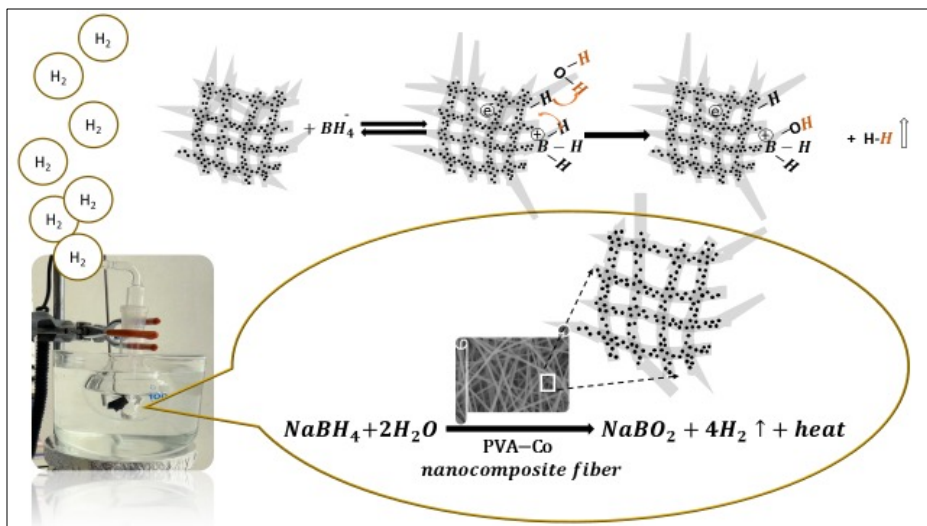


Facile Production of Polymer-Nanometal Composite Nanofiber Catalyst Having Good Catalytic Activity in Hydrogen Generation

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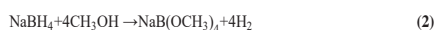
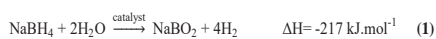
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The need for alternative energy sources is increasing day by day. Among these alternative energy sources, hydrogen has been the subject of many researchers. In this article, for the reaction of hydrogen production via hydrolysis of NaBH_4 , a PVA-Co composite fiber was developed as an effective catalyst, which can be synthesized in a simple one-step route. The characterization studies of PVA-metal composite fibers and optimization studies for hydrogen production have been carried out. As a result of the experiments performed with PVA-Co composite fiber, activation energy, enthalpy and entropy values were calculated by using the Arrhenius equation and Eyring equation. The required activation energy for the NaBH_4 hydrolysis reaction using the PVA-Co composite fiber catalyst was calculated as 40.96 kJ/mol. Hydrogen generation rate (HGR) was found to be 5187 mL H_2 /min.g_{Co} at 343.15 K.



Introduction

Today, the useful energy sources for human need are very limited and the technological developments increase the energy deficit more and more. Therefore, it has become a necessity to find alternative energy sources worldwide. One of the alternatives is hydrogen gas which is reliable and provide environmentally friendly product with usage. It is accepted as the energy of the future because of having a high energy density of $1.42 \times 10^8 \text{ J}\cdot\text{kg}^{-1}$ and its production has been the popular subject of many studies [1, 2]. Compounds such as metal boron hydrides, ammonia borane, hydrazine hydrates, formic acid can be used for sustainable borohydrides, NaBH_4 is rich in hydrogen since its theoretical hydrogen capacity is 10.8% gravimetrically. It is non-flammable, highly soluble in water, environmentally friendly and economical [1, 3]. As a result of the hydrolysis reaction, four moles of hydrogen gas is released with an enthalpy change of $-217 \text{ kJ}\cdot\text{mol}^{-1}$. For reusage, the NaBO_2 product of the process can be reversibly converted to NaBH_4 in closed systems as well [2, 4].



The spontaneous hydrolysis reaction of NaBH_4 proceeds slowly and the conversion rate is 7-8%. Therefore, the reaction efficiency of such reactions can be increased by using a homogeneous or heterogeneous catalyst [5]. Hydrogen gas production via hydrolysis by using catalyst provides H_2 gas with high purity [3]. Therefore, noble metal such as platinum [6], ruthenium [7], palladium [8], gold [9] etc. or transitions metals like cobalt [10], nickel [11], copper [12] etc. have been investigated by many researchers as catalysts for the production of hydrogen in the catalytic hydrolysis of NaBH_4 . Among these catalyst systems, cobalt nanoparticle has been preferred in many studies due

to its catalytical effect. Mahpudiz et al. [13] synthesized a catalyst by supporting cobalt nanoparticles on a magnesium-aluminum double hydroxyl layer. As a result of the experiments, they calculated the activation energy for H_2 production as $56.9 \text{ kJ}\cdot\text{mol}^{-1}$ and the HGR value at 25°C as $4520 \text{ mLmin}^{-1}\text{g}_{\text{Co}}^{-1}$. Ugale et al. [10] synthesized a carbon loaded cobalt oxide ($\text{C-Co}_3\text{O}_4$) catalyst. As a result of the experiments, they calculated the activation energy for H_2 production as $55.9 \text{ kJ}\cdot\text{mol}^{-1}$ and the HGR value at 47°C as $5430 \text{ mLmin}^{-1}\text{g}^{-1}$. Saka et al. [14] synthesized CoB catalyst on kaolin support material activated with acetic acid. As a result of the experiments, they calculated the activation energy for H_2 production as $49.41 \text{ kJ}\cdot\text{mol}^{-1}$ and the HGR value at 50°C as $3400 \text{ mLmin}^{-1}\text{g}_{\text{catalyst}}^{-1}$. Karami et al. [15] synthesized nanocomposites which is CoFe_2O_4 nanoparticles in graphene nanoribbons. According to this article, the activation energy for H_2 production as $31.4 \text{ kJ}\cdot\text{mol}^{-1}$ and the HGR value at 35°C as $3700 \text{ mLmin}^{-1}\text{g}^{-1}$.

