



Short communication

Carbon-supported cobalt catalyst for hydrogen generation from alkaline sodium borohydride solution

Dongyan Xu^{a,*}, Ping Dai^b, Xinmin Liu^a, Changqing Cao^a, Qingjie Guo^a^a College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China^b College of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao 266061, PR China

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ABSTRACT

Low cost transition metal catalysts with high performance are attractive for the development of on-board hydrogen generation systems by catalytic hydrolysis of sodium borohydride (NaBH_4) in fuel cell fields. In this study, hydrogen production from alkaline NaBH_4 via hydrolysis process over carbon-supported cobalt catalysts was studied. The catalytic activity of the supported cobalt catalyst was found to be highly dependent on the calcination temperatures. The hydrogen generation rate increases with calcination temperatures in the range of 200–400 °C, but a high calcination temperature above 500 °C led to markedly decreased activity. X-ray diffraction patterns reveal that the catalysts experience phase transition from amorphous Co-B to crystalline cobalt hydroxide with increase in calcination temperatures. The reaction performance is also dependent on the concentration of NaBH_4 , and the hydrogen generation rate increases for lower NaBH_4 concentrations and decreases after reaching a maximum at 10 wt.% of NaBH_4 .

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1. Introduction

Recently, there is a growing demand on the power systems for portable electronic equipments both in the consumer market and the military fields [1,2]. In this regard, proton exchange membrane (PEM) fuel cell is viewed as a viable option to satisfy these demands. However, one major issue encountered in the large-scale application of portable PEM fuel cell is the storage and supply of hydrogen, which is at least as important as the fuel cell performance. Hydrogen can be stored in tanks as compressed or liquefied H_2 , in hydrogen storage alloys, and on activated carbon or nanoscale materials such as carbon nanotubes. Unfortunately, their volumetric and gravimetric efficiency are still too low to meet the requirements, whereas on-board hydrogen generation is becoming increasingly important as a potential route to supply hydrogen for the PEM fuel cell.

Considerable efforts have been focused on the hydrogen generation via the direct pyrolysis or hydrolysis of various metal hydrides because of the potential feasibility for PEM fuel cell applications [3]. Among these methods, the hydrolysis of sodium borohydride (NaBH_4) is particularly attractive owing to its various advantages [4], including the excellent stability of its alkaline solution, and its high theoretical hydrogen content (10.8 wt.%),

which offers the most promise for meeting the technical target of 6 wt.% hydrogen capacity set by U.S. Department of Energy (DOE) [5]. On demand, high-purity hydrogen can be released controllably by the hydrolysis of alkaline NaBH_4 solution in the presence of appropriate catalysts under ambient conditions. The only disadvantage of this process is the high cost of NaBH_4 feed. However, this deficiency can be partially overcome by regenerating the by-product of the hydrolysis reaction, NaBO_2 , to NaBH_4 [6].

To inhibit the self-hydrolysis reaction, NaBH_4 solutions are usually maintained as a strong alkaline solution by adding NaOH , meaning that the hydrogen generation performance from hydrolysis of alkaline NaBH_4 is dependent on the usage of catalysts to a great extent. Up to now, the most studies on hydrolysis catalysts are mainly centered on nickel borides [7], cobalt borides [8], precious metals supported on anionic exchange resin [9], and LiCoO_2 [10]. It is known that active carbon is very stable in strong basic and acid environments, and that it possesses high specific surface area which is particularly beneficial to the dispersion of active components. The active carbon-supported platinum catalyst has been demonstrated as an effective catalyst for hydrolysis of alkaline NaBH_4 solution in our previous study [11]. Considering the high cost and limited availability of noble metals, it is more practical from the industrial standpoint to develop non-precious catalysts with superior activity and durability. In this study, the active carbon-supported cobalt catalyst was prepared by impregnation-chemical reduction method. The structure of the as-prepared catalysts and

* Corresponding author. Tel.: +86 532 84022506; fax: +86 532 84022757.
E-mail address: xdy0156@sina.com.cn (D. Xu).

the kinetic behavior of the hydrolysis reaction over these catalysts are discussed.

