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STUDIES ON CATALYTIC BEHAVIOR OF $Co–Cr–B/Al_2O_3$ IN HYDROGEN GENERATION BY HYDROLYSIS OF $NaBH_4$

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In this present study, the chemical reduction technique was used to synthesize Al_2O_3 supported Co-Cr-B catalyst (Co-Cr-B/Al_2O_3). The effects of the concentration of $NaBH_4$, NaOH, amount of catalyst, ratio of metal/ $Al_2O_3$and temperature were discussed in detail. The results show that the reaction rate of hydrolysis first rises up and then goes down subsequently with the increase of $NaBH_4$ concentration, as well as the concentration of NaOH. It was observed that the hydrogen generation rate increases with the molar content of metal changing from 2.5% to 5 wt%. However, when the metal/Al_2O_3 molar ratio is located from 5% to 20 wt%, the rate of hydrogen generation goes down. The hydrolysis kinetic order and the activation energy (E_a) of $NaBH_4$ in the presence of Co-Cr-B/Al_2O_3 catalyst were found as 0.15 and 37.34 kJ*mol^{-1}, respectively. According to the results obtained, Co-Cr-B/Al_2O_3 catalyst can be used as a promising material in PEMFC mobile systems.

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Keywords: Co-Cr- B, catalyst, Al_2O_3, hydrogen generation, $NaBH_4$

1. Introduction

Greenhouse gas emissions from fossil fuels contribute to climate change negatively. It has attracted the attention of recent studies on clean renewable energy to solve the important problem for nature [1, 2]. One of the active methods used in the storage of renewable energy is hydrogen with high gravimetric energy density. Thus, proper development of hydrogen storage and production systems has become inevitable for clean hydrogen based technology[3].

Storage of hydrogen is achieved by using different functions such as liquid pressure tanks [4], activated carbon [5] and carbon nanotube [6]. However, the lack of gravimetric energy efficiency of these functions is considered as a major disadvantage. It is of great importance that hydrogen is used as a fuel in the proton exchange membrane fuel cell (PEMFC) [7]. One of the alternative methods that can be used to supply pure hydrogen is the use of chemical hydrides such as $NaBH_4$ [8, 9], NaH [10], KBH_4 [11]. Because they have high gravimetric activity in hydrogen storage.

Among these chemical hydrides, aqueous $NaBH_4$ has more ideal properties than others. The fact that it is non-flammable, non-toxic in nature and has a hydrogen storage capacity of 10.8% makes it more ideal. Since half of the produced hydrogen stems from the water solvent, Hydrogen is generated by water-based hydrolysis reaction of $NaBH_4$. Hydrogen production from the $NaBH_4$ hydrolysis provides an important advantage in supplying hydrogen used as fuel in fuel cells [12, 13].

The provision of the catalyst support during the hydrolysis of $NaBH_4$ significantly affects the rate of hydrogen production. Although many different organic and inorganic acids are used to increase the speed of the reaction in the hydrolysis of NaBH4, the reaction becomes uncontrollable[14]. As an alternative to these acids, metal-based catalysts make the reaction controllable and accelerate. Metals such as Pt [15], Pd [16], Ru [17], Ni [18], Co [19] and Mg [20]

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and their salts are some of the catalysts used to accelerate the hydrolysis reaction of $NaBH_4$. Cobalt borides (Co-B) [19] with low cost and good catalytic activity have an important role in the catalyst. It has been emphasized that Co-B based catalysts exhibit superior catalytic activity in the production of hydrogen from the hydrolysis of $NaBH_4$ in the studies conducted with Co-B based catalysts. Recently, support materials such as activated carbon [5], carbon [21], Al_2O_3 [22], SiO_2 [23], CeO_2 [24] and TiO_2 [25] are used to increase the activity of the catalysts as well as to accelerate the hydrolysis reaction of $NaBH_4$ because the catalysts synthesized using the support material are provided to have high surface areas.

In this present study, the Co-Cr-B/Al_2O_3 catalyst synthesized via the chemical reduction method was used for the hydrolysis of $NaBH_4$. The experimental conditions for the $NaBH_4$ hydrolysis in the presence of Co-Cr-B/Al_2O_3 catalyst were optimized. It was found that Co-Cr-B/Al_2O_3 catalyst has high catalytic activity in the hydrolysis of $NaBH_4$.