Many methods can be used for catalyst synthesis. Among them, electrospinning method is one of the frequently preferred methods. In this method, the solution is provided to form charged droplets with the help of an injection pump. Droplets that exceed the surface tension in the electric field are separated into fine jets. The fiber solvent evaporates and accumulates in the collector plate. Therefore, after choosing a suitable solvent in this method, the concentration of the polymer solution, the voltage to be given, the flow rate, and the distance parameters can be optimized to prepare the suitable fibers for the purpose. It is a simple method used to produce one-dimensional polymer fibers with diameters ranging from 3 nm to 1 mm [16, 17]. Since it offers the advantages of surface functionalization, great porosity, high mechanical properties, low density, extensive surface area and

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volume ratio, low cost etc., it offers a wide range of work opportunities [18] such as biomedical applications [19], adsorption [20, 21], lithium-ion batteries [22] and energy [23]. Due to these advantages, nanofibers have been produced by using various polymer, metal, metal oxide and ceramic composites in order to make the method more efficient [16]. This method makes it possible to work with many materials, from natural polymers to synthetic polymers [18]. The fact that PVA is suitable for use in the electrospinning method, low cost, biodegradable, biocompatible and water-soluble, has chemical and thermal stability has made it preferred in many studies [24–26].

Within the scope of this study, PVA-M (M: Co, Ni, Cu) composite fibers were prepared using the above-mentioned electrospinning method, for the NaBH_4 hydrolysis reaction. After the reduction of PVA-M fibers, the hydrolysis reaction catalyzed with these composite fibers. The hydrogen gas produced by the water displacement method has demonstrated that the PVA-M composite fibers for hydrolysis reaction have a good catalytic effect. In addition, the efficiency of PVA-M composite fibers was also demonstrated by calculating the reaction activation energy. Here in, we report a simple and effective catalyst for the production of hydrogen gas, which is one of the alternative energy sources that is gaining importance today.

Material and Methods

Poly(vinyl alcohol) (PVA, M_w : 130000 g/mol, 99%) was supplied by Aldrich. Sodium hydroxide 98% were supplied by Sigma Aldrich. Sodium borohydride 98% was obtained from Across Organics. Cobalt(II) chloride hexahydrate 99% and copper(II) chloride were provided by Carlo Erba, 1-hexadecyl trimethyl ammonium bromide (CTAB) 98% was provided by Alfa Aesar. Nickel(II) chloride hexahydrate 97% was supplied by Tekkim.

Invenso Ne200 branded electrospinning device was used in experiments to produce fiber. Magnetic stirrer with heater branded Heidolph MR Hei-Tec was used in experiments. Hitachi Regulus 8230 scanning electron microscopy (SEM) and Tetra SII Exster 6000 instrument thermal gravimetric analysis (TGA) was used for characterization studies.

Preparation of PVA-nanometal composite fiber

After preparation of 6% PVA solution followed by addition of 0.782 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.125 g CTAB to reach 130 mM and 13.72 mM concentrations, respectively. The resulting light pink colored solution was

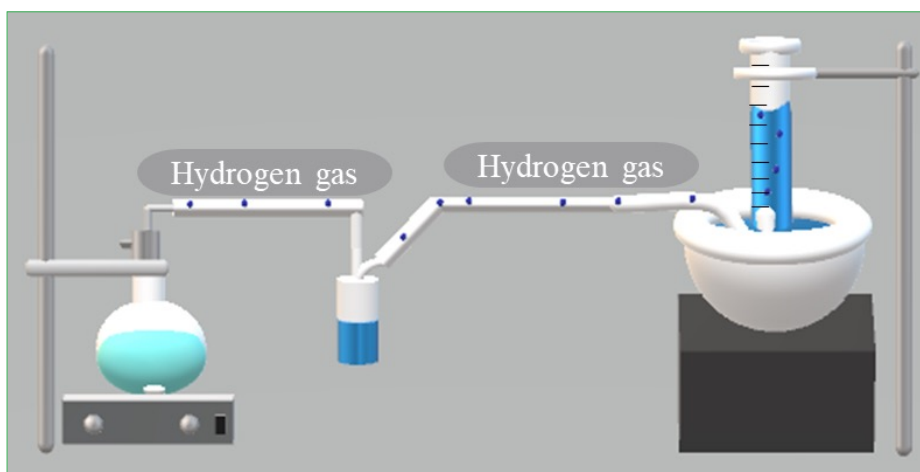


Figure 1. Home-made experimental setup for hydrogen generation

collected on aluminum foil by electrospinning device with 17 kV DC voltage, 1 mL/h flow rate and 12 cm distance parameters. Finally, blue green PVA-cobalt salt composite fiber was taken on the aluminum foil. PVA-Ni and PVA-Cu fibers which were investigated for use as catalysts were produced by the same procedure so as to be 6% PVA with 0.13 M CuCl_2 metal salt. The reduced PVA-Co composite fibers were freshly prepared prior to the experiment. In order to reduce all the cobalt in the fiber content to be fully active in the hydrolysis reaction, the reduction process was carried out in a concentrated NaBH_4 solution. After the gas output was finished, the fibers were washed and used in the hydrolysis reaction. The same processes

given above were also used to produce PVA-Cu and PVA-Ni composite systems.

