

Preparation and Application of Sodium Borohydride composites for portable hydrogen production

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ABSTRACT: A novel composite consisting of CoB catalyst and NaBH₄ compounded with PEG was prepared for portable hydrogen production. The CoB catalyst was synthesized by the reduction of cobalt salt in NaBH₄ solution followed by heat treatment in nitrogen atmosphere. The catalyst and NaBH₄ were mixed in DMF containing PEG. The resulting mixture gel was then dried and ground into composite powder. The composite powder is stable in dry air and can be easily used for hydrogen production. A rate of hydrogen production of 750 ml/min/g was reached when putting the composite powder into water. The humidified pure hydrogen can be used conveniently for fuel cells.

Keywords: composite, catalyst, NaBH₄, hydrogen production, CoB

1. INTRODUCTION

The rapid development of fuel cell technology introduces an efficient and high density power source which is a competitive alternative to secondary batteries [1]. However, the requirement of pure and safe hydrogen on demand supplying for triggering electricity in fuel cells is a bottleneck [2].

In order to solve this problem, many strategies were developed including hydrocarbon reforming [3, 4] and hydrolysis of chemical hydride [5]. Reforming of hydrocarbon, such as methane [6] and ethanol [7, 8], is usually processed at temperature high than 200 °C even using catalysts, in which external heat is required. Furthermore, gases that are poisonous to the fuel cells, such as CO, are produced together with hydrogen gas. Separation of these gases by metal membranes definitely

increases the cost of hydrogen production by hydrocarbon reforming.

Hydrolysis of chemical hydrides, such as NaAlH₄ [9], NaBH₄ [10], and NH₃BH₄ [11], paved a new way for producing hydrogen with high purity since only hydrogen and water vapor are produced in the gaseous product. The water vapor can be removed easily and sometimes the humidified hydrogen is fueled into the fuel cells directly without further purification. However, chemical hydrides, for instance, NaBH₄, have their own disadvantages: 1) in practical application, it should be dissolved in alkaline solution for averting self hydrolysis, making it inconvenient for storage and transportation, 2) the saturated solution has a concentration lower than 40 wt %, which limits its hydrogen density as a hydrogen storage material, and 3) the by-products NaBO₂ tends to attach to the surface of catalysts which deactivates the catalysts.

To overcome the problems mentioned above, many strategies were used for preparation of novel composite materials for hydrogen production. NaAlH₄ impregnated in ordered mesoporous silica was synthesized and used for hydrogen storage materials [12]. However, dehydrogenation of the materials needs a temperature higher than 150 °C or a higher pressure. Sodium borohydride gel was prepared by adsorption of NaBH₄ solution using super absorbent polymer [13]. Hydrogen can be produced by mixing this gel with catalyst solution. Unfortunately, the gel tended to slowly decompose in open air and limited its use. In this study, sodium borohydride composites were prepared using two methods. Method I is directly mixing CoB catalyst and NaBH₄ in DMF with PEG. Method II is confining CoB catalyst in alginate beads and mixed with NaBH₄ in DMF solution with or without PEG. The composites prepared can be easily used by adding it into water and the hydrogen production reaction proceeded instantaneously at room temperature. The composite can be kept in sealed container to separate it from vapour in air. Thus it can be more conveniently stored and transported than NaBH₄ stored in alkaline aqueous solution.

2. Experimental

2.1 Synthesis of CoB-NaBH₄ composites

The CoB catalysts were prepared by directly reducing cobalt chloride with NaBH₄-NaOH alkaline solution followed by heat treatment at 300 °C in a nitrogen atmosphere with a nitrogen flow rate of 2 L/min for 2 hours [14]. 10 mg dried CoB catalyst was added to 10 ml dried DMF solution containing 1.0 g sodium borohydride and varying amounts (0, 0.5, and 1.0 g) of PEG (M_w 1500). After stirring for 10 hours, a homogenous solution was obtained and put into evaporation oven at 60 °C to make a gel. The mixed gel was dried in vacuum oven at 90 °C to remove the

excess solvent DMF. The resulting composite powder was ground and kept in sealed vials until further use. The samples and their corresponding components are shown in Table 1.

Varian 2000 FT-IR was used to obtain the spectrum of each component and each type of composite. Each spectrum was acquired by signal averaging 32 scans at a resolution of 8 cm⁻¹ in transfer mode by pressing the sample with KBr to a pellet. The thermal degradation of all components and the composites were measured using TGA (TG/DSC 92) by heating the samples from 60 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.2 Preparation of CoB/Alginate beads

Alginate solution (1.5 wt.%) containing CoB (0.5 wt.%) was mixed by stirring at room temperature. The mixture was excluded out to 80 mM CaCl₂ solution using a syringe pump. The alginate was crosslinked by the calcium ions and the beads containing CoB were formed. The formed beads were cured in the CaCl₂ solution for 24 hours and then dried in vacuum oven at room temperature. The capacity of swelling of the dried beads in water and DMF were examined by immersing the beads in the solvent for 24 hours. The images of the beads were obtained using optical microscope.