2. Experimental

2.1. Catalyst preparation

Analytical reagent grade cobalt nitrate and sodium borohydride were used without further purification. All the catalysts were prepared by impregnation-chemical reduction method. In a typical preparation procedure, a certain amount of commercial active carbon (BET surface area $1055 \text{ m}^2 \text{ g}^{-1}$, 20–40 mesh) was impregnated with an aqueous solution of cobalt nitrate. After drying at 100°C for 12 h, a certain amount of 5 wt.% NaBH_4 –5 wt.% NaOH solution was dropped into the catalyst precursor. Then, the sample was filtered, washed with distilled water several times, and dried at 100°C for 10 h. At last, the catalysts were calcined under nitrogen atmosphere at 200, 300, 400, and 500°C , respectively. The cobalt loadings in the as-prepared catalysts are 10 wt.%.

2.2. Catalyst characterization

Powder X-ray diffraction patterns of the as-synthesized catalysts were obtained with a D8 ADVANCE X-ray diffractometer using $\text{Cu K}\alpha$ radiation operating at 40 kV and 50 mA. The angle extended from 10 to 90° and varied with a step of 0.05° . Transmission electron microscopy (TEM) analyses were carried out with a JEM-1200EX microscope, operating with an accelerating voltage of 100 kV.

2.3. Catalyst testing

The kinetic studies with as-prepared catalysts were carried out in batch operation and a 50 ml three-necked round-bottom flask was used as the reactor. The left-neck port was equipped with a thermometer inserted into the solution to monitor the temperature, and the middle-neck port was fitted with an outlet to collect the evolved hydrogen gas. In a typical hydrogen generation experiment, 10 ml 5 wt.% NaBH_4 –5 wt.% NaOH solution was initially put into the flask. The hydrolysis reaction was initiated by dropping an amount of catalyst (0.25 g) into the solution quickly through the right-neck port of the flask. The flask was immersed in a water bath to maintain the temperature at relatively constant value. During the reaction, a wet gas meter was used to measure the cumulative volume of the generated hydrogen over time. Because the evolved hydrogen can facilitate the contact between the reactant and the catalysts, no further stirring was adopted during the reaction.

3. Results and discussion

XRD profiles of the prepared catalysts calcined at different temperatures are shown in Fig. 1. In Fig. 1a and b, XRD patterns of the catalysts calcined at 200 and 300°C present broad and diffuse peaks at 25.0° , 36.6° , and 44.3° . The peak centered at $2\theta = 25.0^\circ$ is ascribed to active carbon, and the broad peaks at 36.6° and 44.3° may be caused by amorphous form of Co–B [12,13]. As to the catalyst samples calcined at 400 and 500°C , the XRD patterns (Fig. 1c and d) exhibit quite different diffraction characteristics. One obvious change is that the broad and diffuse peaks of Co–B have disappeared. It was reported that the decomposition of the Co–B amorphous alloy can occur with heat treatment above 300°C [8]. Consequently, the results shown in Fig. 1 indicate that the amorphous Co–B underwent decomposition at calcination temperatures above 400°C . However, no peaks corresponding to metallic cobalt was detected with the decomposition of Co–B because of the

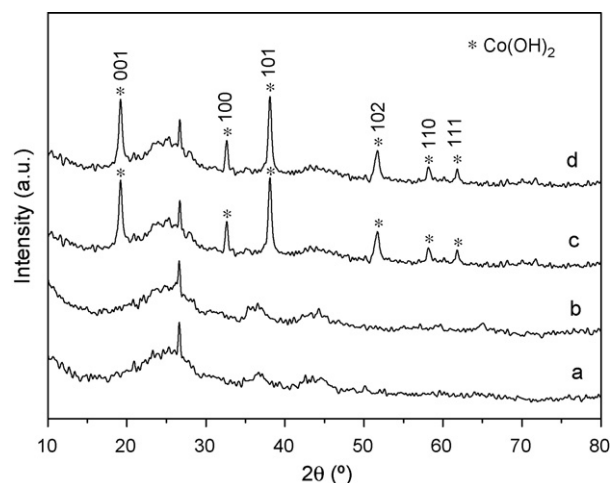


Fig. 1. XRD patterns of the catalysts calcined at different temperatures. (a) 200°C , (b) 300°C , (c) 400°C , and (d) 500°C .

