Preparation of Catalyst for Hydrogen Production Reaction of Sodium Borohydride and Its Effectiveness

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The fundamental purpose of this study is to produce a catalyst for catalyzing the hydrogen production reaction of sodium borohydride (NaBH$_4$). The catalyst for catalyzing this reaction includes a catalyst carrier and a metal catalyst. We use three catalyst bed temperatures with the same γ-Al$_2$O$_3$ carrier and gas sensor, with different chelate concentration processes to make the catalyst. The metal catalyst selected is Co. The effects of the catalyst produced by different catalyst carrier processes on the hydrogen production efficiency and total hydrogen yield of NaBH$_4$ solution are discussed. The experiment shows that when the catalyst soaked in 30 wt% Co/γ-Al$_2$O$_3$ is used at 70 °C, the rate and hydrogen production efficiency are 5300 ml/min g cat and 82.92%, respectively. The catalyst has a vigorous hydrolytic hydrogen production reaction with NaBH$_4$. This catalyst can be combined with a fuel cell system for hydrolytic hydrogen production to generate power in the future, enabling the portability and efficiency of stored hydrogen to be enhanced effectively.

1. Introduction

In recent years, with the development of the hydrogen–oxygen fuel cell, many scholars have studied hydrogen storage. The present hydrogen storage techniques are divided into six main classes, which are compression hydrogen storage, liquefaction hydrogen storage, carbon nanotubes, metal hydrogen storage, recombination hydrogen storage, and chemical hydrogen storage.[1] In comparison with other hydrogen storage techniques, chemical hydrogen storage has high volume energy density and high weight energy density, the hydrogen production rate can be adjusted only by using the catalyst, and the conversion efficiency is high.[2–4] Sodium borohydride (NaBH$_4$) has been paid close attention as a material for chemical hydrogen storage owing to its high hydrogen content (10.8 wt%), its stability in an alkaline liquid and nonflammability, and its controllable, environmentally benign, and renewable hydrolysis reaction.[5,6] With an appropriate catalyst, NaBH$_4$ is hydrolyzed into hydrogen and NaBO$_2$, where the equation is expressed as[7]

$$\text{NaBH}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{catalyst}} 4\text{H}_2 + \text{NaBO}_2 + 217 \text{ kJ}. \tag{1}$$
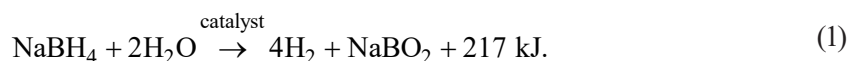
The hydrogen production rate of the hydrolysis reaction of NaBH_4 is related to the metal catalyst applied. The common metal catalysts are Fe, Co, Ni, Ru, Rh, and Pd chlorides, but an aqueous solution of partial metal chlorides reduces the hydrolytic hydrogen production reaction rate.[8] Kreevoy[9] found that pH and temperature had a significant effect on the autohydrolytic hydrogen production rate of NaBH_4 in water. The hydrolytic hydrogen production rate of NaBH_4 at ambient temperature is very low for alkaline byproducts and can be increased effectively by changing the pH and temperature. Kojima *et al.*[10] made a Pt/LiCoO_2 catalyst of multiple metal oxide carriers. Although the metal catalyst was not a metal chloride compound, the carrier supported the metal catalyst. However, these metal catalysts are expensive and rare metals or have little catalytic effect and low economic efficiency, making them inapplicable to mass production in the future. Ye *et al.*[11] found that an $\alpha\text{-Al}_2\text{O}_3$-loaded Co catalyst was very effective owing to its special structure. They used a $\text{Co}/\beta\text{-}\alpha\text{-Al}_2\text{O}_3$ catalyst with 9% catalyst by weight at an ambient temperature of 303 K, and a rate of 220 $\text{mL/min}^{-1}\text{g}^{-1}$ catalyst and about 100% hydrogen production rate were obtained at 303 K. Ke *et al.*[12] found that the rate of the hydrolytic hydrogen production reaction catalyzed by a Co-B catalyst modified by Mo was 4200 ml/min H_2 and indicated that the hydrolytic hydrogen production reaction rate depended on the amount of NaBH_4 adsorbed on the catalyst surface. In addition, the interaction between NaBH_4 and water doubles the hydrogen yield; the reducing reaction of water protons increases the hydrogen yield.[13]

