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# $Al_2O_3$ SUPPORTED Co-Cu-B (Co-Cu-B/$Al_2O_3$) CATALYST FOR HYDROGEN GENERATION BY HYDROLYSIS OF AQUEOUS SODIUM BOROHYDRIDE ($NaBH_4$) SOLUTIONS

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In this study, $Al_2O_3$ supported Co-Cu-B (Co-Cu-B/$Al_2O_3$) catalyst was synthesized by chemical impregnation and precipitation method to be used for catalytic hydrogen generation from $NaBH_4$. Co-Cu-B/$Al_2O_3$ catalyst was synthesized at various ratios using Co-Cu-B/$Al_2O_3$ (5-20%). The effect of some parameters such as NaOH concentration (0-7%), $NaBH_4$ concentration (2.5-7.5%), catalyst amount (25-150 mg) and solution ambient temperature was investigated on the catalytic hydrolysis of $NaBH_4$. The hydrogen generation rate was found as 2519 and 8962 $mL*g^{-1}*min^{-1}$ for Co-Cu-B and Co-Cu-B/$Al_2O_3$ catalysts in $NaBH_4$ hydrolysis, respectively. The order rate kinetics and activation energy for Co-Cu-B/$Al_2O_3$ catalyst were determined as 0.125 and 27 $kJ*mol^{-1}$, respectively. The obtained results suggest that Co-Cu-B/$Al_2O_3$ catalysts can be used for mobile applications of PEMFC systems.

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*Keywords:* Activation energy, Catalyst, Characterization, Hydrolysis, Synthesis

## 1. Introduction

Hydrogen is considered an efficient energy carrier in the future due to its high energy content and renewability. Hydrogen creates zero eco-friendly emissions when it is used in its purest form in a proton exchange membrane fuel cell (PEMFC) [1]. Traditionally, hydrogen generation from natural gas causes greenhouse gases (CO and $CO_2$) to be released. Researchers have examined the environment-friendly hydrogen generation methods for the advancement of the hydrogen economy [2].

Storage of the required hydrogen and its usage are very difficult for the PEMFC. Hydrogen storage applications in pressurized tanks are not very useful. Chemical hydrides ($NaBH_4$, $NH_3BH_3$, LiH and $KBH_4$) are promising as hydrogen storage because they are stable with high amounts of hydrogen stored. Pure hydrogen can be produced from these metal hydrides at room temperature. Among these metal hydrides, $NaBH_4$ is widely used because it stores high amounts of hydrogen [3]. The advantages of $NaBH_4$ can be listed as (i) high hydrogen storage capacity (10.8%), (ii) high stability and high flammability at high pH value, (iii) optimum control over hydrogen generation rate with supported catalysts, (iv) the hydrogen generation rate even at low temperature [4-5].

$NaBH_4$ self-hydrolysis does not occur at high pH values. Therefore, the hydrolysis of $NaBH_4$ takes place in the presence of suitable catalysts. Many catalysts such as Co-B-P [6], Co-W-B [7], Co-Cu-B [8], $Ce_{0.05}$-Ni-W-B [9], the carbon nanotube supported CoB [10] and carbon supported Ru [11] are used in the hydrolysis of $NaBH_4$.

The activity of the catalysts is directly related to the particle size and surface area. As a result, the catalyst with small particle size and high surface area is more effective because it contacts more with the reactant. Higher amounts of catalyst are required to increase the reaction

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rate significantly [12]. Therefore, some materials with high surface area are used as support material.The activated carbon [13], carbon [14], $Al_2O3$ [15], Pd-$TiO_2$ [16] are usually used as support materials.

In this study, $Al_2O_3$ supported Co-Cu-B (Co-Cu-B/$Al_2O_3$) catalyst was synthesized by chemical impregnation and precipitation method to be used for catalytic hydrogen generation from $NaBH_4$. The ratio of support material / catalyst was determined in the catalyst synthesis. The effect of some parameters such as NaOH concentration, NaBH4 concentration, amount of catalyst and solution ambient temperature was investigated on the catalytic hydrolysis of $NaBH_4$.