small amount of formed metallic cobalt. In addition, after calcination at temperatures higher than 400°C , the XRD patterns (Fig. 1c and d) display clear and strong diffraction peaks at 19.1° , 32.6° , 38.1° , 51.7° , 58.1° , and 61.7° , which can be ascribed to the phase of cobalt hydroxide ($\text{Co}(\text{OH})_2$), corresponding to (001), (100), (101), (102), (110), and (111), respectively [14]. These results clearly suggest that the as-prepared catalysts experiences phase transitions from an amorphous Co–B to crystalline $\text{Co}(\text{OH})_2$ with the increase in temperatures. To our knowledge, cobalt hydroxide is most possibly formed during the catalyst reduction process with the NaBH_4 solution containing NaOH rather than formed during the calcination process. Beyond the scope of this study, a more in-depth analysis would be required to identify the surface state of the as-prepared catalysts.

Transmission electron microscopy (TEM) of cobalt catalysts supported on active carbon at varied calcination temperatures is shown in Fig. 2. The surface of all the catalysts are decorated with needle-like metal compound, which is most possibly $\text{Co}(\text{OH})_2$ phase according to XRD results.

To further understand the effect of calcination temperature on the catalytic activity, kinetic studies on hydrolysis of NaBH_4 were carried out with the catalysts calcined at various temperatures. For the catalyst sample without calcination, a linear dependence of generated hydrogen volume with time is observed at the given conditions, as seen in Fig. 3. Additionally, a small induction period is presented. After calcination at 200°C , the catalyst exhibits a remarkably higher hydrogen generation rate than the catalyst without calcination. The reaction starts immediately after the borohydride solution contacts with the catalyst. It must be noted that an obvious slow-down of the reaction rate at the end of experiment has occurred, which may be attributed to a partial blockage of the catalyst surface by produced low-soluble metaborates [15] or the rather low concentration of NaBH_4 at the end of reaction. Increasing calcination temperature from 200 to 300, and 400°C can further improve the catalytic performance but in a smaller extent. These results reveal that the cobalt catalyst with crystal structure can offer higher catalytic performance than that with amorphous structure. A similar result has also been reported by Ingersoll et al. [16] that the hydrogen generation rate increased with the increase in the crystallinity of catalyst. However, a further increase in calcination temperature from 400 to 500°C resulted in a much poor catalytic activity even lower than the catalyst without calcination. The reason for this is still unclear and further investigation is required. Based on above results, a calcination temperature of 400°C was