In this paper, we design a low-cost catalyst for catalyzing the hydrolytic hydrogen production reaction of NaBH_4, which uses a catalyst carrier to load a metal catalyst. The effects of the produced catalyst on the hydrogen production efficiency and total hydrogen yield of the hydrolytic hydrogen production reaction of NaBH_4 are discussed.

2. Materials and Methods

2.1 Design of catalyst production

To design a catalyst for catalyzing the hydrolytic hydrogen production reaction of NaBH_4, we use the process designs and production methods proposed by previous scholars as a reference frame. Kim *et al.*[14] used $\gamma\text{-Al}_2\text{O}_3$ as a catalyst carrier, which was soaked in CoCl_2 solution to load the metal catalyst Co, baked at 350 °C for 3 h, and then reduced. The produced catalyst $\text{Co/Al}_2\text{O}_3$ had a maximum hydrogen production efficiency of 1071 ml/min when the NaBH_4 solution input rate was 3 ml/min. Hsueh *et al.*[15] used AMBERLITE IR–120 PLUS ion-exchange resin (sodium form) as a catalyst carrier, which was soaked in RuCl_3 solution to load the metal catalyst Ru and baked at 80 °C. The produced catalyst Ru/IR–120 had a maximum hydrogen production efficiency of 132 ml/min g cat for NaBH_4 solution at 25 °C and a concentration of 5 wt% NaBH_4+1 wt% NaOH. The low-cost and convenient catalyst carrier $\gamma\text{-Al}_2\text{O}_3$ was used in the references. As a metal catalyst, Kim *et al.*[14] used the non-noble metal

chloride compound $CoCl_2$. In this study, we design a catalyst for catalyzing the hydrolytic hydrogen production reaction of $NaBH_4$ that has the aforementioned catalyst production characteristics. γ-Al_2O_3 is used as a catalyst carrier in this study, with the non-noble metal chloride compound $CoCl_2$. The metal catalyst Co is loaded on the γ-Al_2O_3 catalyst carrier, and different baking temperatures are used for different catalyst carriers.

2.2 Catalyst preparation process

The catalyst carrier used in this study is γ-Al_2O_3, as shown in Fig. 1. The production of the catalyst for catalyzing the hydrolytic hydrogen production reaction of $NaBH_4$ depends on the characteristics of the catalyst carrier.

2.2.1 Production of Co^{2+}/Al_2O_3 catalyst

In the production of the Co^{2+}/Al_2O_3 catalyst, γ-Al_2O_3 is cleaned with DI water and baked in a vacuum oven at 120 °C for 4 h to remove moisture. The oven-dried γ-Al_2O_3 is soaked in 10, 20, or 30 wt% $CoCl_2$ solution for 24 h, so that the Co in $CoCl_2$ solution fully adheres to γ-Al_2O_3, and then the redundant $CoCl_2$ solution is filtered, as shown in Fig. 2. Finally, the γ-Al_2O_3 from the filtered $CoCl_2$ solution is heated in vacuum at 120 °C for 6 h to obtain the catalyst Co^{2+}/Al_2O_3, as shown in Fig. 3.

Fig. 1.   (Color online) Catalyst carrier Al_2O_3.

Fig. 2.   (Color online) γ-Al_2O_3 from filtered $CoCl_2$ solution.

