. This is a major drawback of chemical hydrides, but on the other hand, it presents an opportunity to separately deal with the hydrogen-discharging and recharging aspects. In a general view, chemical hydrogen storage is characterized by the disconnection of technological limitations, and thereby providing a more realistic solution for near-term on-board applications, relative to the reversible metal hydrides.

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\text{NaBH}_4 + (2 + x)\text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{NaBO}_2x\text{H}_2\text{O} + 4\text{H}_2 + 210 \text{kJ}\ (1)
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Sodium borohydride (NaBH₄) is a representative chemical hydride. Its hydrolysis reaction following Eq. (1) can be significantly accelerated using metal or acid catalysts, and effectively inhibited by adding alkaline stabilizer. The aqueous solution of NaBH₄ in combination with metal catalyst and

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alkaline stabilizer, therefore constitutes a controlled HG system. [5]. NaBH₄-based hydrolysis system possesses a series of advantages that merit its potential application as mobile or portable hydrogen sources, such as satisfactory reaction controllability, mild operation temperature, safe fuel storability, negligible environmental impact and free of deleterious impurity in the produced H₂ stream. During the past decade, numerous efforts have been directed towards the development of NaBH₄-based on-demand HG system, which resulted in significant progresses in synthesis of active catalyst [5–9], device design [10, 11] and regeneration chemistry [12, 13]. But even with the aid of these technological advances, the NaBH₄-based hydrolysis system is still greatly limited in the vehicular application. One major drawback is the low hydrogen density. Whereas the stoichiometric hydrolysis reaction of NaBH₄ following Eq. (1) (x = 0) gives a theoretical hydrogen density of 10.8 wt.-%, the practically obtained value is only 2–3 wt.-% [14–16] due primarily to the solubility limitation of sodium metaborate (NaBO₂) by-product in aqueous solution, and the ‘dead weight’ H₂O which existed in the forms of NaBO₂·x·H₂O. Another drawback that limits the practical application of NaBH₄ is its prohibitively high cost. The current price of commercial NaBH₄ gives rise to an equivalent hydrogen cost of around US$ 200 per kg H₂, nearly two orders of magnitude higher than the DOE’s US$ 2–3 per kg H₂ goal [17]. Furthermore, even with the optimistic assumptions about the regeneration technology innovation, it seems highly unlikely to develop NaBH₄ as a competitive transportation fuel in the near future. These drawbacks are the main reasons for the ‘no-go’ decision of US DOE for NaBH₄ for on-board vehicular hydrogen storage [18]. But fundamentally, it is still premature to assert the insurmountability of these technological challenges.

Quite recently, a new method to produce high purity hydrogen using reactions of aluminum (Al) or its alloy and NaBH₄ with aqueous alkaline solutions was reported by Soler et al. [19]. Al is in itself a promising material for chemical hydrogen storage [20, 21], which reacts with water to generate hydrogen gas following Eq. (2) at mild temperature. Actually, the Al/H₂O system received considerable attention as a portable source of hydrogen owing to the resource abundance and the low cost of Al (US $2.4 per kg primary Al) and the well-established regeneration routes for restoring Al(OH)₃ back to metallic Al. But owing to the self-restraining problem that originates from the formation of a passivation layer on the Al surface, the practical application of the Al/H₂O system was greatly restricted. Interestingly, our study further showed that combined usage of NaBH₄ and Al provided a solution for simultaneously solving the problems of the two individual systems. According to the HG performance analysis, this is a result of the mutual-promoting mechanism between the hydrolysis reaction of NaBH₄ and the Al/H₂O reaction. The constituted dual-fuel system exhibited favourable attributes, such as high hydrogen density, reduced material cost and satisfactory controllability at moderate temperatures, which makes it promising for mobile and portable hydrogen source applications.

## 2 Experimental

### 2.1 Materials

NaBH₄ (96% purity), Al powder (100–200 mesh, 99% purity), NaOH (98% purity) and hydrated cobalt chloride (CoCl₂·6H₂O, 99% purity) were purchased from Sinopharm Chemical Reagent Corp. and used as received. Deionized water was used to prepare all the aqueous solutions.