H_2 production via NaBH_4 hydrolysis

The catalytic performance of PVA-Co composite fibers synthesized in the home-made experimental setup given below for hydrogen production was investigated (Figure 1). NaOH is added into 50 mL water to get 5% conc and left for thermal equilibrium. Then, 0.189 mmol Co-containing PVA-Co composite fiber is added into it. Finally, to start experiment, 0.05 M NaBH_4 is added and stirred at 1000 rpm. The amount of H_2 produced over time was determined by using water displacement method and the optimum parameters were decided.

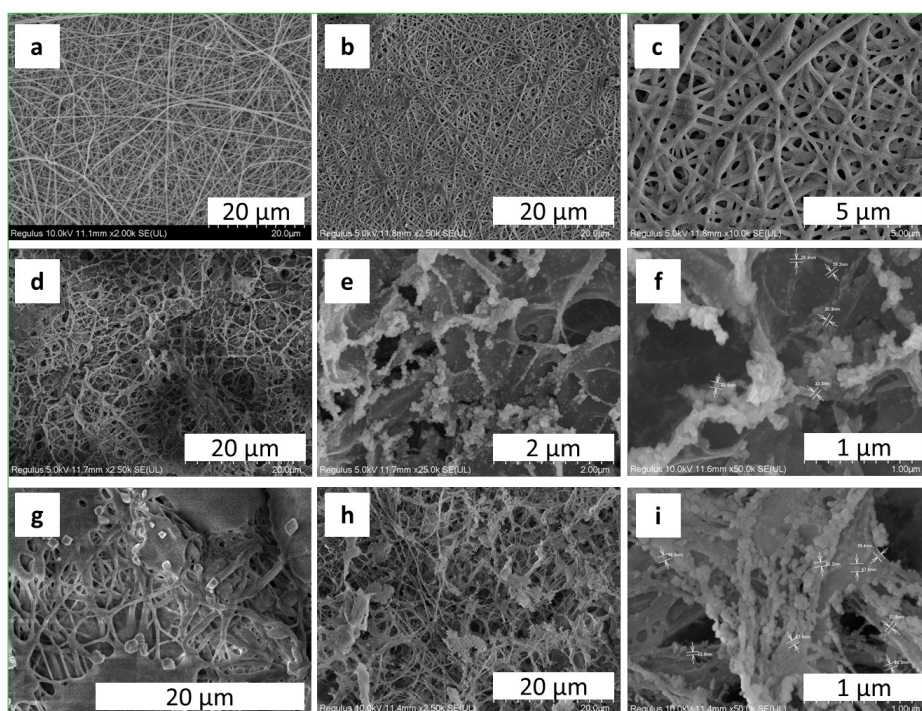


Figure 2. SEM images of the fibers: a) PVA, b) and c) PVA- Co^{2+} composite fiber, d), e) and f) Reduced PVA-Co composite fiber, g) PVA- Ni^{2+} composite fiber, h) and i) Reduced PVA-Ni composite fiber.

Characterization of the composite fiber

SEM analyzes were performed for the characterization of the prepared PVA-nanometal composite fibers. SEM measurements that is under accelerating voltages of 1–10 kV were taken to characterize the surface morphologies of PVA fiber, PVA-Ni, PVA-Co composite fibers. Furthermore, amount of metal in PVA-M composite fiber was determined with TGA. TGA analyzes with under nitrogen atmosphere, under between 30 °C and 900 °C temperatures and 10 °C/min rate were carried out to determine the amount of metal in the composite fibers.

Results and Discussions

Characterization studies

The characterization of the prepared fibers was carried out by SEM studies. First, SEM images were taken in order to examine the surface morphology of PVA fiber and PVA-metal composite fibers produced with the electrospinning. The observed nanosized filamentous structures in SEM images indicated the production of fibers with heterogeneous size distribution (Figure 2a). When SEM images are examined, cobalt salts in unreduced PVA-Co fibers are seen in Figure 2bc. After reduction, SEM images of PVA-Co composite fibers show that they contain cobalt nanoparticles in the range of 25-50 nm (Figure 2def). When Figure 2g is examined, nickel salts are seen in PVA-Ni fibers. Figure 2hi SEM images show that after reduction, PVA-Ni composite fibers contain nickel nanoparticles in the range of 20-70 nm.

After electrospinning process, PVA-Co²⁺ composite fiber was obtained with blue-green color. The pink color, that occurs when the obtained fiber comes into contact with water, indicates that the cobalt is in ionic form and comes out of the fibers by dissolving. In order to determine its catalytic effect in the hydrolysis reaction of NaBH₄, the reduction process was carried out to form PVA-Co⁰ composite fibers. After reduction, its color turned in black due to formation metallic nanocobalt [27, 28].