## 2. Experimental part

### 2.1. Materials

All the chemical substances used in the experiments are in analytical purity and have not been subjected to any purification process. Sodium borohydride ($NaBH_4$,> 98%) was obtained from Merck. $CoCl_2.6H_2O$ and $CuCl_2.2H_2O$ were purchased from Alfa Aesar. Ethanol ($C_2H_5OH$, & gt; 99.9%) was purchased from Sigma-Aldrich. Pure water was used in the experiments.

### 2.2. Synthesis of catalyst

Co-Cu-B/$Al_2O_3$ catalyst was synthesized by chemical impregnation and precipitation method. For the preparation of the catalyst; a certain amount of $CoCl_2.6H_2O$ and $CuCl_2.2H_2O$ were dissolved in 50 ml of ethyl alcohol and then the required amount of $Al_2O_3$ was added to allow the $Al_2O_3$ impregnation of the metals at room temperature for 24 hours. The ethyl alcohol in the medium was then removed at 50 °C and 50 ml of purified water was added to the metal impregnated activated carbon and left in the ice bath. The $NaBH_4$ solution, prepared to be 5 times the total metal moles, was added drop wise to the metal impregnated $Al_2O_3$ in a nitrogen atmosphere. The resultant catalyst was filtered and washed several times with distilled water and ethyl alcohol. The synthesized catalyst was dried in a nitrogen atmosphere at 80 °C for 6 hours. The catalyst was maintained in a closed vessel in a nitrogen atmosphere for using in the hydrolysis of $NaBH_4$.

### 2.3. Characterization of catalyst

Co-Cu-B and Co-Cu-B/$Al_2O_3$ catalysts were characterized by scanning electron microscopy (SEM) (JEOL JSM 5800), Fourier transform infrared spectroscopy (FT-IR) (VERTEX 70v FTIR Spectrometer) and x-ray diffraction (XRD) (Rigaku x-ray diffractometer with Cu Kα ($\lambda$= 154,059 pm) radiation).

### 2.4. Determination of Catalyst Activity

The activity of the synthesized Co-Cu-B/$Al_2O_3$ catalyst was determined using $NaBH_4$ hydrolysis. The used parameters were NaOH concentration (0-7%), $NaBH_4$ concentration (2.5-7.5%), catalyst amount (25-150 mg) and solution ambient temperature (30-60 $^0$C).

## 3. Results and discussion

SEM and EDX results for Co-Cu-B/$Al_2O_3$ and Co-Cu-B catalysts are given in Fig. 1 (a-d). Fig. 1 (a) shows that the Co-Cu-B in Co-Cu-B/$Al_2O_3$ catalyst is retained on the $Al_2O_3$ surface and inside the pores. This leads to a greater amount of hydrogen being produced in the $NaBH_4$ hydrolysis with a small amount of Co-Cu-B catalyst, thus increasing the activity of the catalyst. The surface of the Co-Cu-B catalyst shown in Fig. 2 (c) appears to be porous and not rough. This causes the activity of the Co-Cu-B catalyst to be lowered in the hydrolysis of $NaBH_4$. The EDX spectra shown in Fig. 1 (b, d) show that Co-Cu-B/$Al_2O_3$ and Co-Cu-B catalysts were synthesized successfully, respectively.