2. Experimental part

Chemical reduction technique was used to synthesize Al_2O_3 supported Co-Cr-B catalyst (Co-Cr-B/Al_2O_3). To synthesize Co-Cr-B/Al_2O_3 catalyst, $CoCl_2.6H_2O$ and $Cr(NO_3)_3.9H_2O$ were dissolved in 50 ml of ethanol. The desired amount of Al_2O_3 was added to the above solution and stirred for 24 hours at room temperature. Thus, Co and Cr metals were absorbed onto Al_2O_3. The ethanol in the medium was then removed at 50 °C and 50 ml of distilled water was added on Al_2O_3/Co-Cr-B mixture, then the mixture was left in the ice bath. The 50 ml of The $NaBH_4$ solution, prepared to be 5 times the total metal moles, was added dropwise to Co-Cr-B/Al_2O_3 mixture in the presence of N_2 gas. The resulting catalyst was filtered and washed several times with distilled water and anhydrous ethanol. The synthesized catalyst was dried in a nitrogen atmosphere at 80 °C for 6 hours. The obtained catalyst was maintained in a closed vessel in a nitrogen atmosphere to use in the hydrolysis of $NaBH_4$.

X-ray diffraction (XRD, Rigaku x-ray diffractometer), energy dispersive x-ray (EDX, JEOL JSM 5800), and x-ray photoelectronspectroscopy (XPS, SCIENTA ESCA 200) were used to characterize the properties of Co-Cr-B/Al_2O_3 catalyst.

The effect of different parameters such as concentration of $NaBH_4$ (1.5 -7.5 wt %), concentration of NaOH (0-10 wt %), amount of catalyst (50-150 mg), amount of metal/Al_2O_3 ratio (2.5- 20 wt %) and temperature (20-60 ^{0}C) were investigated on the catalytic activity of Co-Cr-B/Al_2O_3 catalyst for $NaBH_4$ hydrolysis.

3. Results and discussion

3.1. The effect of different parameters on the catalytic activity of Co-Cr-B/Al_2O_3 catalyst for $NaBH_4$ hydrolysis

In order to investigate the effect of the NaOH concentration on the hydrogen generation rate, the amount of NaOH concentration was changed from 0 to 10 wt%. During this process, the temperature, the amount of catalyst and the $NaBH_4$ concentration were kept 30 ^{0}C, 100 mg and 2.5 wt%. Fig. 1 indicates the plot of hydrogen generation volume, as a function of time, obtained from hydrolysis of $NaBH_4$ solution at different NaOH concentrations.

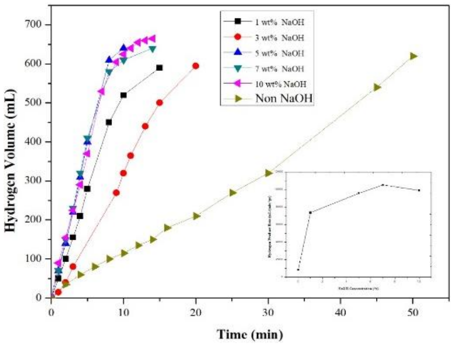

Fig. 1. Hydrogen generation rate of different NaOH concentrations (reaction condition: concentration of $NaBH_4$: 2.5 wt%; amount of catalyst: 100 mg; temperature: 30 ^{0}C).

A significant increase in hydrogen production rate was observed when the NaOH concentration increased to 5% by weight compared to the NaOH-free reaction. Thus, it can be said that in this study the maximum hydrogen production rate is reached when the amount of NaOH concentration is 5% by weight. It was observed that the catalyst had different catalytic activity at different NaOH concentration amounts. The reason for this is that the effect of NaOH on the hydrolysis of $NaBH_4$ depends on the type of catalyst. For example; Jeong et al.[26] studied the performance of Co-B catalyst on the hdyrogen generation from $NaBH_4$. The observed a positive effect on $NaBH_4$ hydrolysis with the increasing NaOH concentration. The optimum NaOH concentration was used as 5% in the study of the effect of other parameters ($NaBH_4$ concentration, amount of catalyst, temperature) on the hydrolysis of $NaBH_4$.

In order to investigate the effect of the $NaBH_4$ concentration on the hydrogen generation rate, the amount of $NaBH_4$ concentration was changed from 1.5 to 7.5 wt%. During this process, the temperature, the amount of catalyst and the NaOH concentration were kept 30 ^{0}C, 100 mg and 5 wt%. Fig. 2 reveals the plot of hydrogen generation volume, as a function of time, obtained from hydrolysis of $NaBH_4$ solution at different $NaBH_4$ concentrations.