Thermal gravimetric analyzes (TGA) were carried out in order to determine the amount of metal in PVA-Co, PVA-Ni and PVA-Cu composite fibers. TGA results were analyzed in Figure 3, it is seen that PVA nanofiber, which has similar results in the literature, degrades to a great extent in the range of 190-485 °C and loses 92% of its mass at 485 °C [29, 30]. The samples used in these analyzes were prepared by mixing 6% PVA with 0.13 M metal salt. It is seen that PVA-Ni composite fiber contains 9.2 % Ni, PVA-Cu

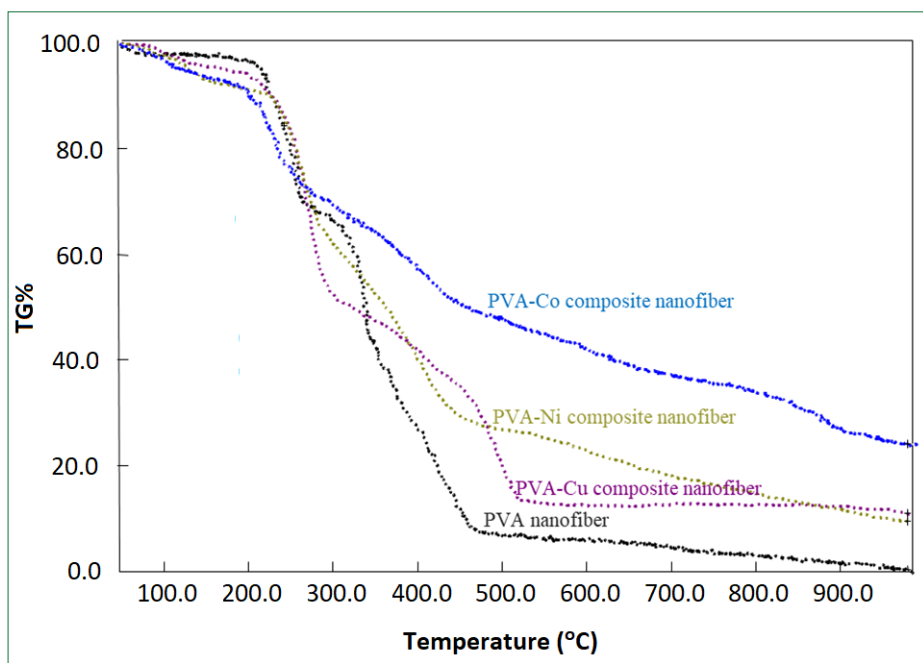


Figure 3. TG% of PVA nanofiber and PVA-Co, PVA-Ni and PVA-Cu composite nanofibers.

composite fiber contains 10.7 % Cu and PVA-Co composite fiber contains 23.8 % Co.

Effect of PVA-metal nanofiber

Because of the slow kinetics of the hydrolysis reactions of borohydrides used for hydrogen storage, catalysts are generally developed for these reactions. Metals are usually used as catalyst [31, 32]. In our study, nanometals in PVA nanofiber structure were used as catalyst. The efficiencies of PVA fiber, PVA-Cu, PVA-Ni, PVA-Co composite fibers were investigated in the H₂ production

by NaBH₄ hydrolysis reaction. Figure 4 indicates that PVA fiber did not have any activity. When composite fibers were compared with each other, the order of activity was Co > Ni > Cu. Since the best results were obtained with PVA-Co composite fiber, optimization studies were carried out for this composite fiber.

Effect of NaOH and NaBH₄ concentration

Spontaneous hydrolysis of NaBH₄ occurs below pH 9. NaBH₄ is preserved in alkaline solutions (pH > 9) to maintain its chemical stability. In energy applications, it is used

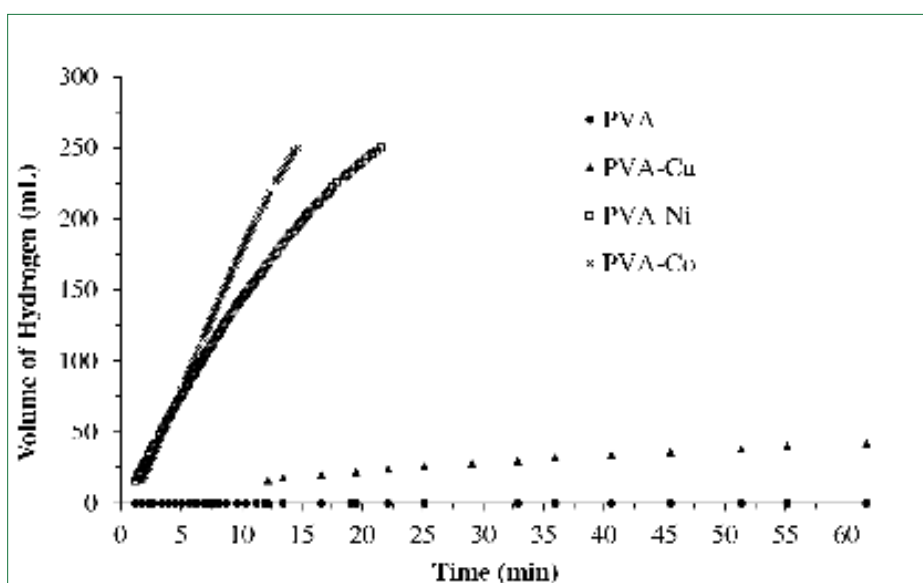


Figure 4. The effect of Co, Cu and Ni metal nanoparticles on the hydrolysis of NaBH₄ [Reaction conditions: 0.189 mmol metal containing PVA-M composite, 50 mL 50 mM NaBH₄ at 50 °C with 5% NaOH, 1000 rpm mixing rate].