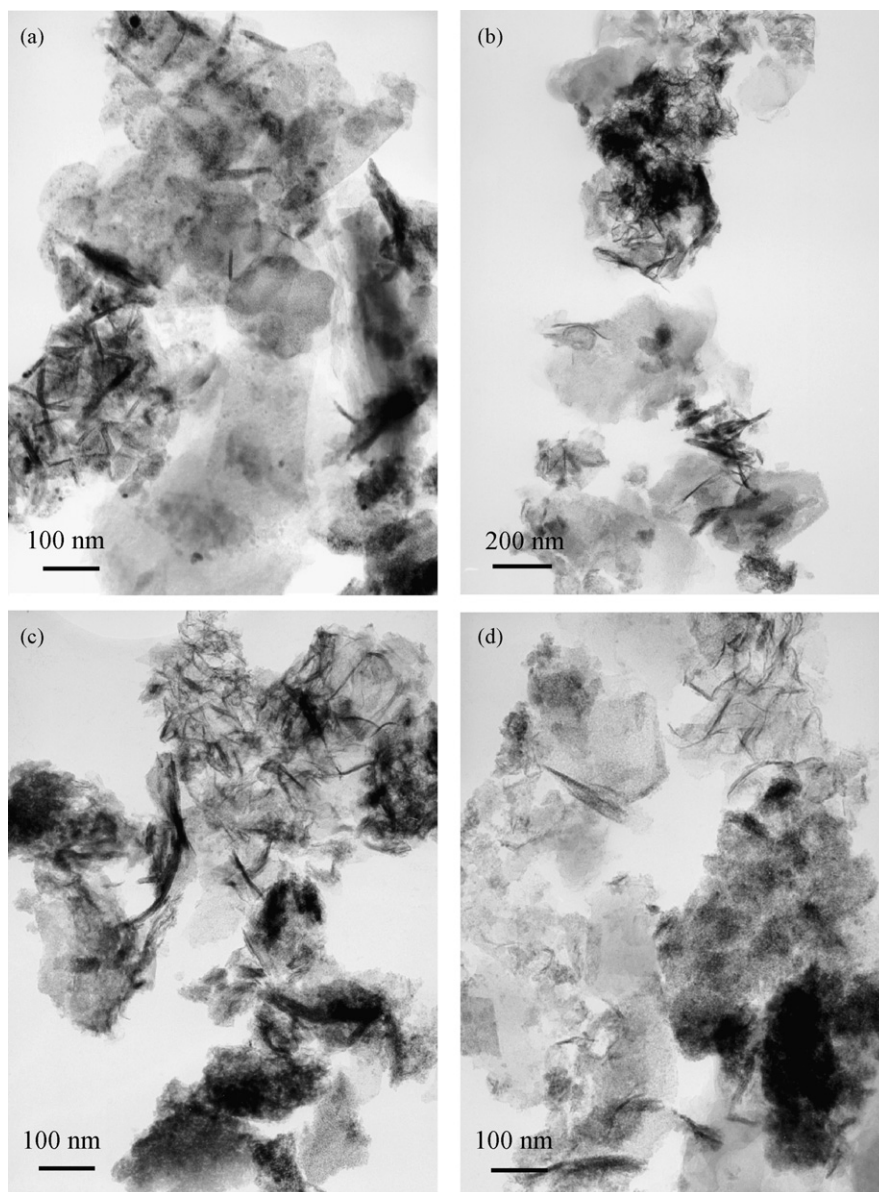


Fig. 2. TEM images of the catalysts calcined at different temperatures. (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

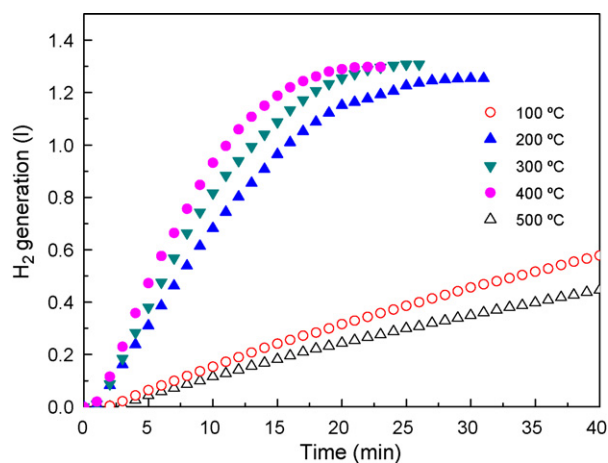


Fig. 3. Catalytic performance of Co/AC catalysts calcined at varied temperatures.

selected in the subsequent experiments to achieve a favorable catalytic activity.

Hydrolysis kinetics is not only dependent on catalyst performances, but also on other factors, such as NaBH_4 concentration and reaction temperature. It is obvious that a higher NaBH_4 concentration would provide more hydrogen density. In order to understand the effect of initial NaBH_4 concentrations on the hydrogen generation rate, a set of experiments were performed with the NaBH_4 concentrations varied from 5 to 25 wt.% while the NaOH concentration was held constant at 5 wt.%. Fig. 4 shows the effects of initial NaBH_4 concentrations on the reaction at 20 °C. A somewhat delay of hydrogen evolution was observed for all the samples possibly due to the initial wetting of catalyst and the pore diffusion resistance. As NaBH_4 concentration increased from 5 to 10 wt.%, the hydrogen generation rate increases. However, the rate decreases gradually when NaBH_4 concentration is further increased in the range of 10–25 wt.%. A similar observation has been made by Krishnan et al. on resin supported catalyst [10]. They suggested that the slower rate of hydrogen generation with 5 wt.% NaBH_4 solution may be