The beads were mixed with NaBH₄ in DMF solution with or without PEG. The mixture was dried in vacuum oven to remove the solvent. The obtained powder was used for hydrogen production.

2.3 The performance of composite powder for hydrogen production

The performance of hydrogen production of the composites powder prepared by method I was tested by putting the composites into water with stirring at 25 °C. The amount of hydrogen produced over time was recorded using water replacement method as previously reported [15]. As a comparison, 10 mg CoB catalyst directly

mixed with 1 g NaBH₄ and varying amounts of PEG (0, 0.5, and 1.0 g) in water was also used for hydrogen production using the same conditions. The performance and composition of the samples are shown in Table 1. Composite prepared by method II was also used to prepared hydrogen using the same method described above.

Table I: components and performance of the composites and mixtures.

Sample	Composition (percent to NaBH ₄)	Rate of hydrogen production (ml/min/g catalyst)
Composite 1	NaBH ₄ + 1% CoB	647.9
Composite 2	NaBH ₄ + 1% CoB + 50% PEG	651.9
Composite 3	NaBH ₄ + 1% CoB + 100% PEG	751.3
Mixture 1	NaBH ₄ + 1% CoB	522.8
Mixture 2	NaBH ₄ + 1% CoB + 50% PEG	526.6
Mixture 3	NaBH ₄ + 1% CoB + 100% PEG	509.6

3. RESULTS AND DISCUSSION

3.1 The performance of composite powder prepared by method I for hydrogen production

Figure 1 shows the FTIR spectra of the components and composites. As shown in curve (a), the CoB catalyst has no characteristic peaks except a broad peak at around 1445 cm⁻¹. Curve (b) shows the characteristic absorption of pure PEG polymers. A peak at 3420 cm⁻¹ was due to O-H stretching vibration while the peak at

2885 cm⁻¹ was due to an alkyl C-H stretching vibration. Moreover, the peaks at 1467 cm⁻¹ and 1351 cm⁻¹ were attributed to C-H vibration of in plane scissoring and deforming, respectively. The asymmetric stretching vibration of C-O-C can be seen at 1114 cm⁻¹ and the C-C skeletal vibration is located at 963 cm⁻¹ and 841 cm⁻¹ [16]. The FTIR spectra of NaBH₄ are shown in curve (f), wherein a peak at 2294 cm⁻¹ was assigned for the vibration of BH₄⁻ ion. The vibration of BH stretches and BH₂ bends can be seen at 2223 cm⁻¹ and 1121 cm⁻¹ respectively [17]. Curve (e) is similar to curve (f) since the components of the two samples are similar except for catalytic amount of CoB that was added in Composite 1 for curve (e). Curves (c) and (d) are the FTIR spectra of Composite 2 and Composite 3. Both composites have peaks at 2885 cm⁻¹ and 2294 cm⁻¹ due to C-H stretching in PEG and BH₄⁻ vibration in NaBH₄ respectively. The ratio of these two peaks as seen in curve (d) is 0.5, and it increases to 0.8 in curve (c) as the ratio of PEG to NaBH₄ increases from 0.5 to 1 from Composite 2 to Composite 3.

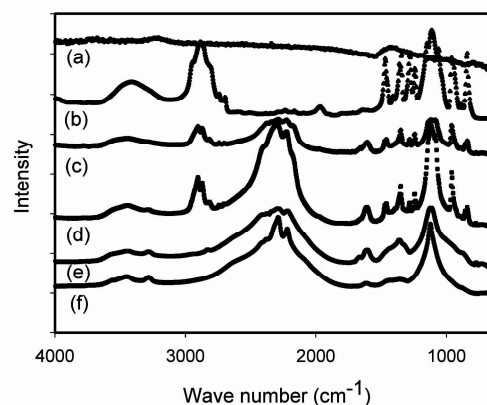


Figure 1: FTIR spectra of (a) CoB catalyst, (b) PEG, (c) Composite 3, (d) Composite 2, (e) Composite 1, and (f) NaBH₄.

The performance of the composites and mixtures for hydrogen production are shown in Figure 3. All of the mixtures have a rate of hydrogen production of around 520

ml/min/g regardless of the amount of PEG it presents. This result confirmed the addition of PEG in the mixture has no effect on the hydrogen production reaction. However, the rates of hydrogen production of the composites, which can reach to 650 ml/min/g, are much higher than those of the mixtures, as shown in Table 1 and Figure 3. The difference of hydrogen production rate between the composite and mixture was due to the better distribution of the catalyst in the composite than that in the mixture. Moreover, the amount of PEG added in the composites influenced the performance of the samples. In Composite 3, the rate of hydrogen production reached 751 ml/min/g. The increasing hydrogen production rate with the addition of PEG in the composite can be attributed to the formation of a complex between PEG and the catalyst during the preparation of the composites. The formed complex is helpful for preventing the aggregation of the catalysts and the adsorption of the byproduct NaBO_2 on the surface of the catalysts.

