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RELEASING HYDROGEN FROM $NABH_4$ VIA HYDROGEL BASED CoF_2 CATALYST

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Abstract: In this paper, the dehydrogenation reaction of $NaBH_4$ was performed in the presence of Co-ion loaded hydrogel catalyst. The reactions took place within 27, 18 and 9 hours at 25, 35 and 45 °C, respectively. In addition, the relation between the initial concentration of $NaBH_4$ and released hydrogen was investigated at 45°C. A linear relationship between initial borohydride concentration and produced H_2 was determined. Also, differential method was used to determine reaction rate constants and rate order. Hence, first-order-kinetics was proved by using experimental data. After that, the activation energy was found as 58.26 kJ/mol by means of the slope of the graph of lnk versus 1/T for the dehydrogenation reaction. This value is nearly equal to 50kJ/mol, which was expected in literature for the studies of the catalytic dehydrogenation. As the hydrophilic and macroporous structure of the prepared poly(acrylamide-co-acrylic acid) (p(AAm-co-AAc)-Co) hydrogel catalyst allowed inlet of $NaBH_4$ solution up to its interior and release of produced H_2, effect of pore diffusion limitation was neglected. Dehydrogenation index of $NaBH_4$ was calculated as 2526.31 mL H_2/g $NaBH_4$ according to the amount of $NaBH_4$ in the aqueous solution.
Keywords: Sodium borohydride, dehydrogenation, hydrogel catalyst, activation energy.

HİDROJEL ESASLI CoF_2 KATALİZÖR İLE $NABH_4$'DEN HİDROJEN SALINIMI

Özet: Bu makalede, $NaBH_4$'ün dehidrojenasyon reaksiyonu, Co iyon yüklü hidrojel katalizör varlığında gerçekleştirilmiştir. Reaksiyonlar sırasıyla 25, 35 ve 45 °C'de 27, 18 ve 9 saat içinde gerçekleşmiştir. Bununla beraber, $NaBH_4$'ün başlangıç konsantrasyonu ile salınan hidrojen arasındaki ilişki 45 °C' de araştırılmıştır. Başlangıç borohidrür konsantrasyonu ile üretilen H_2 arasında doğrusal bir ilişki olduğu belirlenmiştir. Ayrıca, reaksiyon hız sabitleri ve reaksiyon mertebesini belirlemek için diferansiyel yöntem kullanılmıştır. Böylece, deneysel veriler kullanılarak birinci derece kinetik kanıtlanmıştır. Daha sonra, dehidrojenasyon reaksiyonu için lnk'ya karşılık 1/T grafiğinin eğiminden aktivasyon enerjisi 58.26 kJ/mol olarak bulunmuştur. Bu değer, katalitik dehidrojenasyon çalışmaları için literatürde beklenen 50 kJ/mol'e neredeyse eşittir. Hazırlanan poli (akrilamid-ko-akrilik asit) (p (AAm-co-AAc)-Co) hidrojel katalizörün hidrofilik ve makro-gözenekli yapısı $NaBH_4$ çözeltisinin katalizörün iç kısımlarına kadar girebilmesine ve üretilen H_2'nin salınmasına olanak verdiği için gözenek difüzyon sınırlaması etkisi ihmal edilmiştir. $NaBH_4$'ün dehidrojenasyon indeksi, sulu çözeltideki $NaBH_4$ miktarına göre 2526,31 mL H_2/g $NaBH_4$ olarak hesaplanmıştır.
Anahtar Kelimeler: Sodyum borhidrür, dehidrojenasyon, hidrojel katalizör, aktivasyon enerjisi.

INTRODUCTION

Renewable and alternative energy resources have attracted great attention owing to the fact that fossil fuels will not exist forever. In addition, the more population and energy demand have increased, the more energy resources will be needed. A variety of alternatives can be offered instead of gasoline such as natural gas etc. However, hydrogen is a strong candidate among them to overcome the energy problem all over the world (Nayar, 1981). Moreover, fossil fuels are the largest source of carbon dioxide, a greenhouse gas which contributes to climate change, and their production causes both environmental and human health impacts. Hydrogen is a promising candidate as an environment-friendly energy carrier and within this scope lots of studies have been carried out by national labs, industry, and academia separately and in collaborations. Differently from electricity, hydrogen can be stored and easily transported in many forms to keep up with demand by time and place. For that reason, there is considerable interest in its use as a possible fuel to operate industry, heat homes, generate electricity etc. Essentially, two methods identified as physical and chemical are used for hydrogen storage. Hydrogen molecules can be stored in solid compounds using chemical reactions. The chemical bonds (covalent or ionic interactions) between hydrogen and a host compound form relatively safe storage option (Eberle et al., 2009). Among hydride compounds, especially metal borohydrides are the best hydrogen carrier materials due to their properties including hydrogen-storage capacity, kinetics, cyclic behavior, toxicity, pressure and thermal response (Çakanyıldırım and Gürü, 2009). Recently, most of the studies have been carried out to find out a perfect hydrogen release method from sodium borohydrides ($NaBH_4$). In other words, studies are aimed to come out desired uninterrupted energy particularly for the fuel cells (Çakanyıldırım and Gürü, 2010) . Portable electricity generation based on hydrogen and proton exchange membrane fuel cell (PEMFC) has become essential for humans especially in the fields of medical appliances, electronic equipment and toys etc.(Fernandez-Moreno et al. 2013) . In this scope, a portable batch mini-reactor for hydrogen generation from catalytic hydrolysis of $NaBH_4$ was developed in order to supply possible energy for less developed areas in the worldwide (Nunes et al., 2016). Especially, among of all chemical hydrides, sodium borohydride ($NaBH_4$) is the most prevalently used hydrogen carrier because of its high hydrogen storage capacity of 10.8 wt%.