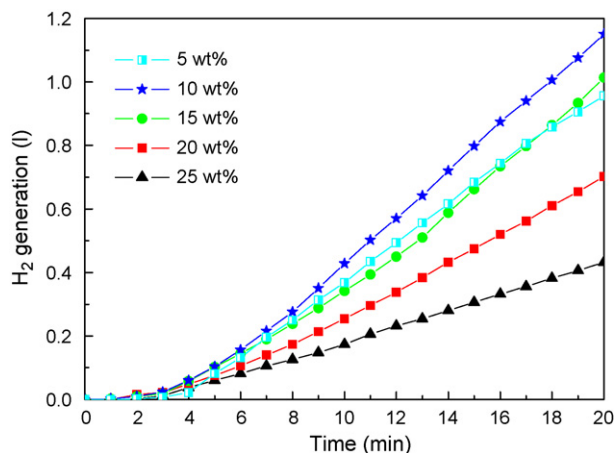


Fig. 4. Kinetic curves for hydrogen generation by hydrolysis of x wt.% NaBH_4 + 5 wt.% NaOH solution ($x=5, 10, 15, 20, 25$) at 20°C .

due to mass-transport limitations inside the resin beads. While the decrease of hydrogen generation rate at high NaBH_4 concentration above 10 wt.% is may be due to an increase in the pH value of the concentrated solutions with a resulting increase in their stability. It must be noted that many researchers [9,17] had found that the hydrogen generation rate decreases with NaBH_4 concentration both at low and high concentration, which is reasonable to be ascribed to the increase of solution viscosity. The increase of the solution viscosity may cause mass-transport limitations of borohydride from the solution to the surface of catalyst.

Kinetic studies at varied temperatures were further carried out using the optimized catalyst. Fig. 5 presents the hydrogen generation kinetic curves at a solution temperature ranging from 20 to 40°C . To minimize the effect of temperature changes resulted by the exothermic hydrolysis reaction, this set of experiments was carried out using 1 wt.% NaBH_4 + 5 wt.% NaOH solution. This measure allows the solution temperature to be controlled to within $\pm 1^\circ\text{C}$ during the reaction. As expected, the initial hydrogen generation rate increases significantly with temperature. The influence of temperature is clearly shown by both the increasing slope values on the linear region of the plots and the decreasing induction period.

For comparison of catalysts activities, the initial hydrogen generation rates k ($\text{mol min}^{-1} \text{g}^{-1}$) were used to determine the activation

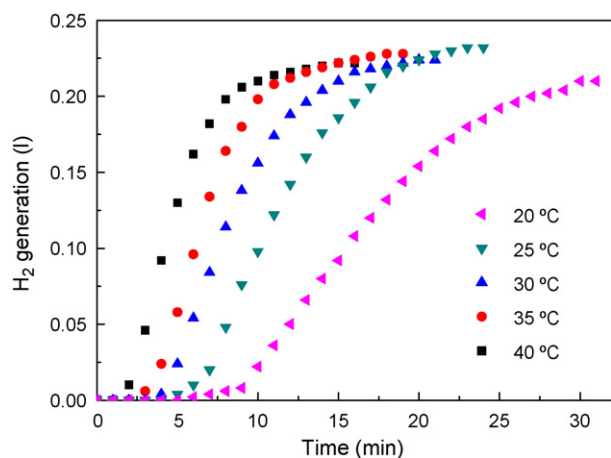


Fig. 5. Kinetic curves for hydrogen generation by hydrolysis of 1 wt.% NaBH_4 + 5 wt.% NaOH solution at varied temperatures.