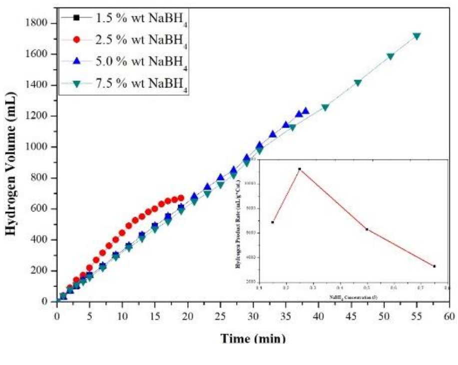

Fig. 2. Hydrogen generation rate of different $NaBH_4$ concentrations (reaction condition: concentration of NaOH: 5 wt%; amount of catalyst: 100 mg; temperature: 30 ^{0}C).

As can be clearly seen in Fig. 2, the hydrogen generation rate decreases when the concentration of $NaBH_4$ is rising up from 2.5 to 10 wt%. Similiar observation was reported by Baytar et al. [21]. They explained the probable reason for the decreasing hydrogen generation rate is due to the high viscosity of solution. For certain catalysts, the concentration of $NaBH_4$ by weight is increased significantly, the high viscosity of product solution will retard mass transfer, which leading to the decrease of hydrogen generation rate Furthermore, the limited solubility of $NaBO_2$ in water, which appears as a by-product in the hydrolysis of $NaBH_4$, can be considered as one of the factors negatively affecting the hydrogen generation rate.

In order to investigate the effect of the amount of catalyst on the hydrogen generation rate, the amount of catalyst was changed from 50 mg to 150 mg. During this process, the temperature, the NaOH concentration and the $NaBH_4$ concentration were kept 30 ^{0}C, 5 wt% and 2.5 wt%. Figure 3 shows the plot of hydrogen generation volume, as a function of time, obtained from hydrolysis of $NaBH_4$ solution at different amount of catalyst.

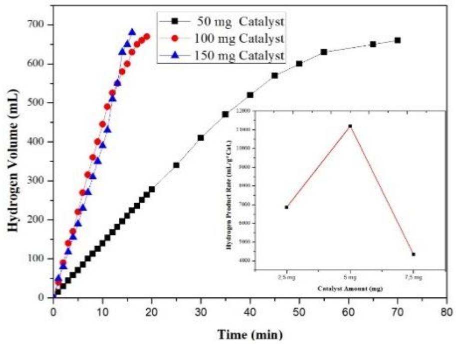

Fig. 3. Hydrogen generation rate of different amount of catalyst (reaction condition: concentration of NaOH: 5 wt%; concentration of $NaBH_4$: 2.5 wt%; temperature: 30 ^{0}C).

It should be noted that as the amount of catalyst increases, the hydrolysis reaction of $NaBH_4$ is completed in a short time. In other words, increasing the amount of catalyst affects the hydrogen generation rate positively. Similar results were obtained in our previous studies [19],[27] for different catalysts. In that case, the hydrogen generation rate can be determined by controlling the catalyst amount.

In order to investigate the effect of metal/Al_2O_3 ratio on the hydrogen generation rate, the amount of metal/Al_2O_3 ratio was changed from 2.5 to 20 wt%. During this process, the temperature, the amount of catalyst, the concentration of $NaBH_4$,and the NaOH concentration were kept 30 ^{0}C, 2.5 wt%, 100 mg and 5 wt%. Fig. 4 demonstrates the plot of hydrogen generation volume, as a function of time, obtained from hydrolysis of $NaBH_4$ solution at different metal/Al_2O_3 ratios.

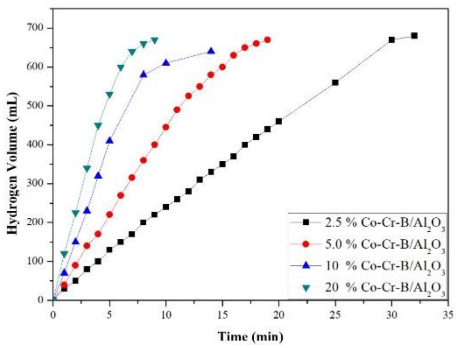

Fig. 4. Hydrogen generation rate of different metal/Al_2O_3 ratios (reaction condition: concentration of NaOH: 5 wt%; amount of catalyst: 100 mg; concentration of $NaBH_4$: 2.5 wt%; temperature: 30 ^{0}C).