Principally two techniques are performed to release the hydrogen of $NaBH_4$, thermal and catalytic dehydrogenation. Catalytic technique comes into the forefront because hydrogen and water can be recovered. On the other hand, thermal dehydrogenation process causes additional operation cost which depends on high-temperature requirement so the kind of dehydrogenation is not preferred (Kaya et al., 2011; Çakanyıldırım and Gürü, 2008).

It is seen that investigations have been performed predominantly by using $NaBH_4$ among metal borohydrides to release hydrogen. Hydrogen can be produced by the reaction between the water and $NaBH_4$ in the presence of a catalyst. In order to obtain hydrogen, an alkaline borohydride solution in water is prepared with its metal hydroxide to prevent sudden hydrogen release. High storage capacities could be achieved on a material basis via metal hydrides because the hydrogen from the hydride besides the hydrogen from the water is liberated (Schüth et al., 2004). According to the reaction given Eq.(1), theoretically four mole hydrogen was generated from the two of them coming from water and the other from $NaBH_4$. The effect of catalyst is very substantial for dehydrogenation reactions of borohydrides.

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} NaBO_2 + 4H_2 + \text{heat} \uparrow \qquad (1)$$

1 g of fully hydrolyzed $NaBH_4$ produces 2.37 L of hydrogen gas at standard temperature and pressure according to the ideal hydrolysis reaction in the literature (Schlesinger et al., 1953). Experimentally, it is expected hydrated crystalline sodium metaborate as a by-product at the end of the reaction, the coefficient x given in Eq.(2) can change depending on the used catalyst type. The hydrogen in the structure of water can be recovered in the presence of the catalyst during the reaction (Çakanyıldırım and Gürü, 2010).

$$NaBH_4 + (2+x)\, H_2O \xrightarrow{\text{catalyst}} NaBO_2 .x\, H_2O + 4H_2 + \text{heat} \uparrow \quad (2)$$

The reaction, dehydrogenation of $NaBH_4$, is exothermic and no heat supply is required. In recent years, researchers prepared a catalyst using a polymeric material as support of metal active sites. These polymers are considerable to make progress the efficiency of the catalyst (Sahiner and Yaşar, 2014). Functional groups in the hydrogel networks, such as –COOH, –OH, $–SO_3H$, –SH and $–NH_2$, differ according to used monomers and among them, carboxylic acid groups have been shown to be highly effective. Pt, Pd, Rh, Ru, Co, Ni and their compounds can be used as a metal source to prepare catalyst but Co and Ni have been widely chosen because of their low cost (Boynuegri et al., 2016; Sahiner et al., 2011). Also, it was reported that Co metal containing hydrogel produced hydrogen faster than Ni metal containing hydrogel composites for the given reaction (Seven and Sahiner, 2013). Obviously, the hydrogen release should be consistent for the fuel cell to operate in desired time so used catalyst has become vital from this perspective. On the other hand, comparable low activation energy values were gained for hydrogen release from $NaBH_4$ in the literature, when NaOH-p(AAM)-Co composite system and super-porous p(AAc)-Co metal composites were used as catalysts (Seven and Sahiner, 2013; Seven and Sahiner , 2014).

Previously, we reported the synthesis of Co-ion loaded poly(acrylamide-co-acrylic acid) (p(AAm-co-AAc)) hydrogel catalyst. According to amounts of cobalt ion, the catalyst was selected and used in the dehydrogenation of $NaBH_4$ reaction. The experimental and theoretical ratio of released hydrogen from 0.0965 g $NaBH_4$ at 25 ºC was found by 90%. Released hydrogen amount was satisfactory in comparison to the given value in literature 240mL and 250 mL, respectively, in the presence of ppm level Co metal active sites (Boynuegri et al, 2016, Seven and Sahiner, 2013).

Still, catalyst is mostly investigated topic in the field of continuous hydrogen production from metal borohydrides. In the current study, synthesized and selected p(AAm-co-AAc)-Co ion loaded hydrogel catalyst was employed in the $NaBH_4$ dehydrogenation reactions at three different temperatures to investigate reaction kinetic. Our aims are identifying the behaviors of the catalyst and carrying out a study to obtain kinetic parameters in detail. Additionally, the effect of dried and swollen hydrogel catalysts usage on catalytic dehydrogenation was observed in this way it was reflected that slow or fast hydrogen release can be supplied by using these catalysts.