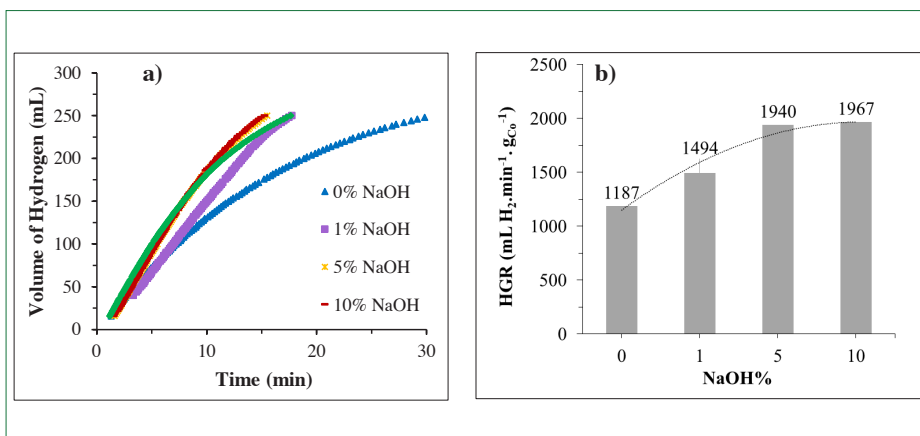


Figure 5. a) The effect of the amount of NaOH on the hydrolysis of NaBH₄, b) The effect of the amount of NaOH on the HGR [Reaction conditions: 0.189 mmol metal containing PVA-Co composite; 50 mL 50 mM NaBH₄ at 50 °C, 1000 rpm mixing rate.]

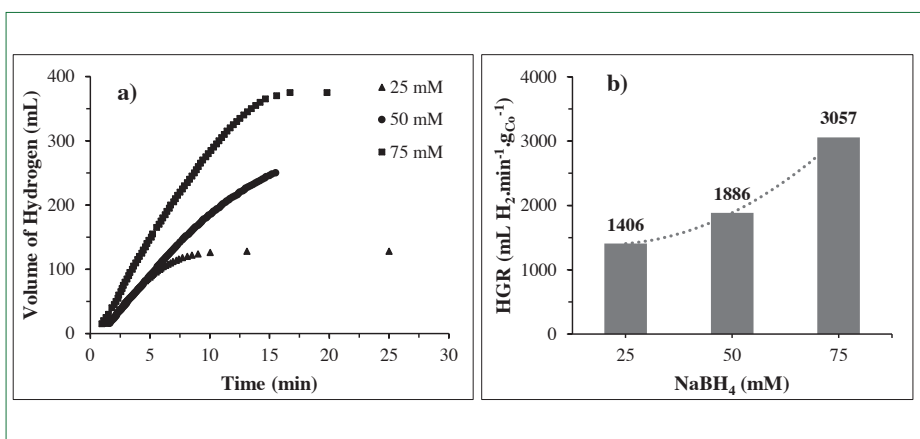


Figure 6. a) The effect of NaBH₄ on the hydrolysis of NaBH₄, b) The effect of NaBH₄ on the HGR [Reaction conditions: 0.189 mmol metal containing PVA-Co composite; 50 mL 25, 50 and 75 mM NaBH₄ at 50 °C with 5% NaOH 1000 rpm mixing rate.]

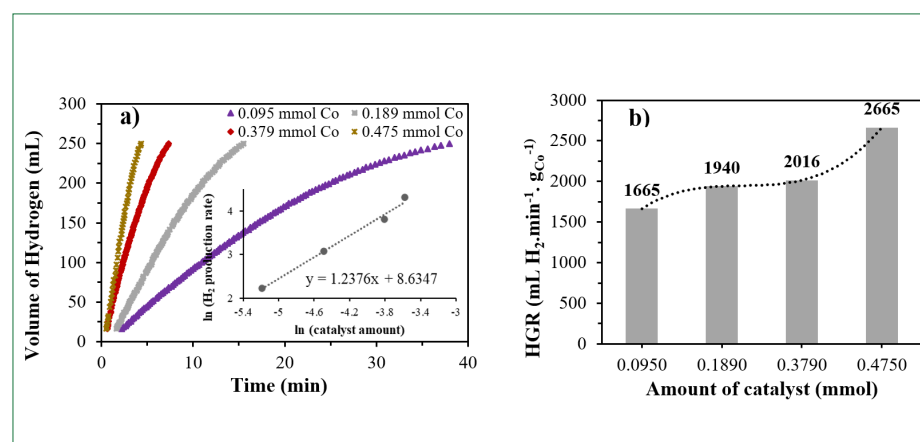


Figure 7. a) The effect of the amount of catalyst on the hydrolysis of NaBH₄, b) The effect of the amount of catalyst on the HGR values. [Reaction conditions: PVA-Co composite containing 0.095-0.475 mmol Co nanoparticles; 50 mL 50 mM NaBH₄ at 50 °C with 5% NaOH, 1000 rpm mixing rate.]

in an alkaline media as it provides controlled hydrolysis [8, 10]. For this reason, the effect of NaOH on the experiment and Figure 5 was examined the efficiency increased as the percentage of NaOH increased. However, the hydrolysis reaction rate of NaBH₄ decreases with the excess NaOH in the environment due to the decrease in the solubility of NaBO₂ and the coating of the catalyst surface [33]. According to these results, HGR values were between 1187-1967 and 5% NaOH was determined as the optimum in terms of cost, since there was no big difference between 5% and 10% NaOH solutions.

Although it is desired to increase the amount of NaBH₄ to obtain more H₂ gas, the solubility of NaBH₄ effect of catalyst are limited due to the NaBO₂ by-product formed in the hydrolysis reaction [34]. For this reason, the effect of NaBH₄ concentration is also evaluated in NaBH₄ hydrolysis reactions experiments. When Figure 6a is examined, as NaBH₄ concentration increases, H₂ production increases depending on time. In Figure 6b, an increase of 25-75 mM in the concentration and an increase in HGR values of 1406-3057 mL·min⁻¹·g_{Co}⁻¹ are observed.