### 2.2 Preparation and Characterization of the Catalyst

The catalyst was prepared in air by using a chemical reduction method, which involves the usage of two solutions of the compositions as follows: solution A contains 60 g L⁻¹ CoCl₂·6H₂O; the reductive solution B contains 40 g L⁻¹ of NaBH₄ and 10 g L⁻¹ of NaOH. The chemical reaction in the preparation of the catalyst is described as Eq. (3) [22]. In a typical preparation process, 100 ml of solution A was first placed in a beaker at 25 °C, and then equal volume of solution B was dropwise added into solution A. The mixture was kept undisturbed under the magnetic stirring until the bubbles generation ceased, which generally took about 30 min. After the reaction, the black precipitate was separated from the solution by vacuum filtration, followed by washing with deionized water and ethanol thoroughly to remove the residual BH₄⁻, Cl⁻ and Na⁺ ions. The catalyst samples were finally dried in vacuum at 40 °C for 48 h, and ready for use.

\[
\text{CoCl}_2 + 2\text{NaBH}_4 + 3\text{H}_2\text{O} \rightarrow 0.5\text{Co}_2\text{B} \downarrow + 2\text{NaCl} + 1.5\text{HBO}_2 + 6.25\text{H}_2 \uparrow
\]  

(3)

The catalyst was characterized by powder X-ray diffraction (PXRD, Rigaku D/MAX-2500, Cu Kα radiation) and scanning electron microscope (SEM, LEO Supra 35) equipped with energy dispersive X-ray analysis unit (Oxford). The specific surface area of the catalyst samples was measured by N₂ adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP 2010). To minimize the measurement error, each sample was measured for three times, from which an average value was given. The composition of the catalyst was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Iris Intrepid).

### 2.3 HG Performance Testing

The experimental setup used for measurement of HG properties is schemed in Figure 1. Catalytic hydrolysis reaction was carried out in a 250 ml three-neck flask, wherein the Al powder and catalyst solid mixtures were preloaded. The
alkaline aqueous solution of NaBH₄ was fed into contact with the Al powder and catalyst using a pressure-equalizing dropping funnel. The dropping rate was controlled at around 4 g min⁻¹, which ensures a reliable comparison of the HG kinetics of different systems. The generated hydrogen gas passed through a trap/heat exchanger to cool to room temperature followed by contacting with a silica drier to remove water vapour. The HG rate was measured using an online mass flow meter that was equipped with a computer. The HG volume was calculated by integrating the measured HG rate over time. 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 mixture and recorded using an online recorder.

3 Results and Discussion

In the present study, the HG system was composed of alkaline aqueous solution of NaBH₄ and Al/the catalyst powder mixture. Here, the selection of cobalt boride (CoₓB) catalyst was mainly based on its high catalytic activity, low cost, easy preparation and its ferromagneticity that allows ready magnetic separation of the catalyst powder from the spent fuel [23–25]. According to the ICP-AES analysis, the as-prepared catalyst possesses a Co/B atomic ratio of around 2:1, thereby is denoted as Co₂B hereinafter. As seen in Figure 2, the XRD pattern of the catalyst sample displays one broad diffraction peak centred around 2θ = 45°, indicative of its amorphous structure. Figure 3 presents the SEM morphology of the as-prepared Co₂B catalyst. The catalyst particles with an average size of around 100 nm were observed to agglomerate together, which is consistent with the relatively low specific surface area (8.4 m² g⁻¹) as determined by using BET method. But after the HG process, the black catalyst particles were observed to mix highly homogeneously with the grey by-products. Presumably, this is a consequence of the dynamic impact that was generated by the vigorous H₂ bubbles from the fuel solution.