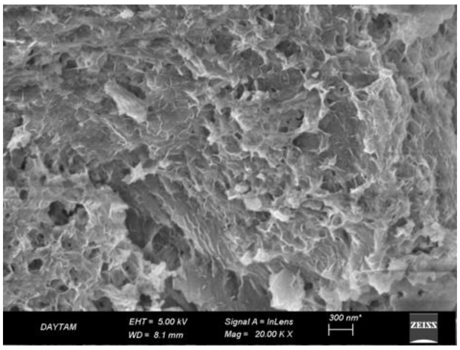

*Fig. 1a. A SEM image of Co-Cu-B/$Al_2O_3$ catalyst.*

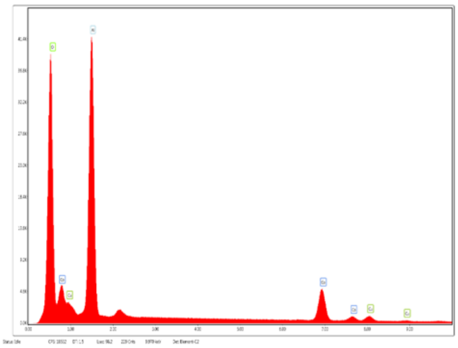

*Fig. 1b. EDX spectra for Co-Cu-B/$Al_2O_3$ catalyst.*

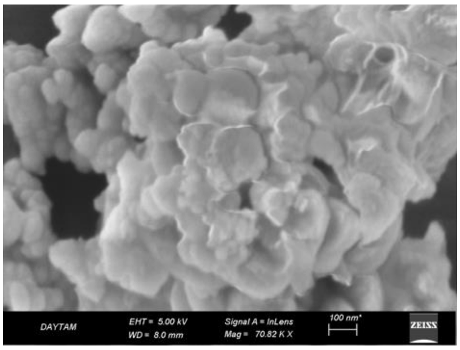

*Fig. 1c. A SEM image of Co-Cu-B catalyst.*

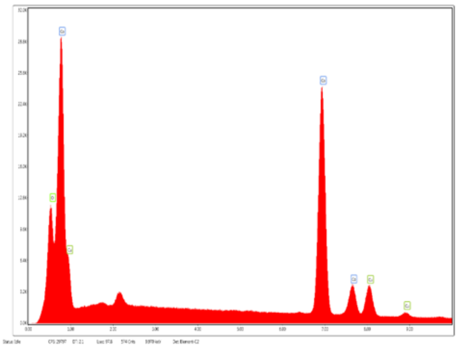

*Fig. 1d. EDX spectra for Co-Cu-B catalyst.*

The recorded XRD patterns for Co-Cu-B/$Al_2O_3$ and Co-Cu-B catalysts are indicated in Fig. 2 (a-b).

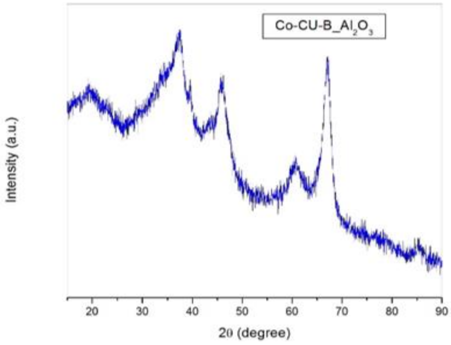

*Fig. 2a.The recorded XRD patterns for Co-Cu-B/$Al_2O_3$ catalyst.*

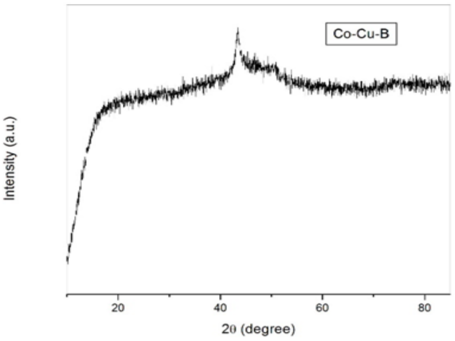

*Fig. 2b. The recorded XRD patterns for Co-Cu-B catalyst.*

As can be seen from Fig. 2 (a), the characteristic patterns of carbon are found at 2θ = 20-$25^0$. This observation is consistent with the result reported by Ding et al. [17]. Ding et al. [17] mentioned that the Co-Cu-B catalyst has a diffraction peak at 2θ = $45^0$. Similar pattern was observed in our XRD patterns for Co-Cu-B/$Al_2O_3$ and Co-Cu-B catalysts. The XRD patterns obtained show that the desired catalysts are synthesized.