MATERIALS AND METHOD

Preparation of Hydrogel Based Catalyst

In this study, Co-ion loaded hydrogel catalyst was used to carry out dehydrogenation experiments. For this purpose, the catalyst's support material had synthesized by using the monomer, acrylamide (AAm) (Merck, purity ≥ 99%) and acrylic acid (AAc) (Merck, purity ≥9 9%), the crosslinker, N,N'-methylenebis acrylamide (MBAAm) (Sigma, purity ≥ 99.5%), the initiator, ammonium persulfate (APS) (Sigma-Aldrich, purity 98%), and the accelerator, N,N,N',N'-tetramethylenediamine (TEMED) (Merck, purity ≥ 99%) by means of free-radical crosslinking polymerization and then metal ion was loaded to polymeric matrices. Specific amount of CoF_2, metal ion source, was dissolved in 100 mL deionized water (DI-water), and 0.1 g hydrogel was placed in this solution for the duration of 24 h with the aim of metal ion uptake. Metal ion-loaded hydrogel was washed with deionized water 2 h or so to remove free metal ions from hydrogel support material. After all these steps, Atomic Absorption Spectroscopy (AAS, Varian, AA240FS) analysis was performed to determine amounts of metal ions. Thus, metal-ions was transferred from hydrogel material to solution, the metal-ion loaded hydrogel was placed in a 50 mL 5 M HCl solution for 12 h repetitively two times.

Catalytic Dehydrogenation of $NaBH_4$

Dehydrogenation reactions were performed by using 50 ml 50 mM (0.0965 g) $NaBH_4$ (Merck, purity ≥ 98%) aqueous solution with 0.5 g NaOH (Merck, purity ≥ 98%). As metal hydrides are sensitive to moisture in the air, the enclosed chambers, GLOVE-BOX (LABstar, MBRAUN), was used to weight $NaBH_4$. It is known that self-hydrolysis of borohydrides must be prevented by using its metal hydroxide. Here, the amount of NaOH is important as mentioned in the literature. It was represented that released hydrogen from $NaBH_4$ solution diminished via increasing NaOH concentration because of suppression of hydrogen formation by hydroxide ions (Jeong et al., 2005). In other words, the hydrogen generation rate increases for lower NaOH concentrations in the alkaline $NaBH_4$ solution and decreases after reaching a maximum value. During the process, pH value remains between 12 and 14 because of the presence of NaOH (Ingersoll et al., 2007). It can be inferred that amount of NaOH is arranged according to pH. In addition, this pH value can eliminate probable toxic fluorine (F) exposure according to graph of the equilibrium concentrations of various fluorine species versus solution pH given in literature (Zhao et al., 2016). F ions exist in the state of the soluble form in the aqueous solution having pH 7 and above.

The aqueous solution was poured into the reactor and then 0.1 g of p(AAm-co-AAc)-Co hydrogel catalyst was added to it. p(AAm-co-AAc)-Co hydrogel catalyst involve 135.82 mg Co for per gram of hydrogel as given in the literature (Boynuegri et al., 2016). The reactor lid was closed tightly whenever catalyst was placed in the dehydrogenation reactor containing the solution. Released hydrogen was measured with the inverse burette system, as seen in Fig. 1.

Dehydrogenation reaction of $NaBH_4$ occurs according to the Eq.(1) given above. P(AAm-co-AAc)-Co hydrogel catalyst should be washed with water at the end of the reaction. It can help removing borate compounds probably remained on the pores of the catalyst (Xu et al., 2007).

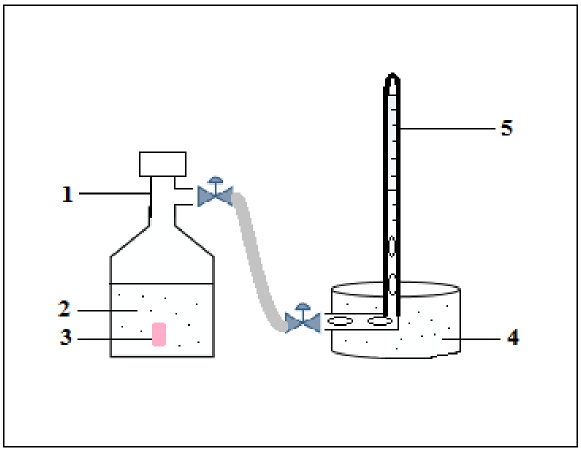

Figure 1. Inverse burette system: (1) Reactor, (2) $NaBH_4$ and NaOH solution, (3) catalyst, (4) water reservoir, and (5) burette.