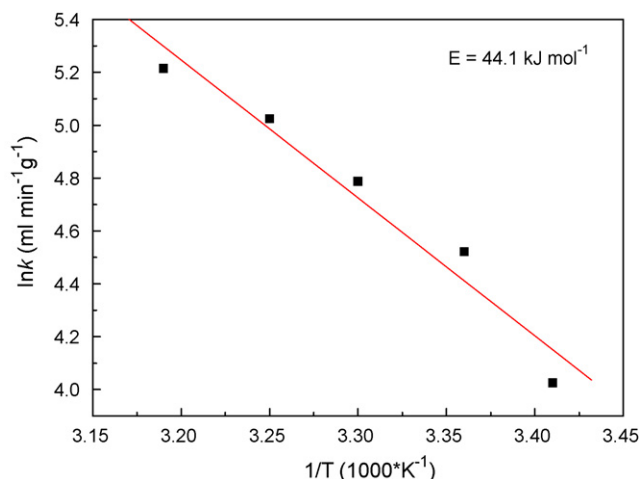


Fig. 6. Arrhenius plots for catalyzed hydrolysis of 5 wt.% NaBH_4 + 5 wt.% NaOH solution.

energy by the following Arrhenius equation:

$$\ln k = \ln k_0 - \left(\frac{E_a}{RT} \right)$$

where k_0 is the rate constant ($\text{mol min}^{-1} \text{g}^{-1}$), E_a the activation energy (kJ mol^{-1}), R the gas constant ($8.3143 \text{ kJ mol}^{-1} \text{K}^{-1}$), and T is the reaction temperature (K). An Arrhenius plot, in which $\ln k$ is plotted against the reciprocal of absolute temperature ($1/T$), was plotted in Fig. 6. From the slope of straight line, the activation energy was calculated to be 44.1 kJ mol^{-1} . This value compares favorably with the reported results for Co–Mn–B electrodeposited on Ni-foam (55 kJ mol^{-1}) [15], Ni–Co–B (62 kJ mol^{-1}) [16], Co–B powder catalyst (65 kJ mol^{-1}) [17], and Ru-promoted sulphated zirconia (76 kJ mol^{-1}) [18].

Fig. 7 shows the hydrogen generation rate measured using the optimized catalyst and 1 wt.% NaBH_4 + 5 wt.% NaOH solution at 20°C . To examine the effects of catalyst loading on the hydrogen generation rate, 0.25, 0.50, and 0.75 g of the catalysts were employed. As observed in Fig. 7, using more catalyst increases the H_2 production rate, implying that hydrogen generation rate can be determined by controlling the catalyst loading used in the reactor.

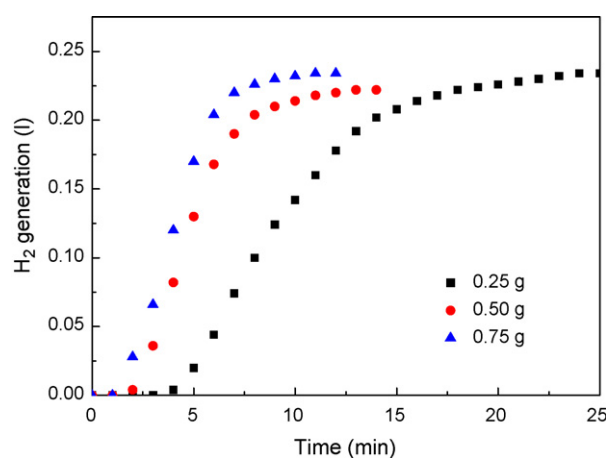


Fig. 7. Kinetic curves for hydrogen generation by hydrolysis of 1 wt.% NaBH_4 + 5 wt.% NaOH solution using varied catalyst amounts.

4. Conclusion

The calcination temperature exhibits evident influence on the catalyst structure and its performance. Increasing calcination temperature in the range of 200–400 °C induces the transitions of active component from an amorphous structure to a crystalline structure, and improves the catalytic activity towards hydrolysis of alkaline NaBH₄ solution. Calcination at temperature above 500 °C, however, induces a decrease in the catalytic activity, which is even lower than the sample without calcination. Increase in NaBH₄ concentrations higher than 10 wt.% resulted in negative effect on hydrogen generation rate. Hydrogen generation rate increases with an increase in reaction temperature, and activation energy for the NaBH₄ hydrolysis reaction was calculated to be 44.1 kJ mol⁻¹. The H₂ production rate can be controlled by adjusting the amount of catalysts used.

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