FT-IR spectra scanning in the range of 4000-400 $cm^{-1}$ for Co-Cu-B/$Al_2O_3$ and Co-Cu-B catalysts are indicated in Fig. 3 (a-b).

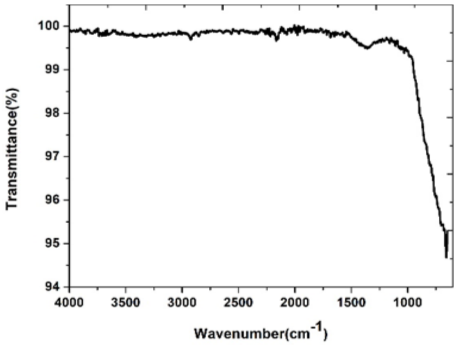

*Fig. 3a. The recorded FT-IR spectra for Co-Cu-B/$Al_2O_3$ catalyst.*

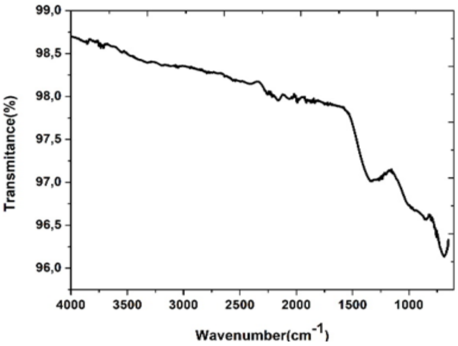

*Fig. 3b. The recorded FT-IR spectra for Co-Cu-B catalyst.*

As can be seen from Fig. 3(b), two vibration modes were observed at 1470 and 700 cm$^{-1,}$ respectively. The band located at 700 cm$^{-1}$ appears due to metal oxide groups while the FT-IR band positioned at 1470 cm$^{-1}$ corresponds to B-O groups. Similar FT-IR spectra shown in Fig. 3 (a) was observed for Co-Cu-B/$Al_2O_3$ catalyst. The intensity of current bands is weakening. The observation was in agreement with results reported by Izgi et al. [18].

$Al_2O_3$ was used at different ratios to investigate the effect of the ratio of Co-Cu-B/$Al_2O_3$ catalysts on hydrogen generation rate. The graph obtained is shown in Fig. 4.

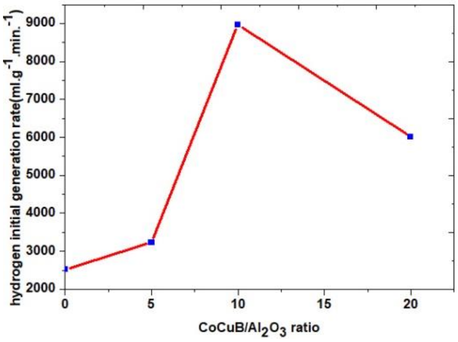

*Fig. 4. Effect of the ratio of Co-Cu-B/$Al_2O_3$ catalysts on hydrogen generation rate.*

The obtained hydrogen generation rate in the presence of Co-Cu-B/$Al_2O_3$ (5-20%) catalyst is given in Table 1.

*Table 1. The hydrogen generation rate in the presence of Co-Cu-B / $Al_2O_3$ (5-20%) catalyst.*

| The different ratio of Co-Cu-B/$Al_2O_3$ | The hydrogen generation rate (mL*g$^{-1}$*min$^{-1}$) |
|---|---|
| 0 | 2520 |
| 5 | 3000 |
| **10** | **8962** |
| 15 | 6912 |
| 20 | 5413 |

