Preparation of magnetic cobalt-based catalyst for hydrogen generation from alkaline NaBH$_4$ solution[1]

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Abstract

A fast and simple fabrication process was utilized for preparation of cobalt-based catalysts. Compared with other noble-metal catalysts, it is cost-effective, because of the low price of cobalt and capability of rapid-production and easiness in scale-up manufacturing of such catalysts. The magnetic property of the cobalt-based catalysts makes it convenient for recycling spent catalysts. Furthermore, magnetic catalysts can be removed easily to stop the hydrogen production, when hydrogen is no more required in applications. Certainly, this promotes the safe and reliable production of hydrogen and makes it as a safe portable energy source. The rates of hydrogen generation from hydrolysis of alkaline NaBH$_4$ solution were determined as a function of temperature, NaBH$_4$ concentration, and NaOH concentration in presence of prepared catalysts. Production rate of ultrapure hydrogen, as high as 329 ml·min^{-1}·g^{-1}, was reached at 55ºC. This high purity of hydrogen could be directly used as the fuel to PEMFC without additional requirement in hydrogen purification.

1. Introduction

The advancement of technology and the increase of worldwide populations amplify energy consumption significantly, of which most energy comes from fossil origins. Thus, over-consumption of fossil fuels has resulted in climate change and global warming due to the elevated concentration of carbon dioxide in atmosphere. With increasing awareness and necessity of using more efficient and cleaner energy, hydrogen energy has become more and more attractive. However, challenge in hydrogen storage and release in safe and economic ways has been the focus of many researches. Steam reforming of natural gas is the common industrial process to generate hydrogen, but carbon monoxide contained in produced hydrogen will poison certain catalysts [1], such as platinum. Thus, it is imperative to find out a reliable and stable method for continuous supply of pure hydrogen.

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Up to now, there are several hydrogen storage methods, such as high pressure tanks, liquefied hydrogen, metal hydrides and chemical hydrides (e.g., KBH_4, $NaBH_4$, NaH and LiH). In terms of energy cost, high pressure and liquefaction are not preferred due to the fact that extra energy losses must be taken into account. Moreover, the content of hydrogen stored in chemical hydride is much more than that stored in metal hydride [2]. Consequently, in order to meet the goals of 6 wt% and 9 wt% hydrogen capacity by 2010 and 2015, respectively, declared by the U.S. Department of Energy (DOE) [3], chemical hydrides are promising materials for hydrogen supply and storage due to their capability in supplying ultrapure H_2 and large storage capacity of hydrogen. Furthermore, some chemical hydrides, such as $NaBH_4$ and KBH_4, are quite stable in alkaline conditions at ambient temperature. Consequently, proper catalysts are required in hydrogen production from hydrolysis of $NaBH_4$ and KBH_4.

Among chemical hydrides, sodium borohydride ($NaBH_4$) is one of the potential compounds for hydrogen storage. Because of its high hydrogen storage capacity, about 10.8 wt%, its high stability in alkaline solution and non-flammability, it is often applied in controlled generation of hydrogen with specific catalysts. In addition, hydrogen can be generated from $NaBH_4$ even at 0°C, which indicates its feasible application in frigid weather. Besides, the main reaction product, sodium metaborate ($NaBO_2$), shown as Eq. (1), can be properly recycled [4–6] back to $NaBH_4$ to lower the cost of using $NaBH_4$ as hydrogen storage materials.

$$NaBH_4 + 2H_2O \xrightarrow{\quad catalyst \quad} NaBO_2 + 4H_2 + 300kJ \tag{1}$$
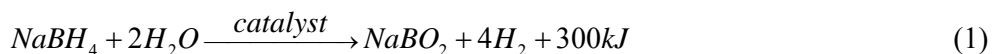
In general, $NaBH_4$ solutions are preserved at high pH conditions by adding $NaOH$ to prevent it from self-hydrolysis [7] and maintaining it at chemically stable state. Thus, the rate of hydrogen generation mainly depends on catalysts used.