The amount of PVA-Co to catalyze the hydrolysis reaction of 50 mM NaBH₄ in 5% NaOH solution was investigated and the results were given in Figure 7. It indicates that an increase on the amount of catalyst caused an increase on the amount of hydrogen produced. 1665 mL H₂·min⁻¹·g_{Co}⁻¹ for catalyst containing 0.095 mmol Co, 1940 mL H₂·min⁻¹·g_{Co}⁻¹ for catalyst containing 0.189 mmol Co, 2016 mL H₂·min⁻¹·g_{Co}⁻¹ for catalyst containing 0.379 mmol Co, 2665 mL H₂·min⁻¹·g_{Co}⁻¹ for catalyst containing 0.475 mmol Co was produced as seen in Figure 7b. The slope of the inside graph given in Figure 7a was found to be 1.2. This result shows that the reaction kinetics is pseudo first order.

The effect of temperature on the reaction rate is a well-known fact. Therefore, the effect of temperature for the hydrolysis reaction occurring is shown in Figure 8a. When 50 mM NaBH₄ hydrolysis experiment was performed under 0.189 mmol metal containing PVA-Co composite in 5% NaOH solution at different temperatures, 830 mL H₂·min⁻¹·g_{Co}⁻¹ for 303.15 K, 1250 mL H₂·min⁻¹·g_{Co}⁻¹ for 313.15 K, 1942 mL H₂·min⁻¹·g_{Co}⁻¹ for 323.15 K, 3681 mL H₂·min⁻¹·g_{Co}⁻¹ for 333.15 K, 5187 mL H₂·min⁻¹·g_{Co}⁻¹ for 343.15 K was produced (Figure 8b). As can be seen from the results, as the temperature increases, the reaction time shortens and the HGR values increase.

Activation energy (E_a) was calculated by using Arrhenius equation (Equation 1).

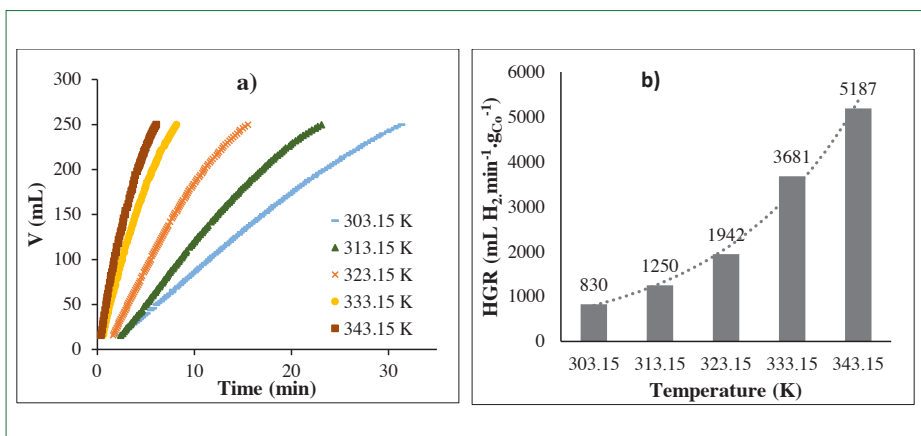


Figure 8. a) The effect of temperature on the hydrolysis of NaBH_4 , b) The effect of temperature on HGR values [Reaction conditions: 0.189 mmol metal containing PVA-Co composite; 50 mL 50 mM NaBH_4 with 5% NaOH, 1000 rpm mixing rate].

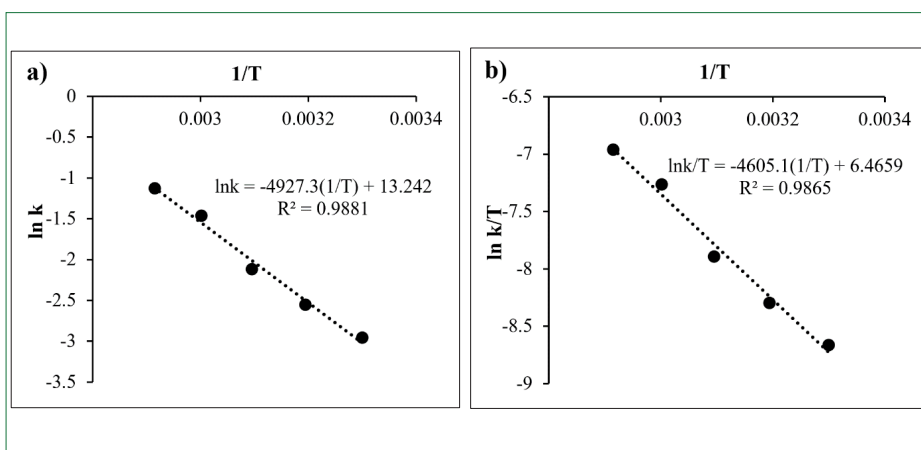


Figure 9. a) $1/T$ vs $\ln k$ according to Arrhenius equation, b) $1/T$ vs $\ln(k/T)$ according to Eyring equation [Reaction conditions: 0.189 mmol cobalt containing PVA-Co composite; 50 mL 50 mM NaBH_4 with 5% NaOH, 1000 rpm mixing rate].