Combined usage of NaBH₄ and Al offers new possibilities for the development of high-performance chemical hydrogen storage systems. Figure 4 presents a comparison of the HG performance among the dual-fuel system and the single-fuel systems containing individual NaBH₄ or Al. In the first trial, we selected a dual-fuel system containing 10 g...
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of aqueous solution (10 wt.-% NaBH₄ + 5 wt.-% NaOH), 1 g of Al powder and 0.1 g of Co₂B catalyst. For comparison purpose, the single-fuel systems were constituted in an identical way to the dual-fuel system except for the presence of NaBH₄ or Al. In all the three systems, vigorous hydrogen release was immediately initiated upon feeding the fuel solution into contact with the solid fuel and/or the catalyst powder. In comparison with the single-fuel systems, the NaBH₄+Al dual-fuel system showed a much higher maximum HG rate, reaching up to ∼1,350 ml min⁻¹. Furthermore, the dual-fuel system exhibited a higher fuel conversion than the Al/H₂O system. Notably, the favourable HG performance of the dual-fuel system was achieved at a much lower H₂O/fuel ratio relative to the single-fuel systems. This clearly means an increase of hydrogen density of the HG system.

The property advantages of the dual-fuel system over the single-fuel systems clearly suggested that there exists a mutual-promoting mechanism between the hydrolysis reaction of NaBH₄ and the Al/H₂O reaction [19]. Fundamentally, it should be understood from the coupling effects as follows: the catalytic hydrolysis of NaBH₄ results in elevated alkalinity of the aqueous solution, and thereby promoting the Al/H₂O reaction through disrupting the passivation layer following Eq. (4). As the highly exothermic Al/H₂O reaction proceeds, the fuel solution temperature is further elevated, which in turn promotes the hydrolysis reaction of NaBH₄. This mechanistic understanding was strongly supported by the measurement results of the reaction temperature. As shown in Figure 4c, the dual-fuel system showed higher reaction temperature than the single-fuel system throughout the HG process.

Al₂O₃ + 2NaOH + 3H₂O → 2NaAl(OH)₄

In an effort to optimize the HG performance of the dual-fuel system, we performed a systematic study of the property dependence of the component parts of the system. Firstly, we examined the effect of alkaline concentration on the HG kinetics and fuel conversion. As shown in Figure 5, increasing the alkaline concentration resulted in consistent increases in both HG kinetics and fuel conversion of the dual-fuel system. But in the parallel studies of the two single-fuel systems, we observed marked opposite effects of NaOH. More exactly, NaOH exerted positive effect on the Al/H₂O system, but negative effect on the hydrolysis reaction of NaBH₄ with the presence of Co₂B catalyst. A combination of these results indicates that the HG process of the dual-fuel system is dominated by the Al/H₂O reaction. Actually, this is quite understandable from comparison of the exothermicity of the Al/H₂O and NaBH₄/H₂O reactions (the reaction enthalpy of the former nearly doubles that of the latter reaction). Once the Al/H₂O reaction is initiated, the released reaction heat causes rapid increase of the fuel temperature, which may compensate the inhibitory effect of high alkaline concentration on the NaBH₄/H₂O reaction. This was further supported by the measurement results of the reaction temperature. As seen in Figure 4c, the reaction temperature profile of the dual-fuel system strongly resembled that of the Al/H₂O system, but differed significantly from that of the NaBH₄ hydrolysis system. In the dual-fuel system containing 10 g of
10 wt.-% NaBH₄ solution and 1 g of Al powder, a 100% fuel conversion was achievable upon increasing the NaOH concentration to 10 wt.-%. Meanwhile, the NaBH₄ aqueous solution containing 10 wt.-% NaOH was stable at room temperature [26]. In an overall consideration of the hydrogen density, fuel conversion, HG rate and shelf life of fuel solution, we selected the dual-fuel system containing 10 wt.-% NaOH for further investigation.

Next, we carried out another set of experiments to evaluate the effect of the Al amount on the HG performance of the dual-fuel system. Figure 6 presents the HG rate and fuel conversion curves of the systems containing varied amounts of Al powder. As expected, increasing the amount of Al powder resulted in increase of HG rate, but decrease of fuel conversion. The former was associated with the increase of reaction temperature; the latter should be ascribed to the transportation limitation in the H₂O-deficient environment. At the late stage of HG process, the slurry-like by-products became the predominant constituent of the system. In the case of deficient H₂O supply, the by-products may fully cover the surface of the catalyst and unreacted Al powder, thereby restraining the HG reactions. In the practical design of the HG system, the amount of Al powder is selected mainly on the basis of the requirement of maximum HG rate. The amount of H₂O is then adjusted to pursue a balance of hydrogen density and fuel conversion.