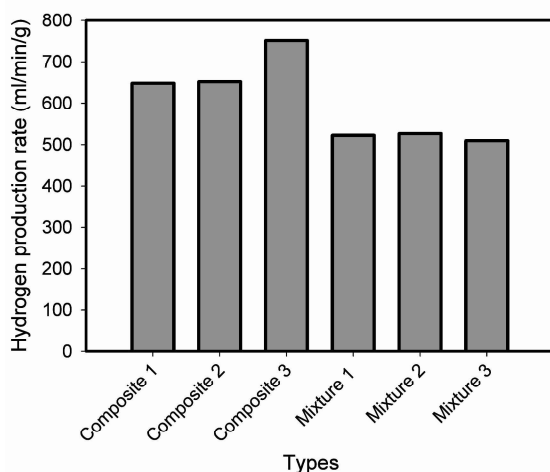


Figure 2: Hydrogen production rate of the composites and mixtures

3.2 The performance of composite powder prepared by method II

The capacity of swelling of the dried beads in water and DMF was measured by weighting the mass of the beads before and after immersing in the solvent for 24 hours.

As shown in Table 2, the beads swelling in water is reversible and the weight can be reached 10 times of its dry weight. This swelling capability makes the transition of reactants easy when the CoB/Alginate beads are used for hydrogen production. While the swelling of the beads in DMF is impossible since DMF is a bad solvent for alginate. And because of the lost of CoB catalysts, the bead in DMF has a swell ratio less than 0.

Table II: capacity of swelling of CoB/alginate beads in water and DMF.

Solvent	Water	DMF
Solvent uptake	950%	-7.2%

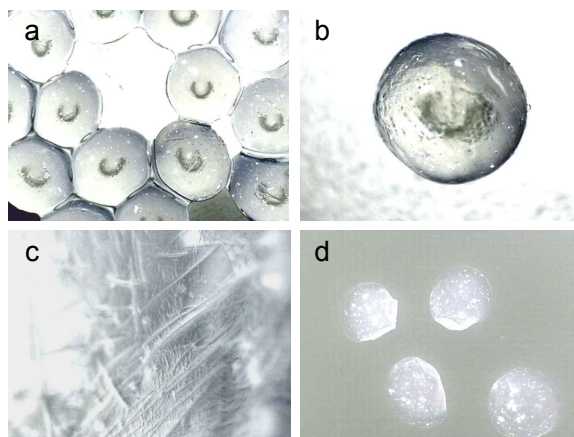


Figure 3: optical images of CoB/alginate beads in wet (a) 10 $\times$, (b) 20 $\times$, (c) 100 $\times$ and dry state (d) 20 $\times$.

The images of the CoB/alginate beads were shown in figure 3. Figure 3 (a), (b), and (c) showed the wet beads in different magnification. As we can see the beads in wet states has round sharp with a loose surface which makes NaBH_4 can be easy to transfer into the beads when they are added in NaBH_4 solution. Furthermore, the alginate polymer chains in the beads play a role as a barrier for the reactant as well as the by-products NaBO_2 . Although it would decrease the rate of hydrogen production, it is helpful to extent the activity of the catalysts since it hinders the adsorption of NaBO_2 on to the surface of the catalysts.

Figure 3 (d) showed the beads in dry state with a volume shrink and distortion of round sharp.

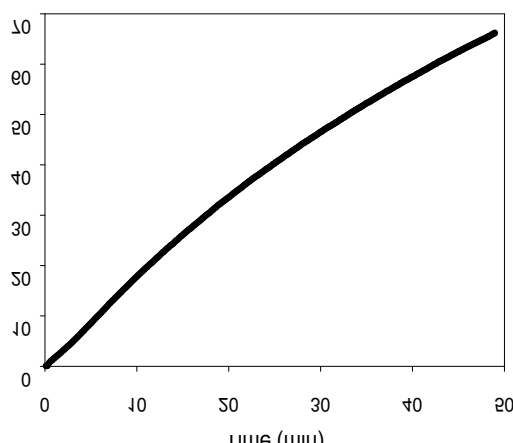


Figure 4: Hydrogen production using composite prepared by method II (0.01 g CoB/alginate bead mixed with 0.2 g NaBH₄ and 0.2 g PEG in DMF)

The performance of the NaBH₄-CoB/alginate beads composites prepared by method II was also obtained by adding the composites in water for hydrogen production. Unfortunately, the rate of hydrogen production is much lower than that of the composite prepared by method I. But the hydrogen production keeps stable as the hydrogen volume is a linear function as time as shown in Figure 4. The reason can be contributed to the confine of the CoB catalyst in the alginate beads.

4. CONCLUSION

On demand hydrogen production can be made available by putting a novel composite into water with a rate of hydrogen production of 750 ml/min/g at room temperature. Two methods were used to prepare the composites containing CoB catalyst, sodium borohydride, alginate beads and PEG. The composite can be prepared by simply mixing, annealing and grinding. The prepared composite is stable in dry air, which makes it easier to be stored and transported.

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