It was found that Co-Cu-B/$Al_2O_3$ (10%) catalyst has the best hydrogen generation rate. The probable cause of this situation is the increase of the surface area of Co-Cu-B/$Al_2O_3$ catalyst and the increase of active sites on the $Al_2O_3$ surface due to the support material. Baytar et al. [19] studied the effect of activated carbon supported Co-Cr-B and Co-Cr-B catalyst on the hydrogen generation rate. They found that the hydrogen generation rate is 30226 mL*g$^{-1}$*min$^{-1}$ in the presence of activated carbon supported Co-Cr-B catalyst whereas the hydrogen generation rate is 6495 mL*g$^{-1}$*min$^{-1}$ in the presence of Co-Cr-B catalyst. It can be seen in Table 1, the rate of hydrogen generation increases as the ratio of Co-Cu-B/$Al_2O_3$ increases from 5% to 10% and the rate of hydrogen generation decreases after the maximum value reaches 10%. This is probably due to the formation of multilayered catalyst layers on the $Al_2O_3$ surface as the amount of Co-Cu-B increases. Co-Cu-B/$Al_2O_3$ (10%) catalyst was used in experimental studies in which other parameters of $NaBH_4$ hydrolysis were investigated.

Since $NaBH_4$ aqueous solutions with high pH values do not self-hydrolyze, the NaOH is used to increase the pH value of the solution. The NaOH concentration is one of the most important parameters affecting the activity of the catalyst and therefore needs to be optimized. The effect of different concentrations of NaOH on $NaBH_4$ hydrolysis is shown in Fig. 5.

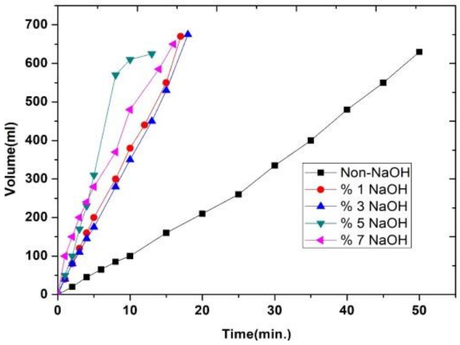

*Fig. 5. Effect of different concentrations of NaOH on $NaBH_4$ hydrolysis.*

As can be seen from Fig. 5, when the NaOH concentration is increased from 1% to 5%, the hydrogen generation rate increases whereas when the NaOH concentration is more than 5%, the hydrogen generation rate decreases. This is probably due to the two different effects of $OH^-$ ions in catalytic hydrolysis reactions. The first of these is the increase of the contact between the resulting catalyst and $NaBH_4$, which increases the electrostatic interaction between $Al_2O_3$ and the Co-Cu-B catalyst at low NaOH concentrations. Hence, when the NaOH concentration is increased from 1% to 5%, the hydrogen generation rate is increased. The second is that $OH^-$ ions present in the environment in large quantities have inhibitory effect on $NaBH_4$ hydrolysis. Another possible cause of this situation is that NaOH, which is present in excess in the solution medium, reduces the aqueous solubility of $NaBO_2$, which is the byproduct of hydrolysis of $NaBH_4$. Therefore, $NaBO_2$ in the solution will collapse and block the active sites of the catalyst, reducing the hydrogen generation rate. Ye et al. [15] used $Al_2O_3$-supported CoB catalysts for the $NaBH_4$ hydrolysis in the presence of different NaOH concentrations and found the same results. The optimal NaOH concentration for the hydrolysis of $NaBH_4$ was determined to be 5% and all subsequent experiments were carried out in the presence of a 5% NaOH concentration.

The hydrolysis of $NaBH_4$ depends not only on catalyst activity but also on factors such as $NaBH_4$ concentration, NaOH concentration and temperature. The effect of different concentrations of $NaBH_4$ on $NaBH_4$ hydrolysis is shown in Fig. 6.