Theoretically, the amount of released hydrogen is twice as many as expected due to hydrolysis of the water. Dehydrogenation reactions were carried out both dried and swollen p(AAm-co-AAc)-Co catalysts to clarify its effect at 45°C. In addition, the effect of the catalyst's surface area was investigated according to measured hydrogen volume. For this purpose, two catalysts which have the same weight and the different surface area were prepared and the amounts of their released hydrogen were compared. We, also, investigated effect of hydrogel catalyst's surface area on the reaction of $NaBH_4$ dehydrogenation

Kinetic studies

Dehydrogenation reactions of $NaBH_4$ were performed to clarify catalyst's kinetic properties at 25, 35, 45 °C. All of these experiments were performed to find out the reaction rate order and the activation energy (Ea) of the related hydrolysis reaction. P(AAm-co-AAc)-Co hydrogel catalyst was used in each experiment and the amount of hydrogen released was continuously recorded. Furthermore, the pre-exponential factor (A) presented in Arrhenius equation was calculated according to the related equation given below (Eq.(3)).

$$k = A.e^{-Ea/RT} \qquad (3)$$

While the reactions were occurring at selected temperature, a water bath was used to maintain the constant temperature. Thus, the reaction temperature did not change by the exothermic nature of the hydrolysis reaction. The amounts of released hydrogen of the dehydrogenation reactions catalysed by p(AAm-co-AAc)-Co hydrogel catalyst were calculated for different $NaBH_4$ initial concentrations. Hence, the relation between the initial concentration of the reactant and the amount of released hydrogen was clarified.

RESULTS AND DISCUSSION

Recently, studies demonstrate that metal ion loaded hydrogel catalysts have had a pleasant performance in dehydrogenation reactions of metal borohydrides because of their high capabilities to load metal active sites and high catalytic activities (Sahiner and Yaşar, 2014; Sahiner et al., 2011; Sahiner et al., 2012).

In this study, it is estimated that hydrogel support material’s egg-shaped porous structure having pore size from 11 µm to 231 µm proven by SEM (Scanning electron microscope)analysis display a significant role as for activity of the catalyst.

In the end of catalyst preparation procedure given previously, amount of the Co-ion was found as 135.82 mg Co/g hydrogel according to Atomic Absorption Spectroscopy (AAS) (Varian, AA240FS) as given previous research study in detail (Boynuegri et al., 2016). Dehydrogenation reactions were carried out by using this characterized p(AAm-co-AAc)-Co hydrogel catalyst.

Released hydrogen amounts and reaction times were measured as 225, 230, 240 mL and 27, 18, 9 hours at 25, 35, 45 °C, respectively. When the dehydrogenation reaction of $NaBH_4$ temperature was increased, the reaction time decreased as seen in Fig. 2.

When the released hydrogen amount compared with the results given in the literature, the produced H_2 amount (No:3) via dehydrogenation of 0.095 g $NaBH_4$ (prepared as 50 mM $NaBH_4$ solution) was almost same with the amounts of released H_2 (No:1, 2, 4) given in the literature as seen in the Table 1.

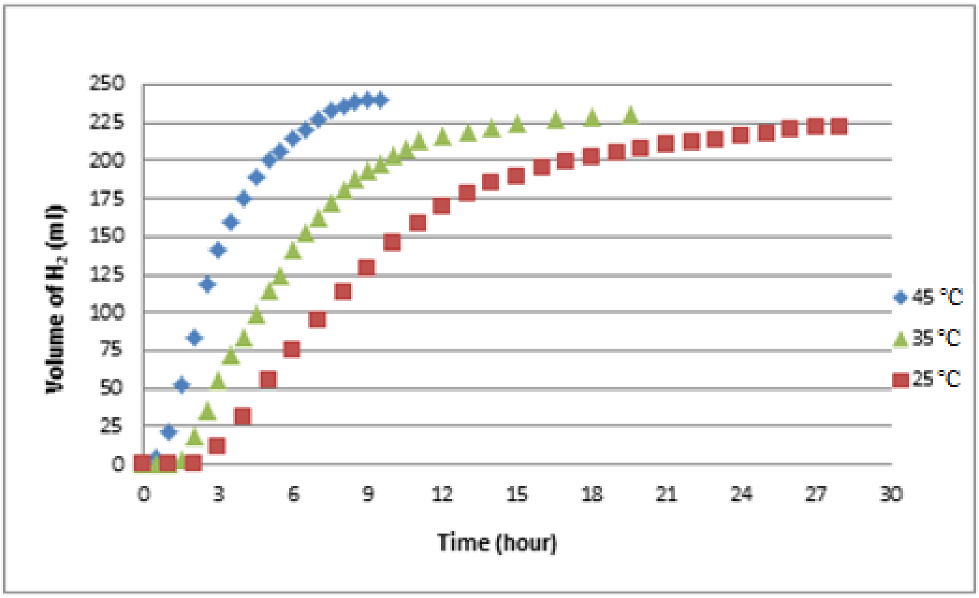

Figure 2. The effect of temperature on dehydrogenation reaction of $NaBH_4$
(T= 25, 35, 45 °C, 0.0965 g $NaBH_4$, 0.5 g NaOH)