It was observed that the hydrogen generation rate increases with the molar content of metal changing from 2.5% to 5 wt%. However, when the metal/Al_2O_3 molar ratio is located from 5% to 20 wt%, the rate of hydrogen generation goes down. This might be that a small quantity of Cr doped in Co-Cr-B/Al_2O_3 catalysts, which is favorable to the dispersion of Co active sites. However, a large amount of Cr content covers the active Co sites to some degree. The maximum hydrogen generation rate of $NaBH_4$ hydrolysis using different Co-Cr-B/Al_2O_3 catalysts as a function of metal molar content is given in Fig. 5. It can be seen clearly from the Fig. 5, the catalysts show the best activity with the molar content of metal being 5%.

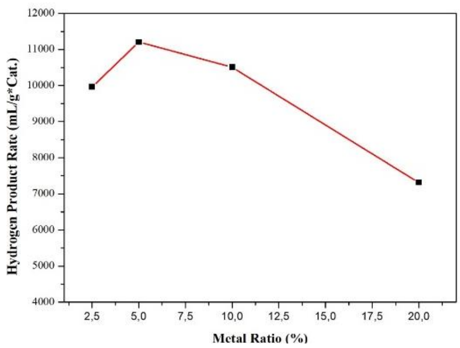

Fig. 5. The maximum value of hydrogen generation of different molar ratios of Co-Cr-B/ Al_2O_3 at 30 ^{0}C.

The temperature plays an important role on the hydrolysis of $NaBH_4$ for hydrogen generation. In order to determine the activation energy of $NaBH_4$ hydrolysis, four different temperatures (30, 40, 50, 60 ^{0}C) were chosen. The hydrogen generation rate at different temperatures is indicated in Fig. 6 a. As expected, the hydrogen generation rate increases depending on the temperature.

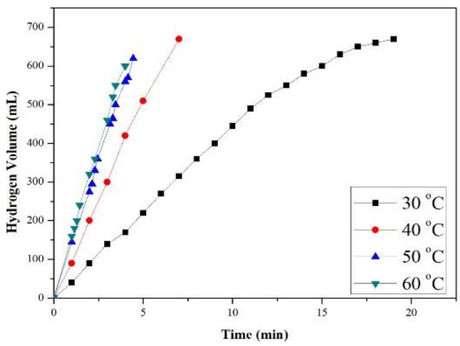

Fig. 6a. Hydrogen generation rate at different temperatures (reaction condition: concentration of NaOH: 5 wt%; amount of catalyst: 100 mg; concentration of $NaBH_4$: 2.5 wt%; temperature: 30 ^{0}C).

The activation energy of the $NaBH_4$ hydrolysis can be determined by plot lnk as a function of $1/T$ (Fig. 6b) using the Arrhenius relation given in the Equation (1).

$$lnk = lnA - \frac{E_a}{RT} \quad (1)$$

where E_a is the activation energy value. The E_a value was found as 37.34 kJ*mol^{-1}. It can be clearly seen that the obtained value low. The favorable E_a value determined in the present study is attributed to both high surface area acquired by Co-Cr-B/ Al_2O_3 and promoting effect of Al_2O_3 species to enhance the catalytic hydrolysis reaction. Moreover, the hydrolysis of $NaBH_4$ reaction degree was determined as 0.15 in the presence of Co-Cr-B/ Al_2O_3. The result indicates that the hydrolysis obeys zero order reaction.

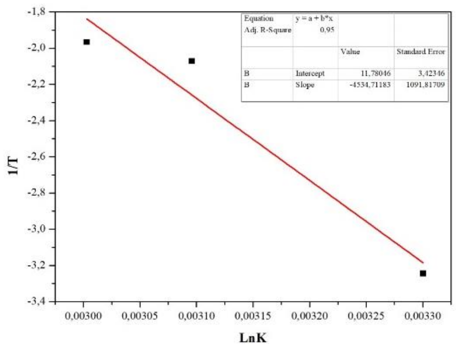

Fig. 6b. The Arrhenius plot for the hydrolysis of $NaBH_4$ in the presence of Co-Cr-B/ Al_2O_3.

3.2. Characterization of Co-Cr-B/Al_2O_3 catalyst

Fig. 7 shows XRD patterns of Co-Cr-B /Al_2O_3 catalyst synthesized by chemical reduction techniques.

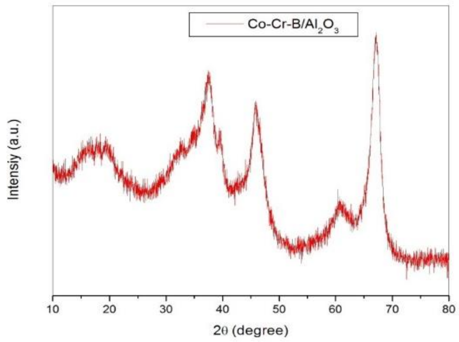

Fig. 7. XRD patterns of Co-Cr-B /Al_2O_3 catalyst.