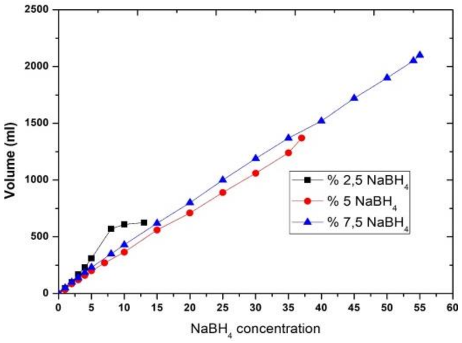

*Fig. 6. Effect of different concentrations of $NaBH_4$ on $NaBH_4$ hydrolysis.*

As can be seen from Fig. 6, as the concentration of $NaBH_4$ increases, the hydrogen generation rate decreases. Especially when the NaBH4 concentration is 7.5%, there is a very serious decrease in the hydrogen generation rate. The probable cause of this situation is that the solubility of the by-product $NaBO_2$ in water is limited in the hydrolysis of $NaBH_4$. Another reason for this is that the concentration of $NaBH_4$ and $NaBO_2$ in the medium is high and therefore the solution viscosity increases and accordingly, the $NaBH_4$ slows the mass transfer to the catalyst surface. Similar observation was reported by Izgi et al. [19].

The effect of different catalyst amounts on $NaBH_4$ hydrolysis is shown in Fig. 7.

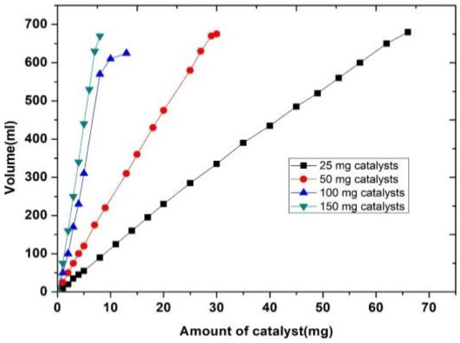

*Fig. 7. Effect of different catalyst amounts on $NaBH_4$ hydrolysis.*

As can be seen from Fig. 7, as the amount of catalyst increases, the hydrogen generation rate also increases. This suggests that $NaBH_4$ hydrolysis is catalyst-controlled. It can be seen that when the amount of catalyst is increased from 25 mg to 100 mg, the hydrogen generation rate increases and then decreases. It is thought that as the amount of catalyst increases, the catalyst is agglomerated in solution.

The effect of temperature on $NaBH_4$ hydrolysis is shown in Fig. 8. As can be seen from Figure 8, there is a significant increase in the volume of hydrogen obtained as a result of $NaBH_4$ hydrolysis as the temperature increases. The hydrolysis of 2.5% $NaBH_4$ takes place at 30 °C for 13 minutes at 40 °C for 8 minutes and at 60 °C for 5 minutes.

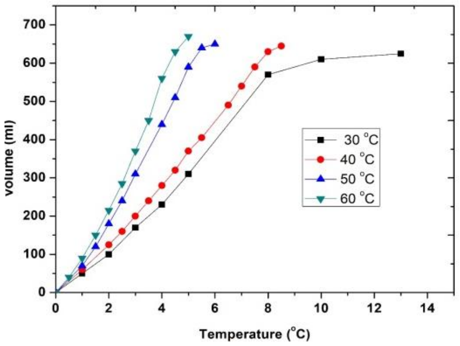

*Fig. 8. The effect of temperature on $NaBH_4$ hydrolysis.*

One of the most basic reasons for measuring the reaction time of any reaction at different temperatures is to determine the reaction rate constant and to determine the activation energy required for the reaction to take place accordingly. For this reason, an $n^{th}$ order reaction is used to determine the rate constants at different temperatures. Thus, the reaction rate constant for this reaction is determined by the equation (1) given below.

$$\frac{1}{C_A^{n-1}} = (n-1)kt + \frac{1}{C_{A_0}^{n-1}} \tag{1}$$

Fig. 9 indicates $C_{\mathrm{NaBH4}}^{n-1}$ versus t plots for different temperatures. After the most suitable n value has been determined, the value of k is obtained from the slope of the obtained curve.