Table 1. Comparison of released H_2 amount and activation energy from 0.095 g $NaBH_4$

No	**Amount of mg Co/g hydrogel**	**Released H_2 (mL)**	**Released H_2 ($x10^{-2}$ mol)**	**Activation Energy (kJ/mol)**	**Dehydrogenation Parameters**
1	92.0	≈250	1.11	26.62	%5 NaOH, 30°C (Sahiner, Butun and Turhan, 2012)
2	128.0	247	1.10	38.14	%5 NaOH, 30°C (Sahiner, Ozay, Inger and Aktas, 2011)
3	135.8	230	1.03	58.26	%1 NaOH, 35°C
4	218.5	248	1.11	20.36	%5 NaOH, 30°C (Seven and Sahiner 2014)

According to the ideal hydrolysis, it is expected that 0.1 g of fully hydrolyzed $NaBH_4$ produces mL of hydrogen gas at standard temperature and pressure. If we take into account temperature effect, produced H_2 gas should be 241 mL and 245 mL at 30 °C and 35 °C be regarding ideal gas law. As a result, in this study (No: 3), amount of released H_2 was nearly equal anticipated theoretical value. In addition, it is remarkable that the amount of released hydrogen is in coherent with expected theoretical value for released H_2 was 1.02 $x10^{-2}$ mol according to Eq.(1).

This reaction can be accelerated by the increase of temperature or by addition of any acidic compound as stated in the literature (Balbay and Şahin , 2014). It is possible to arrange hydrogen release time which depends on amount of loaded active metal source, different features of polymer like the percentage of swelling degree and reaction temperature and etc. It was reported that hydrogen release time changed from nearly 60 min to 3000 min in literature.

When amounts of theoretically and experimentally released hydrogen were compared, the ratio was found by 90 %. $NaBH_4$ was weighted at the inert atmosphere in GLOVE-BOX, so there was an experimental error nearly 5% because of the change in pressure. As a result of this, the yield could be taken by 95 %. After the hydrogen released via catalytic dehydrogenation process used Co-ion loaded hydrogel catalyst's color turned over from pink to black as seen in Fig. 3.

This figure represents in situ metal particle preparation in the p(AAm-co-AAc) hydrogel matrice, and their camera images. Metal ion absorption from their solution occurred via the functional groups such as –COOH and –OH which exist on the p(AAm-co-AAc) hydrogel matrice. As soon as metal ion loaded hydrogels contact with a reducing agent like $NaBH_4$, these metal particles can be formed in situ within the hydrogel. This kind of change in color corresponds to literature (Seven and Sahiner, 2013) .

Amount of loading metal particles was determined by using Atomic Absorption Spectroscopy (AAS) as given in the literature in detail (Boynuegri et al., 2016).

In addition, dehydrogenation reaction of $NaBH_4$ was carried out at 45 °C to show the effect of area of p(AAm-co-AAc)-Co hydrogel catalyst on the production of hydrogen. The areas of these two catalysts were calculated by using mathematical equations according to their geometric shapes without any other measurement technique like BET (Brunauer, Emmett and Teller) or etc. The reason is that noticeably high the percentage of swelling degree in aqueous phase of the prepared hydrogel material (p(AAm-co-AAc)), 6500 %, could not allow proper analysis of BET.

In this study, probable impact of size or area of hydrogels investigated by using two catalysts having same weight but different size as given Table 2, 125 and 150 mm^2 , hydrogen was released by 91.0 % and 91.2 % yield, respectively.

Table 2. Effect of catalyst area on released hydrogen

Used $NaBH_4$ ($x 10^{-4}$mol)	**Area of catalyst (mm^2)**	**Volume of released H_2 (mL)**	**Yield (%)**
8.46	125	80	91.0
8.19	150	78	91.2

It was inferred that released hydrogen does not change remarkably with catalyst surface area according to given results in Table 2. Besides, hydrogel catalyst was used as dried and swollen, and reaction time was determined as 9 and 25 hours, respectively as given Fig. 4. Thus, the option of using dried or swollen state of the catalyst can be done by the expectation of its place of use.

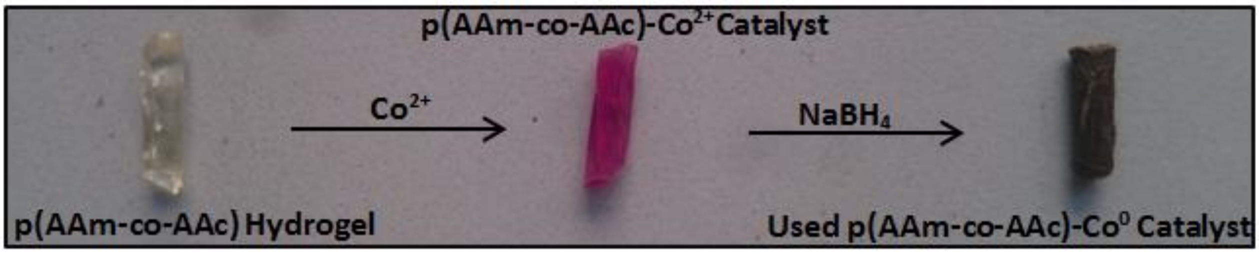

Figure 3. Color changing of hydrogel catalyst. Images of dried p(AAm-co-AAc) hydrogel, Co(II) ions absorbed p(AAm-co-AAc) hydrogel and the reduction of these ions within hydrogel matrices, respectively.