(a)   (b)   (c)

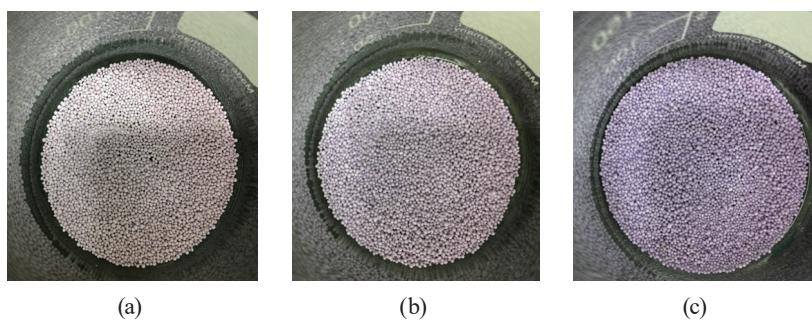Fig. 3.   (Color online) γ-Al_2O_3 from $CoCl_2$ solutions at different concentrations. (a) 10 wt%, (b) 20 wt%, and (c) 30 wt%.

2.3   Experimental setup for evaluating hydrogen production efficiency

The experimental setup for evaluating hydrogen production efficiency is shown in Fig. 4. The NaBH$_4$ solution with a concentration of 10 wt% NaBH$_4$+1 wt% NaOH is injected into the hydrogen production container, and then the catalyst is placed in it to generate hydrogen. The hydrogen flows through the gas-drying tower, and the hydrogen mass sensor reads the hydrogen production efficiency and total hydrogen yield of various catalysts. Finally, the flow recording program records the hydrogen production efficiency and total hydrogen yield. When the reading of the hydrogen mass sensor is zero, the experiment is terminated and recording is stopped.

2.3.1   Hydrogen production container

In the initial experiment, as general conical flasks cannot be used to control the catalyst bed temperature, a special two-layer hydrogen production reaction container is made. The inner layer is the hydrogen production reaction chamber and the outer layer is the insulating layer, the water temperature in which controls the catalyst reaction temperature. The catalyst bed temperature can be controlled by this design during the experiment.

2.3.2   Gas filter flask

In addition to pure hydrogen, the hydrogen generated in the hydrogen production container contains fine water globules and water vapor; thus, an instrument for removing the moisture is required. We use a gas filter flask to remove the moisture in the gas. A silica-gel dryer is placed in the gas filter flask to adsorb the moisture in the mixed gas of hydrogen and water vapor generated in the hydrogen production container, so as to purify the hydrogen. As a result, the hydrogen mass sensor only reads the mass flow of hydrogen.

Fig. 4.   (Color online) Experimental setup for evaluating hydrogen production efficiency: (a) hydrogen production container, (b) gas filter flask, (c) hydrogen mass sensor, (d) catalyst bed flow pump, and (e) catalyst bed constant temperature water tank.

2.3.3 Hydrogen mass flowmeter and mass flow recording program

The flowmeter used in this study can read and display the hydrogen mass flow through the hydrogen mass sensor, and can obtain the cumulative total hydrogen volume through the hydrogen mass sensor. The hydrogen mass flow and cumulative total hydrogen volume are recorded once per second by setting the mass flow recording program.

3. Experimental Results

3.1 Test for hydrogen production efficiency of Co^{2+}/Al_2O_3 catalyst

Table 1 shows the Co/Al_2O_3 catalyst manufacturing parameters: the three chelate concentrations are 10, 20, and 30%, the three chelate soaking times are 24, 36, and 72 h, the bake-out period is 6 h, the baking temperature is 120 °C, the drying time after the alumina is cleaned is 4 h, and the hydrogen production container is filled with 5.56 g of 10 wt% $NaBH_4+1$ wt% NaOH. The experimental measurement data are shown in Fig. 5. The hydrogen production rates of catalysts at 25 °C are compared. The experimental measurement data show that the 30 wt% catalyst has the highest hydrogen production rate and the 10 wt% catalyst has the lowest efficiency. Table 2 shows the experimental hydrogen production rates. It is observed that the 30 wt% Co/Al_2O_3+2 wt% NaOH has the highest efficiency. The experimental measurement data in Fig. 6 show the hydrogen production rates of the catalysts at 25 °C. These data also show

Table 1
Co/Al_2O_3 catalyst condition parameters.