There are already many reports in the open literature related to hydrogen production from $NaBH_4$ using different catalysts, which focuses mainly on precious metals, such as ruthenium [8], nickel-boride [9], $LiCoO_2$ [10], cobalt-boride [11–13] on various supports. However, the recycle of used and spent catalysts, is of grave concern, especially when being applied to supply hydrogen for polymer electrolyte membrane fuel cell (PEMFC) or on-board automobile applications. In our previous study [14], we have developed a fast and simple method to synthesize the polymer template-Ru composite to catalyze the hydrolysis of $NaBH_4$ for hydrogen generation. High generation rate of hydrogen was thus achieved. Furthermore, lower activation energy in the hydrolysis reaction of $NaBH_4$ for hydrogen generation was also obtained at about 49.72 kJ·mol^{-1}.

It is, therefore, our aim in this study to develop catalysts effective in the hydrolysis of $NaBH_4$ for hydrogen generation, but also easily recycled from spent $NaBH_4$ solution. Cobalt-based catalysts called Co/IR-120 were successfully synthesized by using a cost-effective and simple chemical reductive method. Characteristics of these catalysts, such as magnetism and capability in hydrogen production were determined accordingly. Because of its magnetic property, these catalysts can be easily recycled with permanent magnets and be reused easily again. Moreover, factors affecting the rate of hydrogen generation, including concentrations of $NaOH$ and $NaBH_4$ as well as the temperature, were studied and discussed in this report.

2. Experimental

2.1 Preparation of Co/IR-120 catalysts

Analytical reagent grade sodium borohydride (Riedel – de Haën) and cobalt chloride (II) (Sigma–Aldrich) were utilized without further purification. A strongly acidic cation exchange resin, Amberlite IR–120 in hydrogen form (16–45 mesh size), used as catalyst support was purchased from Supelco Chemical Co. (Bellefonte, PA, USA). The properties of Amberlite IR–120 in detail were also given in our previous publication [14]. The active site on IR-120 is mainly the $-SO_3H$ functional group.

Amberlite IR-120 resin beads of weight amount were placed into Co^{2+} solution to initiate the chelation reaction. After uniformly stirring for 1 hour at the ambient temperature, the cobalt ion chelated IR-120, called Co^{2+}/IR-120, were taken out from the solution and washed with deionized water repeatedly to remove the residual unchelated Co^{2+} on the surface of IR-120. Subsequently, the reductive catalysts Co/IR-120 was obtained by reducing the Co^{2+}/IR-120 complexes with suitable concentration of $NaBH_4$ at ambient temperature. The synthesized catalysts, Co/IR-120, were vacuum-dried at 60°C to get rid of water and hydrogen.

2.2 Characterization of Co/IR-120 catalysts

The morphology of prepared Co/IR-120 catalyst was identified by scanning electron microscope (SEM; JEOL, JSM-6700F) whereas the element compositions on catalyst surface were analyzed with the energy dispersive spectra (EDS) gained from an Oxford INCA-400 spectrometer.

2.3 Hydrogen generation

The volume and the rate of hydrogen generated in presence of Co/IR-120 catalysts were measured by using a water-displacement method, which was described in details along with its experimental setup in our previous work [14]. 15 ml of $NaBH_4$ solution containing appropriate concentration of NaOH were thermostatically kept in a sealed flask at the preset temperature using thermostatic circulator, with temperature variation within ±0.1°C in water bath. The onset of the H_2 generation reaction started at one minute from the moment when a fixed amount, *ca.* 500 mg, of Co/IR-120 catalysts was introduced into the flask containing $NaBH_4$ solution. One minute was assumed enough for catalysts to be moistened with $NaBH_4$ solution. An outlet tube connecting the flask was placed under an inverted water-filled burette, which was situated in a graduated glass column filled with water. The volume of hydrogen released was equal to the volume change of water in the burette.