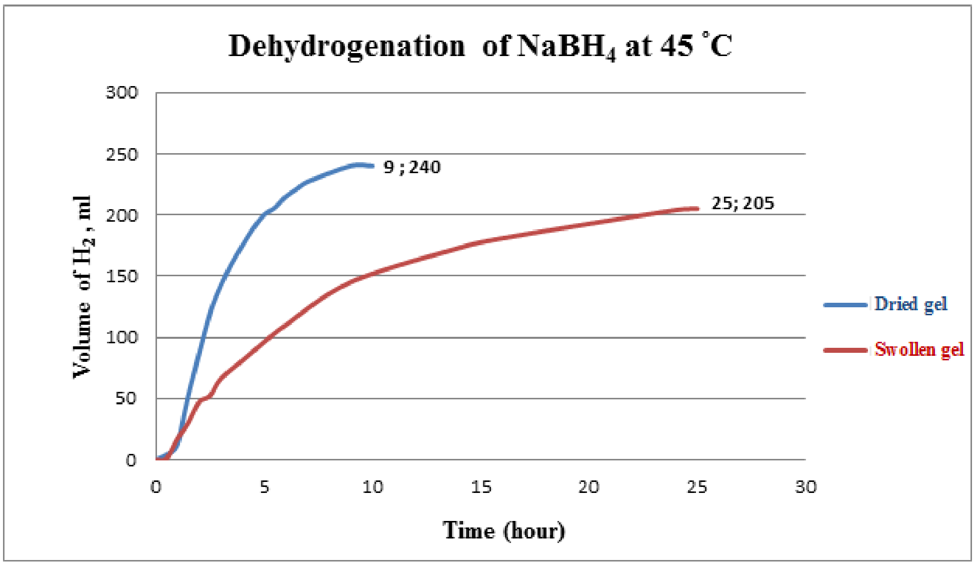

Figure 4. Dehydrogenation of $NaBH_4$ by using dried and swollen Co-ion loaded hydrogel catalyst (T=45 ºC, 0.0965 g $NaBH_4$, 0.5 g NaOH)

Previously, catalytic dehydrogenation reactions were performed by using dried hydrogel based catalyst, as given in Fig. 1. We used the same data to plot the blue line that represents produced H_2 versus time for the dehydrogenation reaction, carried out at 45 ºC by using dried hydrogel in Fig. 4. In this experiment, hydrogel based catalyst was immersed in deionized water and then kept in it to swell.

It was predicted that swollen hydrogel caused smaller pore sizes in compared to pores in the structure of dried hydrogel so the released amount of hydrogen was less than that of dried hydrogel catalyst. In this scope, it is obvious that pore sizes important as for diffusion. It means that when the specific pore sizes in the structure of catalyst support materials decrease, the pore diffusion limitation will emerge because of their sizes. Previously, we determined pores sizes of freeze-dried hydrogel and selected using dried p(AAm-co-AAc) hydrogel catalyst. Hence, we carried out the dehydrogenation reaction by neglecting the pore diffusion limitation.

The dehyrogenation reactions were carried out by taking different initial amount of $NaBH_4$ to produce H_2. It was found that initial amount of $NaBH_4$ and amounts of released hydrogen increased linearly as seen in Fig. 5.

It is obvious that there is a lineer relationship between used initial amount of $NaBH_4$ and the released hydrogen. In other words, H_2 production rate does not change with the increase in the amount of $NaBH_4$. As a result of this, it can be approved that specific dehydrogenation rate does not change according to initial amount of $NaBH_4$. In addition, it is clear that amount of the used metal catalyst source is already enough to proceed the reaction so its amount is not confining parameter for the dehydrogenation reaction of $NaBH_4$.