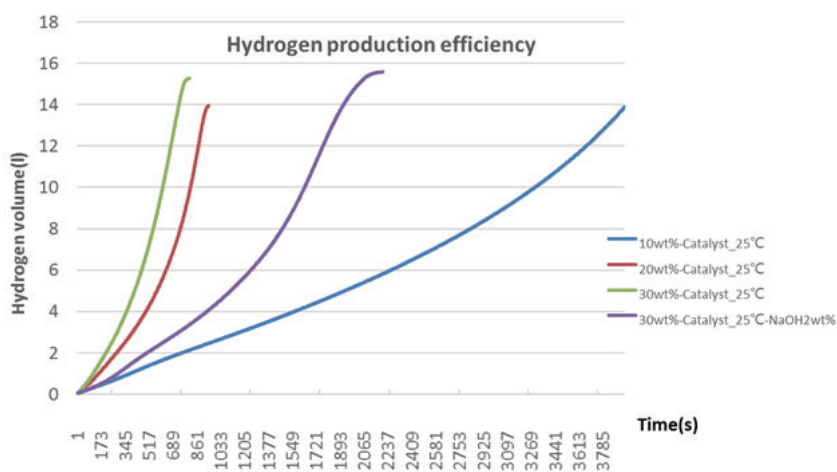| Experimental conditions	Chelate $CoCl_2$ concentration (wt%)	Chelate $CoCl_2$ soaking time (h)	Drying time (h)	Baking temperature (°C)	Al_2O_3 oven-drying dewatering time (h)
1	10	24	6	120	4
2	20	48	6	120	4
3	30	72	6	120	4

Fig. 5.   (Color online) Hydrogen production rates at Co/Al_2O_3 catalyst bed temperature of 25 °C.

Table 2
Hydrogen production rates as percentages when Co/Al_2O_3 catalyst bed temperature is 25 °C.

Experimental conditions	Total hydrogen yield (L)	Theoretical hydrogen production rate (L)	Hydrogen production rate (%)
10 wt%+NaOH_1wt%	13.898	15.605	89.06
20 wt%+NaOH_1wt%	13.952	15.605	89.4
30 wt%+NaOH_1wt%	15.281	15.605	97.92
30 wt%+NaOH_2wt%	15.585	15.605	99.87
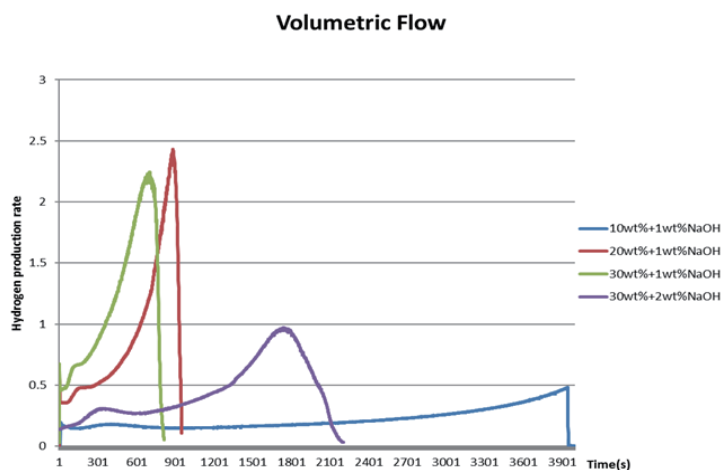
Fig. 6.   (Color online) Hydrogen production rates at Co/Al_2O_3 catalyst bed temperature of 25 °C.

that the 20 wt% catalyst has the highest hydrogen production rate with a maximum hydrogen production efficiency of 2434 ml/min g cat, the total hydrogen yield is 14.01 L, and the 10 wt% catalyst has the lowest hydrogen production rate.