3. Results and discussion

3.1 Characterization of Co/IR-120 catalysts

The activity of a catalyst is known to be mostly dependent on its surface properties, such as morphology and surface chemistry. Thus, it is necessary to examine the surface properties of obtained catalysts. Figure 1 shows synthesized Co/IR-120 catalysts strongly attracted by permanent

magnets with a residual magnetic flux density of *ca.* 12,000 G, which clearly indicates ferromagnetism present intrinsically in Co/IR-120 catalysts. The good ferromagnetic property of Co/IR-120 catalysts gives a convenient way to separate the catalysts from spent $NaBH_4$ system and, thus, makes it easier in continuous operation of hydrogen generation from such $NaBH_4$ system. Furthermore, this magnetic characteristic certainly gives an advantage on recycle of waste catalysts from $NaBH_4$ solutions used in hydrolysis of $NaBH_4$ to produce hydrogen. A simple procedure using magnet could easily separate the catalysts from solutions to reduce the operation cost in waste treatment.

The surface morphology of Co/IR-120 catalysts was further examined by an SEM. Figure 2 are the SEM micrographs of the IR-120 resin beads as substrates and Co IR-120 catalyst. In general, the IR-120 resin beads has quite smooth surface, while highly concentrated groups of flower-shaped structures are observed uniformly in Figure 2(e) and Figure 2(f) after cobalt was reduced on IR-120 by $NaBH_4$. Nanoscale dispersion of approximately 300 – 500 nm is also found in Figure 2(f). From the microscopic point of view, the surface of Co/IR-120 is covered with flakes and calyces, in contrast to almost smooth terrain on IR-120 beads. It is, thus, reasonable to infer that flake-like materials are originated from cobalt. Several fissures exist between two adjacent cobalt sheets in lower magnification (130×) as shown in Figure 2(e). Moreover, wrinkled structure observed on surface of Co/IR-120 also implies an increasing surface area and, thus, may enhance H_2 generation rate.

Figure 3 exhibits the EDS analyses of IR-120 resin beads and cobalt-loaded IR-120 (Co/IR-120). Elements, such as carbon, oxygen and sulfur were found to be major components in original IR-120. The platinum detected should not be intrinsic, as specimens must be deposited with a thin layer of platinum to increase their surface conductivity prior to SEM/EDS analysis. After cobalt was reduced on the surface of IR-120, two apparent peaks representing cobalt were detected at around 0.6 keV and 7 keV, shown as curve b on Figure 3, which confirmed that cobalt was successfully coated on the resin. Table 1 lists the surface compositions of both IR-120 resin beads and Co/IR-120 catalyst. For example, carbon content dropped from 65.3 at% (or 53.2 wt%) on IR-120 to 12.86 at% (or 4.95 wt%) on Co/IR-120. Simultaneously, Co was not detected on neat IR-120 resin beads, but found around 36.25 at% or 68.43 wt% on Co/IR-120. This certainly confirmed that flower-like and calyx structures shown on Figure 2(d), 2(e) and 2(f) are mostly cobalt.

3.2 Hydrogen generation

Some factors influencing the catalytic performance of Co/IR-120 catalysts on hydrogen generation were studied and discussed below. In addition to the existence of catalysts, pH value of solution has also profound influence on the hydrolysis of $NaBH_4$ especially in acidic environment [15].

3.2.1 Hydrogen generation using pristine IR-120

The supports used in this study, IR-120 resin beads, are ion exchange resin in acidic form and

could lead to small production of hydrogen due to the low pH value near 3.1 when IR-120 resin beads are dispersed in water. In previous work [14], catalytic effects of pristine IR-120 resin beads were studied on hydrolysis of $NaBH_4$. Only considerably small amount of hydrogen was generated, compared to that when Co/IR-120 catalysts are used. Therefore, catalytic effect of original IR-120 on hydrogen generation is negligible in this work.