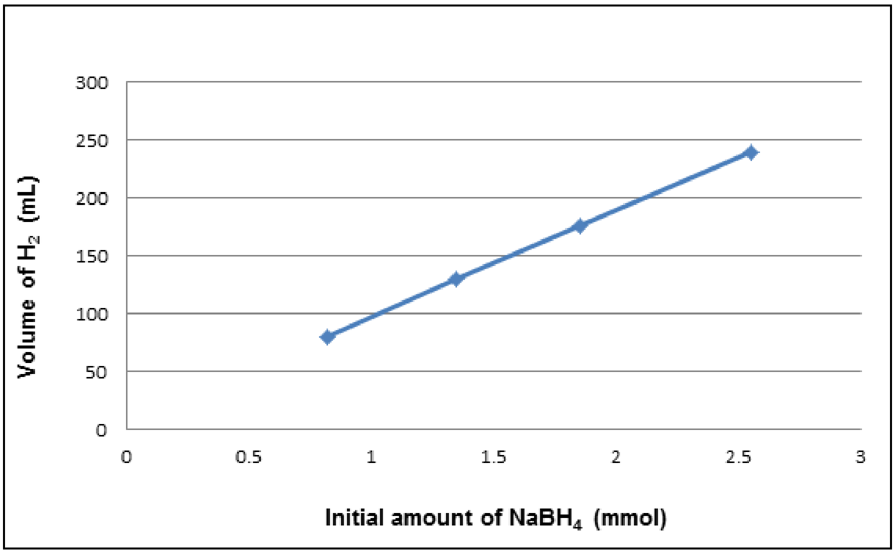

Figure 5. Released H_2 by changing initial amount of $NaBH_4$ (T= 45 ºC, 0.5 g NaOH)

We assumed that the amount of H_2O was very high in compared to the amount of $NaBH_4$ in aqueous solution so we neglected it in the reaction equation as given in the Eq.(4). As a result of this, the reaction equation turned into Eq.(5).

$$-\frac{dC_A}{dt} = kC_A^n C_B^m \qquad (4)$$

$$-\frac{dC_A}{dt} = kC_A^n \qquad (5)$$

According to the differential method, kinetic calculations were made to determine the rate constants and the reaction rate order. Graphs were plotted by using these data and reaction rate order (n) was found as 1 from the slope of these graphs.

Here, the graph which was plotted for the dehydrogenation reaction performed at 25 ºC are demonstrated in Fig.6.

As a result of this, the differential equation was arranged as given Eq. (6) and (7). Rate constants were calculated depending on time and concentration differences by using experimental results for both three dehydrogenation reactions carried at 25 ºC 35 ºC and 45 ºC.

$$-\frac{dC_A}{dt} = kC_A^n \text{, n=1} \qquad (6)$$

$$k = (-\frac{dC_A}{dt})/C_A \qquad (7)$$

These rate constants and other essential data for getting lnk versus 1/T graph are given in Table 3.

Table 3. Data for lnk versus 1/T graphs

T(K)	**1/T(x10^{-4})**	**k (x10^{-1})**	**lnk**
298	33.56	1.37	-1.98
308	32.47	3.27	-1.12
318	31.45	5.99	-0.51

It is known that the slope of the graph of lnk versus 1/T as given Fig. 7 is used to obtain the activation energy. However, if Arrhenius Equation is rearranged as seen Eq.(8), why we used the slope of this graph should be more apprehensible.

$$lnk = lnA - \frac{Ea}{R.T} \qquad (8)$$

The activation energy was calculated as 58.26 kJ/mol by using the slope of lnk versus 1/T graph.

The activation energy is almost equal 50 kJ/mol as it is demanded and compatible with the literature (Seven and Sahiner, 2013). As mentioned before carboxylic acid groups have been shown to be highly effective in the networks of hydrogels and also NaOH-p(AAm)-Co composite system and super-porous p(AAc)-Co metal composites, as catalysts, enable to get low Ea values respectively 20.07 ± 0.05 kJ/mol and 29.35 kJ/mol. However, prepared and used p(AAm-co-AAc)-Co hydrogel catalyst was not show Ea value as low as reported in literature (Seven and Sahiner, 2014; Ingersoll et al., 2007).