According to the maximum hydrogen production efficiency of three chelate concentrations, the maximum hydrogen production efficiency and the hydrogen production rate increase significantly when the chelate concentration is increased. When the NaOH concentration is increased from 1 to 2 wt%, the hydrogen production rate is significantly reduced, but the hydrogen production efficiency is increased to 99.87%.

3.2   Test for hydrogen production efficiency of Co^{2+}/Al_2O_3 catalyst on 65 °C catalyst bed

The hydrogen production container is filled with 1.5 g of 10 wt% $NaBH_4$+1 wt% NaOH. The experimental measurement data in Fig. 7 show the catalyst hydrogen production rates when the catalyst bed temperature is 65 °C. These data also show that the 20 wt% catalyst has the highest hydrogen production rate and that the 30 wt% catalyst has the lowest hydrogen production rate. Table 3 shows a comparison of hydrogen production rates. The maximum hydrogen production rate is 99.13% when the concentration is 20 wt%. The experimental measurement data in Fig. 8 show the catalyst hydrogen production rates at 65 °C. These data also show that the 30 wt% catalyst has the highest hydrogen production rate with a maximum hydrogen production efficiency of 5300 ml/min g cat and that the 10 wt% catalyst has the lowest hydrogen production rate.
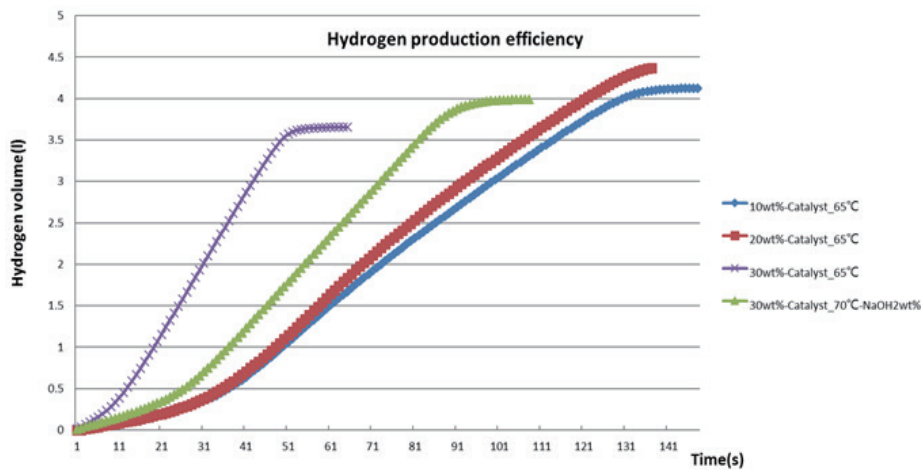
Fig. 7.   (Color online) Hydrogen production rates at Co/Al$_2$O$_3$ catalyst bed temperatures of 65 and 70 °C.

Table 3
Hydrogen production rates as percentages at Co/Al$_2$O$_3$ catalyst bed temperatures of 65 and 70 °C.

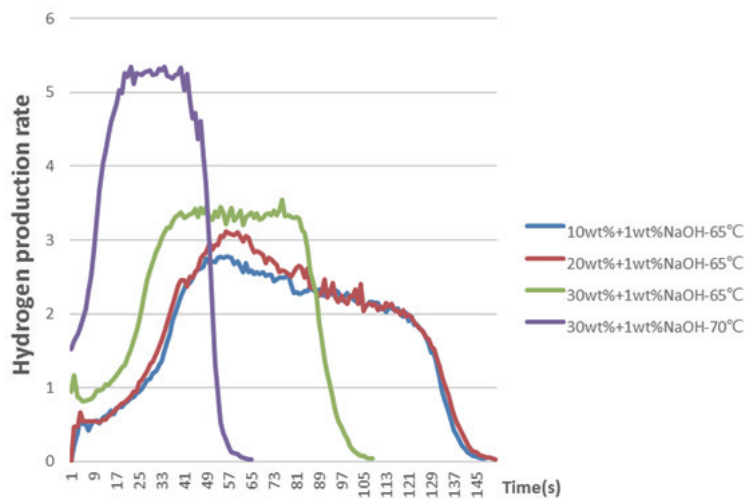| Experimental conditions	Total hydrogen yield (L)	Theoretical hydrogen production rate (L)	Hydrogen production rate (%)
10 wt%–65 °C	4.125	4.408	93.58
20 wt%–65 °C	4.37	4.408	99.13
30 wt%–65 °C	3.991	4.408	90.54
30 wt%–70 °C	3.655	4.408	82.92

Fig. 8.   (Color online) Comparison of hydrogen production rates at Co/Al$_2$O$_3$ catalyst bed temperatures of 65 and 70 °C.