Finally, we examined the effect of NaBH₄ concentration on the HG performance of the dual-fuel system. From an application point of view, high NaBH₄ concentration is desirable for achieving high hydrogen density. But due to the solubility limitation of NaBO₂ by-product in water, particularly in the presence of alkaline stabilizer, the NaBH₄ concentration is limited to around 12 wt.-% at room temperature [14–16]. Nevertheless, the practical operation of the hydrolysis system may involve higher NaBH₄ concentration since the solubility of NaBO₂ increases with increasing the fuel solution temperature. In this regard, addition of Al powder is clearly of benefit to the increase of NaBH₄ concentration. Figure 6 presents the HG performance of the dual-fuel systems with different NaBH₄ concentrations. It was found that the HG rate increased with increasing the NaBH₄ concentration and reached its maximum of ∼1,600 ml min⁻¹ at a NaBH₄ concentration of 15 wt.-%. Further increasing the NaBH₄ concentration resulted in a decrease of HG rate, which evidently originated from the transportation limitation in the H₂O-deficient environment. Here, it should be noted that the given NaBH₄ concentrations are nominal values for the aqueous solution. After taking the H₂O consumption in the Al/H₂O reaction into account, the actual NaBH₄ concentrations are 25% higher than the given values. It means that the optimal NaBH₄ concentration at the applied experimental conditions is ∼19 wt.-%. Notably, even at such high NaBH₄ concentration, the dual-fuel system fulfilled 97% fuel conversion within
6 min. The achievement of high fuel conversion at high NaBH₄ concentration should clearly be ascribed to the high solution temperature that is associated with the highly exothermic Al/H₂O reaction. According to the online temperature-monitoring results, the maximum solution temperature in the HG process reached up to around 100 °C. These experimental results agree well with the recent thermodynamic modeling study by Shang and Chen [14], which predicted an optimal NaBH₄ concentration of ∼21 wt.-% in the presence of 10 wt.-% NaOH at 100 °C. Here, the slightly lower experimental value of NaBH₄ concentration than the computational value may partially come from the water evaporation in the HG process.

The NaBH₄+Al dual-fuel system exhibited an overall property improvement relative to the NaBH₄-based hydrolysis system. Besides the higher HG rate (Figure 4), the dual-fuel system showed increased fuel conversion and remarkably higher hydrogen density than the NaBH₄ system, as shown in Figure 8. For the system containing 10 g of aqueous solution (25 wt.-% NaBH₄ + 10 wt.-% NaOH), 1 g of Al powder and 0.1 g of Co₂B catalyst, the deliverable hydrogen density reached up to 5.2 wt.-%. This is much higher than the achievable level in the NaBH₄-based hydrolysis systems. Additionally, the dual-fuel system possessed significantly reduced H₂ production cost relative to the NaBH₄ system. For example, addition of 1 g of Al powder to the system containing 10 g of 10 wt.-% NaBH₄ aqueous solution resulted in an around 30% discount of H₂ production cost. The favourable combination of high HG rate, satisfactory fuel conversion, high hydrogen density and reduced H₂ production cost makes the (NaBH₄+Al)/H₂O system promising for mobile/portable hydrogen source applications.

4 Conclusions

A high-performance HG system has been demonstrated, which is composed of alkaline aqueous solution of NaBH₄ and solid powder mixture of Al and Co₂B catalyst. In this system, HG can be readily controlled by regulating the NaBH₄ aqueous solution to contact with the Al powder and catalyst mixture. In comparison with the conventional NaBH₄-based hydrolysis system, the (NaBH₄+Al)/H₂O system exhibited a series of property advantages, such as higher HG rate, increased fuel conversion, higher hydrogen density and reduced H₂ production cost. Fundamentally, the improvements on the HG properties originate from the mutual-promoting mechanism between the hydrolysis reaction of NaBH₄ and the Al/H₂O reaction. In this regard, the detailed studies are still required to further mechanistic understanding of the complicated multi-phase reaction process, which may lay renewed basis for designing practical HG systems for mobile/portable hydrogen source applications.

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