3.2.2 Effect of $NaBH_4$ concentration

Effect of $NaBH_4$ concentration (1 wt%, 5 wt%, 10 wt%, 15, wt%, 25 wt%) in presence of 1 wt% NaOH on H_2 generation rate using 500 mg of Co/IR-120 catalysts at 298 K is presented in Figure 4. The amount of hydrogen generated is almost linearly proportional to the reaction time for all concentration of reactants studied, revealing the constant generation rate of hydrogen and stable catalytic activity of the catalysts. Furthermore, the linear relationship between amount of hydrogen generated and reaction time indicates that such a $NaBH_4$ hydrolysis reaction is of the zero order.

As $NaBH_4$ concentration increased from 1 wt% to 5 wt%, an apparent increase in H_2 generation rate from 23.3 ml·min^{-1}·g^{-1} to 53.1 ml·min^{-1}·g^{-1} was observed. It has to mention that all weights of catalyst used and presented in this work were based on the bulk weight of Co/IR-120 catalyst. However, with a further increase in $NaBH_4$ concentration from 5 wt% to 25 wt%, the rate of hydrogen production was reduced to 26.5 ml min^{-1} g^{-1}. That is, 5 wt % of $NaBH_4$ solution with 1 wt% of NaOH in presence of catalysts gives the highest production rate of hydrogen in this study.

Similar results were reported by Ye et al. [11], who utilized a γ–Al_2O_3 supported Co catalyst to find out 5 wt% $NaBH_4$ as the optimal concentration in H_2 generation. Amendola et al. [16] attributed it to the increase of viscosity in $NaBH_4$ solution for the reduced rate of $NaBH_4$ hydrolysis with an excessive increase in $NaBH_4$ concentration. Furthermore, Suda et al. [17] pointed out that the hydrolyzed product of $NaBH_4$ is mainly sodium metaborate, $NaBO_2$, which has a relatively smaller aqueous solubility, approximately 28 g/L, at 25°C, compared with the higher aqueous solubility of $NaBH_4$ near 55 g/L at 25°C. Such a lower aqueous solubility of $NaBO_2$ will result in precipitation of $NaBO_2 \cdot 4H_2O$, which interferes in mass transfer between $NaBH_4$ molecules and Co/IR-120 catalysts or wraps the catalysts to cover up the active sites on the surface of catalysts to prevent $NaBH_4$ molecules from hydrolysis over the active sites of catalysts. In addition, the precipitated $NaBO_2$ will possibly poison the catalyst. Consequently, when $NaBH_4$ concentration increases over 5 wt%, generation rate of H_2 will decrease apparently.

4. Conclusion

The stable low-cost Co/IR-120 catalysts with high remnant magnetism suitable for hydrogen generation from hydrolysis reaction of $NaBH_4$ were synthesized using a chemical reduction method. Such a wet chemical method provides a fast and simple way to produce Co/IR-120 catalysts in large quantity. The good ferromagnetic property of Co/IR-120 catalysts gives a convenient way to separate the catalysts from spent $NaBH_4$ system and, thus, makes it easier in continuous operation of hydrogen generation from such $NaBH_4$ system. As Co/IR-120 catalysts were used for H_2 generation, a hydrogen production rate of 53 ml·min^{-1}·g^{-1} at 25°C was achieved in solution having 5

wt% of $NaBH_4$ and 5 wt% NaOH. Rates of H_2 generation increase with increasing temperatures. The activation energy of $NaBH_4$ hydrolysis reaction was found at 54.62 kJ·mol^{-1}, which was lower than others reported in the open literatures.

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Table 1: Surface compositions present in polymer template (Amberlite IR-120 resin) and catalyst (Co/IR-120) analyzed by EDS.

Elements	Amberlite IR-120 resin		Co/IR-120	
	wt%	at%	wt%	at%
C	53.17	65.30	4.95	12.86
O	28.49	26.26	25.52	49.81
S	18.34	8.44	1.10	1.07
Co	0	0	68.43	36.25

Figure 1: Photographs of prepared Co/IR-120 catalysts placed in bottle in a magnetic field with magnetic strength near 12,000 G show their intrinsic magnetism.