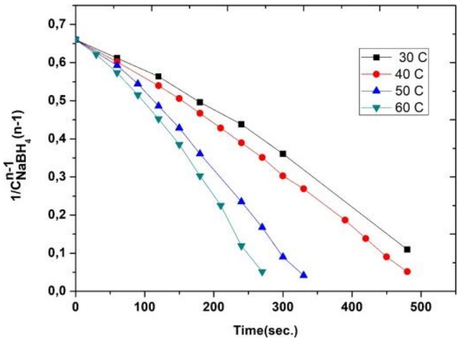

*Fig. 9.* $C_{NaBH4}^{n-1}$ *versus t plots for different temperatures.*

As you can see in Fig. 9, the selected n values are consistent at all temperatures and are all linear. The order rate kinetics for Co-Cu-B/$Al_2O_3$ catalyst were determined as 0.125. The rate constants at different temperatures are given in Table 2. Activation energy was determined by Arhenius equation (2) based on these rate constants at different temperatures.

*Table 2. The rate constants at different temperatures.*

| Temperature ($^{o}$C) | Rate constant,k(mL*g$^{-1}$*min$^{-1}$ ) | Kinetic order |
|---|---|---|
| 30 | 0,0621 | 0.125 |
| 40 | 0,0906 | 0.125 |
| 50 | 0,1359 | 0.125 |
| 60 | 0,1622 | 0.125 |

$$\ln(k) = lnA - \frac{E}{RT} \tag{2}$$

The obtained ln(k) versus (1/T) plot is demonstrated in Fig. 10. It was determined that the activation energy required for the hydrolysis of $NaBH_4$ in the presence of Co-Cu-B/$Al_2O_3$ catalyst is 27 kJ*mol$^{-1}$. This value is very low and indicates that the activity of the catalyst is very high.

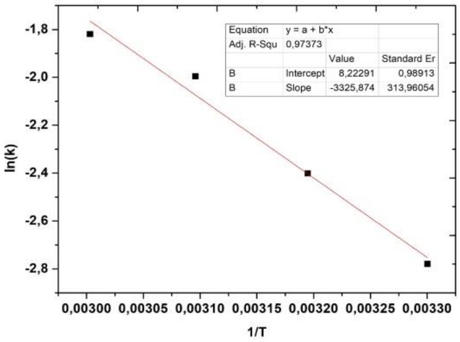

*Fig. 10. Plot of ln(k) versus (1/T) to determine activation energy.*

## 4. Conclusions

In this study, Co-Cu-B/$Al_2O_3$ catalyst was synthesized by chemical impregnation precipitation method for using in the hydrolysis of $NaBH_4$. The hydrogen generation rate of the synthesized Co-Cu-B/$Al_2O_3$ catalyst was found to be 8962 $mL*g^{-1}*min^{-1}$ while the hydrogen generation rate of Co-Cu-B catalyst was 2519 $mL*g^{-1}*min^{-1}$. It was determined that the activity of the Co-Cu-B catalyst by its attachment to the $Al_2O_3$ surface is increased about 4 times. The effect of some parameters such as NaOH concentration, $NaBH_4$ concentration catalyst amount and solution temperature was investigated on the catalytic hydrolysis of $NaBH_4$.

It was determined that the hydrogen generation rate is best when the NaOH concentration is 5%. It was found that the increased $NaBH_4$ concentration reduces the hydrogen generation rate and the increasing amount of catalyst increases the hydrogen generation rate. It was determined that the rate of hydrogen generation increases significantly with increasing temperature. The order rate kinetics and activation energy for Co-Cu-B/$Al_2O_3$ catalyst were determined as 0.125 and 27 $kJ*mol^{-1}$, respectively. The obtained results suggest that Co-Cu-B/$Al_2O_3$ catalysts can be used for mobile applications of PEMFC systems.

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