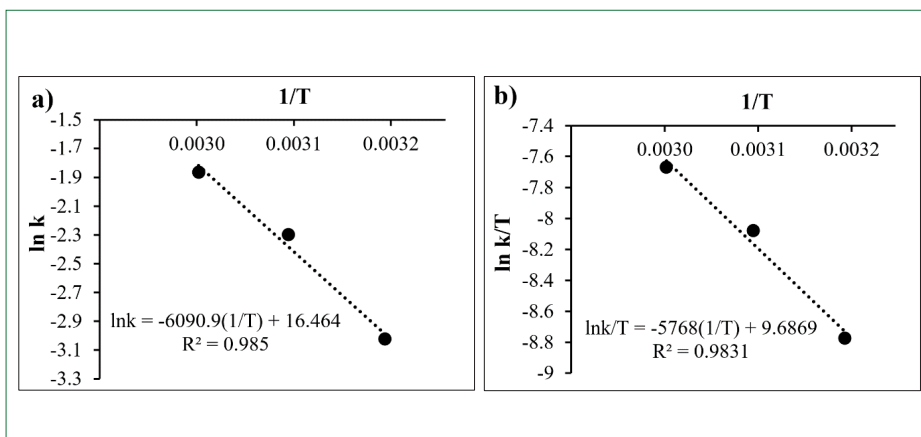


Figure 10. a) $1/T$ vs $\ln k$ according to Arrhenius equation, b) $1/T$ vs $\ln(k/T)$ according to Eyring equation [Reaction conditions: 0.189 mmol nickel containing PVA-Ni composite, 50 mL 50 mM NaBH_4 with 5% NaOH, 1000 rpm mixing rate].

Enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) values were calculated by using Eyring equation (Equation 2). The R constant $8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$, Boltzman constant (k_B) $1.38 \times 10^{-23} \text{ J.K}^{-1}$ and Planck constant (h) $6.626 \times 10^{-34} \text{ J.s}$ values were used in these equations.

$$\ln k = \ln A - \left(\frac{E_a}{RT} \right) \quad \text{Equation 1}$$

$$\ln \frac{k}{T} = \ln \left(\frac{k_B}{h} \right) + \left(\frac{\Delta S^\ddagger}{R} \right) - \left(\frac{\Delta H^\ddagger}{R} \right) \left(\frac{1}{T} \right) \quad \text{Equation 2}$$

E_a was calculated for PVA-Co composite fiber as 40.96 kJ/mol , using the slope found when plotting $1/T$ versus $\ln k$ according to the Arrhenius equation given in Equation 1 (Figure 9a). According to Eyring equation (Equation 2), ΔS^\ddagger and ΔH^\ddagger values are calculated by using $1/T$ versus $\ln k/T$ graph. ΔS^\ddagger and ΔH^\ddagger values are calculated as $-143.78 \text{ J.K}^{-1} \text{ mol}^{-1}$, $38.29 \text{ kJ.mol}^{-1}$, respectively (Figure 9b).

In addition, in the system where PVA-Ni composite fibers were used as catalysts, E_a was calculated as $50.64 \text{ kJ.mol}^{-1}$, using the slope found when plotting $1/T$ versus $\ln k$ according to the Arrhenius equation given in Equation 1 (Figure 10a). According to Eyring equation (Equation 2), ΔS^\ddagger and ΔH^\ddagger values were calculated by using $1/T$ versus $\ln k/T$ graph. ΔS^\ddagger and ΔH^\ddagger values were calculated as $-117.0 \text{ J.K}^{-1} \text{ mol}^{-1}$, $47.96 \text{ kJ.mol}^{-1}$, respectively (Figure 10b).

In Table 1, the HGR and E_a values obtained from the studies conducted for the production of H_2 by the hydrolysis of NaBH_4 are compared with the values obtained from this study. As can be seen, effective PVA-Co composite fiber was prepared for hydrogen production.

The reuse studies of 0.189 mmol cobalt containing PVA-Co composite in the NaBH_4 hydrolysis reaction were performed and the results were demonstrated in Figure 11. As can be seen that the conversion is 100%. The catalyst maintains its activity at a rate of 69.28% after six measurements and 51.89% after 10 measurements. In the literature, it has been stated that such decrease on the catalyst activity occurs due to various reasons such as catalyst poisoning, formed by-products, corrosion of the catalyst, precipitation of borates on the catalyst surface, and degradation of the catalyst [43].

Conclusion

Many catalysts have been developed for hydrogen production in the literature. In general, such catalysts are synthesized in more than one step and have a higher cost.

Table 1. Catalytic activity and activation energy values for the hydrolysis of NaBH₄ catalyzed by different Co catalysts.

Catalyst	Hydrogen Generation Rate (HGR) Catalytic activity	Activation Energy (E _a)	Ref.
Co/MCM41-0.5w	915.2 mL.min ⁻¹ .g _{cat} ⁻¹ at 25 °C	108.70 kJ.mol ⁻¹ .	[35]
Co(20)/AC _{ox} catalyst	6420 mL.min ⁻¹ .g _{Co} ⁻¹ at 80°C	59.00 kJ.mol ⁻¹	[36]
CoB/bentonite	921.94 mL.min ⁻¹ .g _{cat} ⁻¹ and	55.76 kJ.mol ⁻¹	[37]
CoB/Na-bentonite	1601.45 mL.min ⁻¹ .g _{cat} ⁻¹ at 70 °C.	56.61 kJ.mol ⁻¹	
C-Co ₃ O ₄	5430 mL.min ⁻¹ .g ⁻¹ at 47 °C	55.90 kJ.mol ⁻¹	[10]
Co-Fe-B	10690.3 mL.min ⁻¹ .g ⁻¹ at room temp	55.60 kJ.mol ⁻¹	[4]
Ru/CoOx@NPC	8019.5 mL.min ⁻¹ .g _{cat} ⁻¹ at 25 °C	54.20 kJ.mol ⁻¹	[7]
Fe3O4@SiO2@KCC-1@Co	3830 mL.min ⁻¹ .g _{Co} ⁻¹ at 30 °C	53.63 kJ.mol ⁻¹	[38]
Co@C	1680 mL.min ⁻¹ .g ⁻¹ at 30 °C	45.00 kJ.mol ⁻¹	[39]
Co@P ₄ VPGB@PMC	4499 mL.min ⁻¹ .g _{cat} ⁻¹ at 58.9 °C	41.27 kJ.mol ⁻¹	[40]
Halloysite-supported Co-B catalyst	33854 mL.min ⁻¹ .g _{Co} ⁻¹ at 39.96 °C	-	[41]
p(AMPS)-Co composite	5351.5 mL.min ⁻¹ .g _{Co} ⁻¹ at 70 °C	35.46 kJ.mol ⁻¹	[42]
CoFe ₂ O ₄ /GONRs catalyst	3700 mL. min ⁻¹ .g ⁻¹ at 35 °C	31.40 kJ.mol ⁻¹	[15]
PVA-Co composite	5187mL.min ⁻¹ .g _{Co} ⁻¹ at 70 °C	40.96 kJ.mol ⁻¹	This work