Figure 2: Scanning electron micrographs of (1) IR-120: (a) 130×; (b) 10,000×; (c) 30,000×; (2) Co/IR-120 (d) 130×; (e) 10,000×; (f) 30,000×.

(a) IR-120, 130×
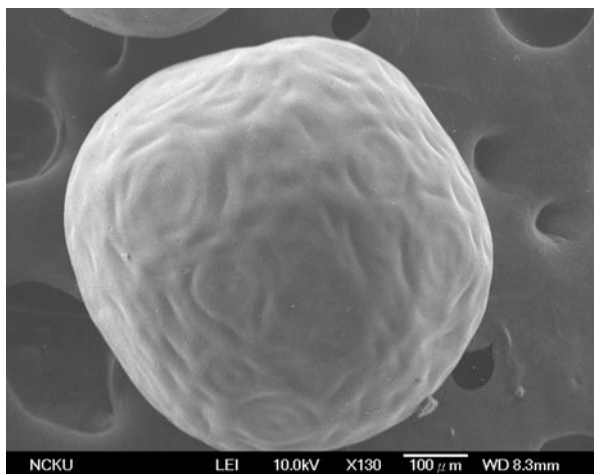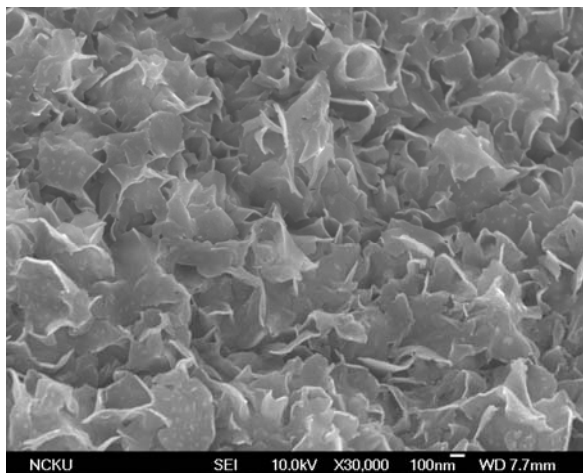
(d) Co/IR-120, 130×
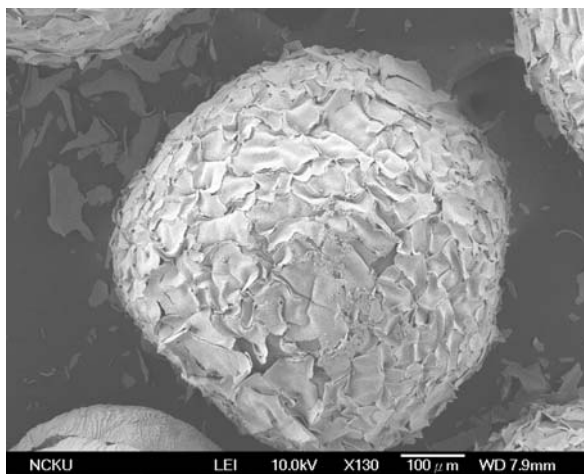
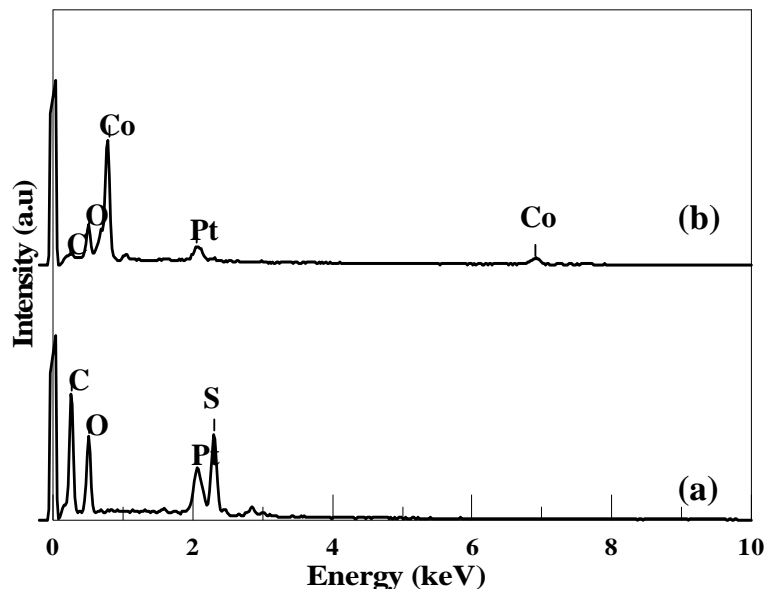(b) IR-120, 10,000×
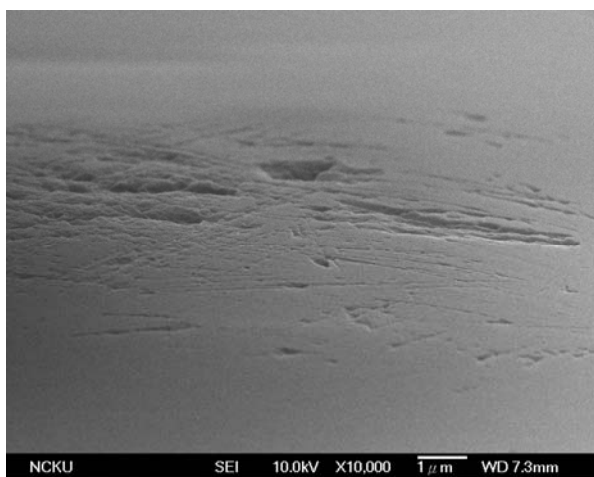
(e) Co/IR-120, 10,000×