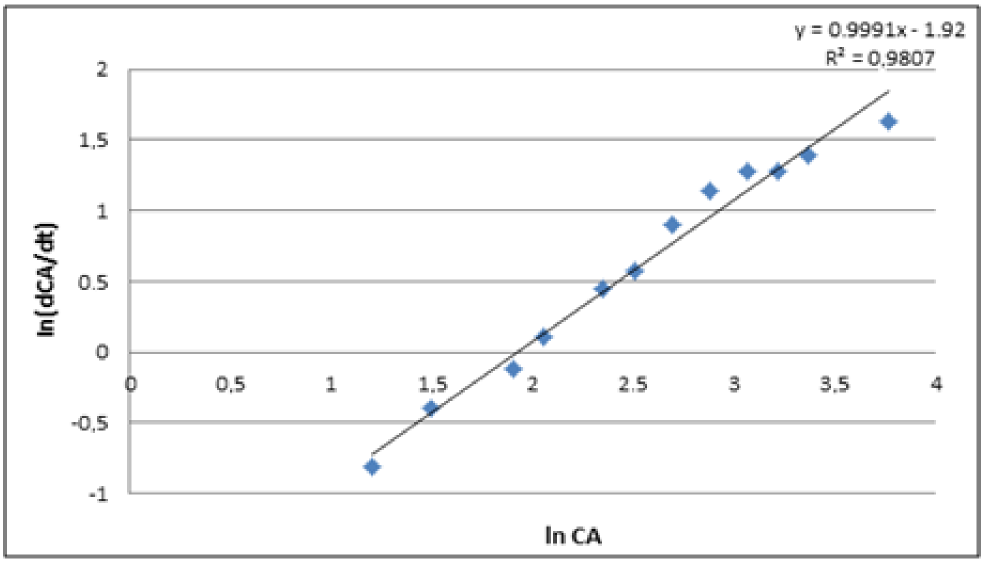

Figure 6. Graph of ln (dC_A/dT) versus ln C_A for the reaction at 25 ºC

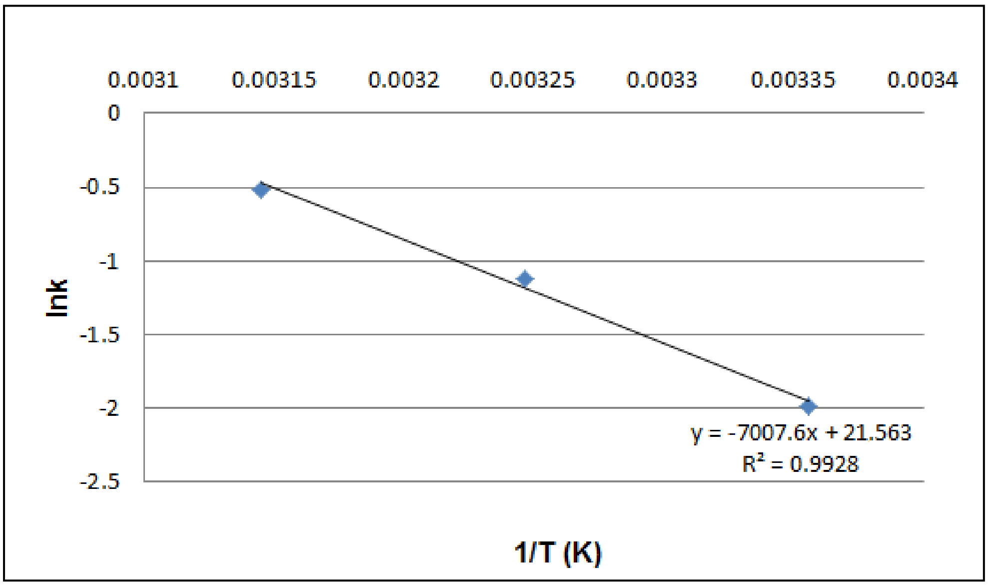

Figure 7. Graph of lnk versus 1/T

On the other hand, calculated Ea is lower than gained in the literature, 132 kJ/mol and 79 kJ/mol, when diatomite and γ-Al_2O_3 supported heterogeneous Co based catalyst was used for the dehydrogenation of $NaBH_4$ (Çakanyıldırım and Gürü, 2010). It is obvious that low-level Ea in a chemical reaction is ideal therefore this novel p(AAm-co-AAc)-Co catalyst should be preferred in comparison to heterogeneous Co based catalyst. This study mentioned that hydrogel based catalysts are the most preeminent among other types of catalysts as for this given feature.

In this study, the effect of pore diffusion limitation was not taken into consideration. Because, the hydrophilic and macroporous structure of the prepared p(AAm-co-AAc)-Co hydrogel catalyst allowed inlet of $NaBH_4$ solution up to its interior and release of produced H_2.

CONCLUSION

In this study, dehydrogenation reactions of $NaBH_4$ were carried out at three different temperatures for investigation of kinetic parameters. P(AAm-co-AAc)-Co hydrogel catalyst was synthesized and prepared by using CoF_2 metal source as given our previous study and was used to figure out hydrogen release characteristic of NaBH4 in this study. Dehydrogenation index of $NaBH_4$ was calculated as 2526.31 mL H_2/g $NaBH_4$ according to the amount of $NaBH_4$ in the aqueous solution. It was seen that this value is relatively higher than given value in literature, 2387 mL H_2/g $NaBH_4$, when the comparison was made. On the other hand, used Co amount, 135.82mg, was less than that of literature, 167.93mg (Çakanyıldırım and Gürü, 2009). Despite the less amount of Co, p(AAm-co-AAc)-Co hydrogel catalyst provided higher dehydrogenation index for same amount of metal borohydride hydrolysis. In addition, the reaction rate was found as first order and activation energy of the reaction calculated as 58.26 kJ/mol.

Cobalt metal active sites can be taken away from hydrogel support material in an acidic solution so reusability of these sites is possible. Previously, p(AAm-co-AAc)-Co hydrogel catalyst was used in 10 consecutive runs to perform reusability test for the catalyst in the dehydrogenation reaction of $Ca(BH_4)_2$. It was reported that the produced hydrogen amount diminished gradually when the run number has risen. However, the activity of the catalyst was compatible with relatively similar catalyst given in the literature (Boynuegri and Guru, 2017).

To sum up, this novel catalyst has great potential especially for the generation of hydrogen from metal borohydrides. $NaBH_4$ is mostly used source for H_2 production among metal borohydrides. Thus, this study provides opportunity to compare experimental results and make evaluation for getting additional improvements in related scopes.

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