It was observed that the Co-Cr-B /Al_2O_3 catalyst has a crystalline structure. XRD patterns of Co-Cr-B /Al_2O_3 catalyst showed only diffraction planes of γ-Al_2O_3 with reflections located at 2Ɵ 19.4^0 (111), 37.48^0 (011), 39.3^0 (222), 45.8^0 (400), 60.7^0 (511), 66.90 (440), and 84.8◦ (444), respectively. (PDF Card 00-050 0741). None of them revealed diffraction lines associated with Co or Cr metals that accounts for the good dispersion of the metal, with a particle size under the detection limit of XRD technique.

The XPS spectrums for the Co-Cr-B /Al_2O_3 catalyst are indicated in Fig. 8.

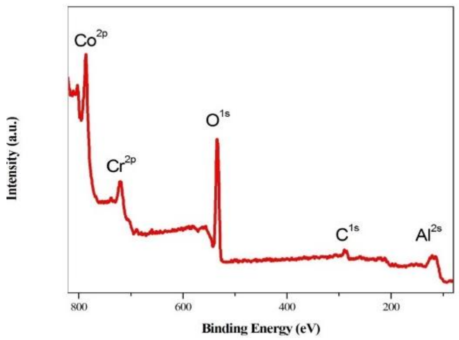

Fig. 8. XPS spectra for Co-Cr-B /Al_2O_3 catalyst.

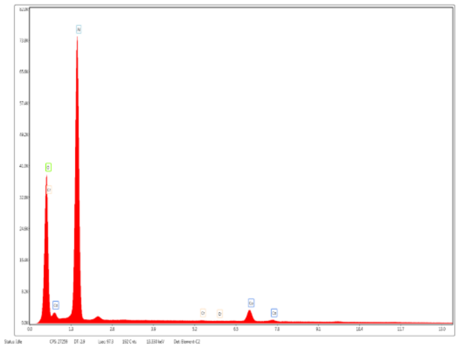

Fig. 9. The EDX spectra of Co-Cr-B /Al_2O_3 catalyst.

The observed all narrow scan spectra are related to Al^{2s} (120.1 eV), C^{1s} (285.1 eV) and O^{1s} (533.4 eV), Cr^{2p} (721.1 eV) and Co^{2p} (786 eV), respectively. Our result is consistent with data reporpted by Tsuchida et al. and Feng et al. [28].The EDX measurement was carried out to support the XPS data obtained. The EDX spectra of Co-Cr-B /Al_2O_3 catalyst are shown in Figure 9. As is clearly seen from Figure 8 and Figure 9, observation of the spectrum of Al, O, Cr and Co elements is another indication that Co-Cr-B /Al_2O_3 catalyst is efficiently synthesized.

4. Conclusion

Our conclusions can be listed as (1) Co-Cr-B/Al_2O_3 catalyst was successfully synthesized by the chemical reduction method. (2) The effect of different parameters such as amount of $NaBH_4$ (1.5 -7.5 wt %), amount of NaOH (0-10 wt %), amount of catalyst (50-150 mg), amount of metal/Al_2O_3 ratio (2.5- 20 wt %) and temperature (20-60 ^{0}C) were investigated on the catalytic activity of Co-Cr-B/Al_2O_3 catalyst for $NaBH_4$ hydrolysis. (3) A significant increase in hydrogen generation rate was observed when the NaOH concentration increased to 5% by weight compared to the NaOH-free reaction. (4) The hydrogen generation rate decreases when the concentration of $NaBH_4$ is rising up from 2.5 to 10 wt%. Thus, the optimum concentration of $NaBH_4$ was observed as 5 wt%. (5) The hydrogen generation rate increases with the molar content of metal changing from 2.5% to 5 wt%. However, when the metal/Al_2O_3 molar ratio is located from 5% to 20 wt%, the rate of hydrogen generation goes down. The catalysts show the best activity with the molar content of metal being 5%. (6) The hydrolysis kinetic order and E_a value of $NaBH_4$ in the presence of Co-Cr-B/Al_2O_3 catalyst were found as 0.15 and 37.34 kJ*mol^{-1}, respectively. According to the results obtained, Co-Cr-B/Al_2O_3 catalyst can be used as a promising material in PEMFC mobile systems.

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