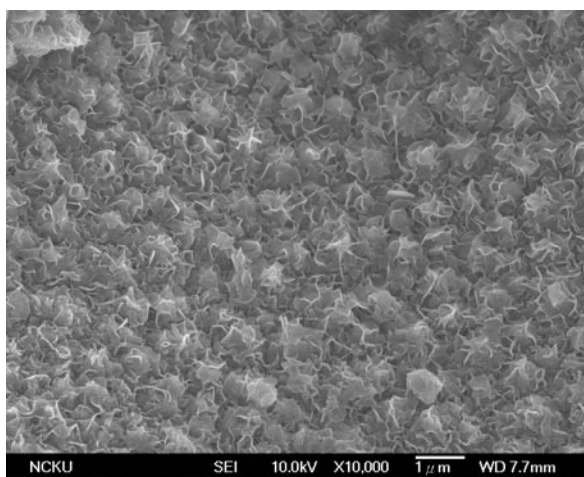
(c) IR-120, 30,000×
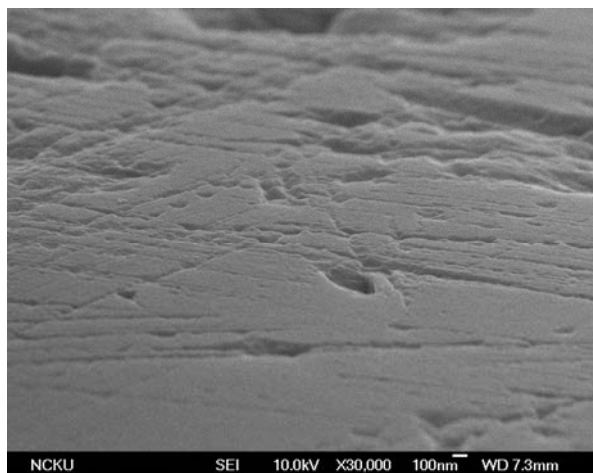
(f) Co/IR-120, 30,000×

Figure 3: EDS spectra of (a) IR-120 and (b) Co/IR-120. Pt was sputtered on samples prior to SEM/EDS analysis to increase the electric conductivity of these samples.

Figure 4: Volume of hydrogen generated as a function of time in different $NaBH_4$ concentrations (25 °C, 1 wt% NaOH solution, 500mg Co/IR-120 catalyst).