It is a great advantage that the composite fiber can be prepared in a single step and economically. With this study, we report one step pathway for the production of PVA-nanometal composite fiber as catalyst. Nano-sized metal particles are clearly seen in the SEM images of the composite fibers. The NaBH₄ hydrolysis reaction was successfully catalyzed by these metal

nanoparticles and yielded with the production of hydrogen gas, which is one of the alternative energy sources. It has been observed that PVA-Co composite fibers catalyzed the reaction more effectively than nickel and copper containing composite systems. When experiments were made between 303.15 and 343.15 K temperature values, the activation energy was calculated

to be 40.96 kJ.mol⁻¹. Moreover, HGR value was 5187 mL_{H₂}.min⁻¹.g_{Co}⁻¹. Having the advantage of being prepared in a simple way that catalyzes the hydrolysis reaction of NaBH₄, PVA-Co composite fibers are expected to be promising for future energy studies.

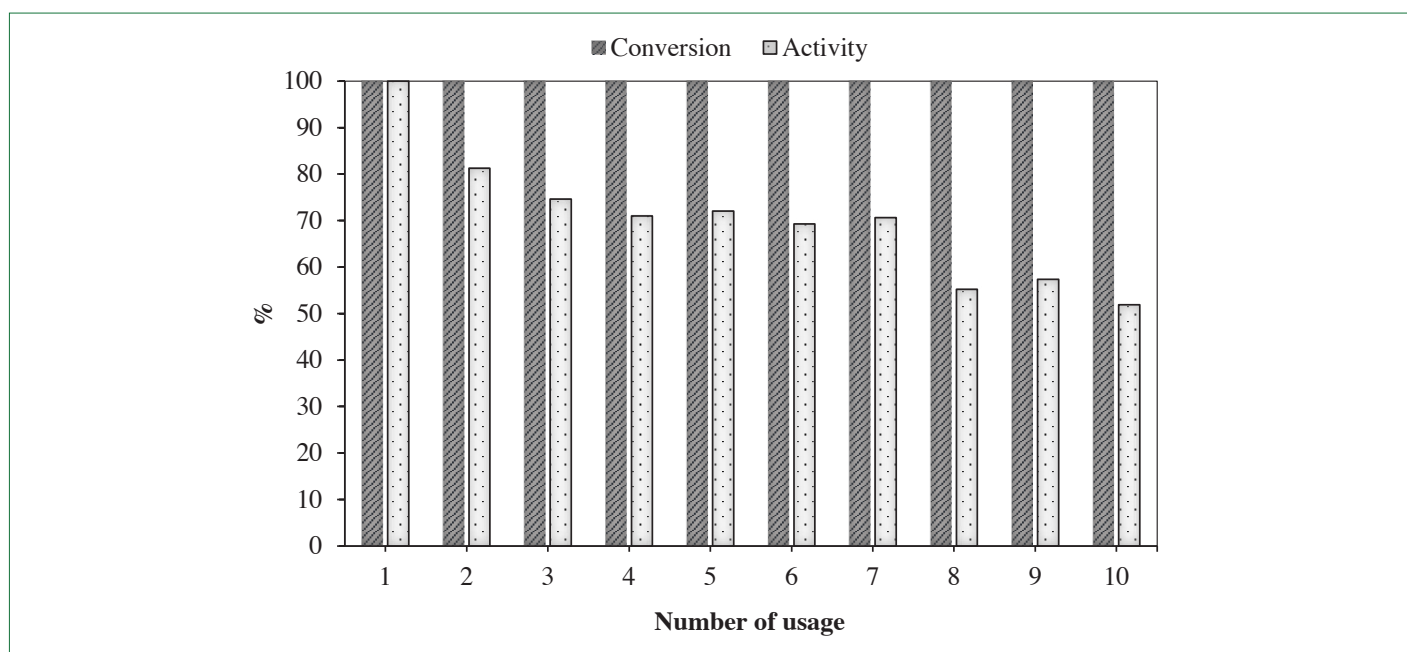


Figure 11. The change in the activity and conversion of the catalyst with time for repetitive use of PVA-Co catalyst in hydrolysis of NaBH₄, [Reaction conditions: 0.189 mmol cobalt containing PVA-Co composite; 50 mL 50 mM NaBH₄ at 50 °C with 5% NaOH, 1000 rpm mixing rate].

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