By comparing the maximum hydrogen production efficiency and hydrogen production rate at the two catalyst bed temperatures, it was observed that the temperature rose to 70 °C. However, a very drastic hydrolysis reaction gasifies the water solution, reducing the hydrogen production rate.

4. Discussion

We use γ-Al_2O_3 to load the non-noble metal catalyst Co with three catalyst bed temperatures (25, 65, and 70 °C) and three chelate concentrations (10, 20, and 30 wt%) to produce a catalyst for catalyzing the hydrolytic hydrogen production reaction of NaBH4, and we test the hydrogen production efficiency of the $NaBH_4$ solution at the same concentration of 10 wt% $NaBH_4$+1 wt% NaOH.

The results of comparing the catalyst efficiencies are summarized as follows:

(1) In comparison with the catalyst produced by Kim *et al.*,[14] high-temperature calcination is not required, and the hydrogen production efficiency remains good after the baking temperature is reduced. Lowering the baking temperature also reduces the time and increases the convenience of production.

(2) The catalyst carrier is γ-Al_2O_3, and the metal catalyst soaking time is extended from 24 to 72 h, so that the catalyst can produce more hydrogen within the same time.

(3) Hsueh *et al.*[15] used $RuCl_3$ as the raw material of the metal catalyst. The non-noble metal chloride $CoCl_2$ used as the raw material in this study is 10 times less expensive than $RuCl_3$, allowing more catalyst to be produced at the same cost.

(4) The hydrogen production efficiencies obtained in this study are shown in Fig. 8. It is clear that the hydrogen production efficiency of the catalyst carrier at a chelate concentration of 30 wt% is higher than those at other chelate concentrations, and that the Co^{2+}/Al_2O_3 catalyst with a catalyst bed temperature of 70 °C has the maximum hydrogen production rate of 5300 ml/min g cat.

(5) The hydrogen production efficiency of the Co^{2+}/Al_2O_3 catalyst at a chelate concentration of 10 wt% is lower than that of the catalyst of the same catalyst carrier under different conditions. Because this batch of the catalyst has a lower chelate concentration and a shorter chelation time, Co^{2+} cannot adhere to the catalyst surface effectively during chelation, which may reduce the content of the metal catalyst on the catalyst carrier surface. The chelate concentration and time will be optimized in future work.

5. Conclusion

The non-noble metal catalyst Co is loaded on a γ-Al_2O_3 catalyst carrier, then subjected to Table 1 manufacturing to produce a catalyst for catalyzing the hydrolytic hydrogen production reaction of $NaBH_4$. The catalyst is added in 10 wt% $NaBH_4$+1 wt% NaOH solution to generate hydrogen. According to the experimental results, the Co^{2+}/Al_2O_3 catalyst with a chelate concentration of 30 wt% has the maximum hydrogen production rate of 5300 ml/min g cat at a catalyst bed temperature of 70 °C, and the Co^{2+}/Al_2O_3 catalyst with a chelate concentration of 20 wt% has the maximum hydrogen production rate of 99.13% at a catalyst bed temperature of 65 °C. This catalyst is characterized by convenient production and a low cost, and it is expected to contribute to reducing the cost of hydrogen production from $NaBH_4$.

Acknowledgments

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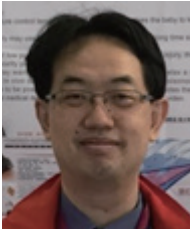
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