Research Article GU J Sci 38(4): x-x (2025) DOI: 10.35378/gujs.1602928

Gazi University
Journal of Science
http://dergipark.gov.tr/gujs

Use of Alumina Supported Co-P and Ni-P Catalysts Synthesized By Electroless Plating Method in $NaBH_4$ Hydrolysis

Ebru ARINAN[1], Meltem DOGAN[2], Duygu UYSAL[2,*], Ozkan Murat DOGAN[2]

[1] *ROKETSAN, P.K. 30, Elmadağ 06780 Ankara, Türkiye*
[2] *Gazi University, Faculty of Engineering, Chemical Engineering Department, Maltepe, Ankara, 06570, Türkiye*

Highlights

- This paper focuses on hydrogen generation from $NaBH_4$ hydrolysis.
- Catalysts used in research are synthesized by the electroless plating method.
- Co-P and Ni-P loaded on commercial alumina is used as catalysts.
- Parametric study is conducted on the generation of hydrogen.
- In repeat experiments, 74% of the initial performance was preserved after the tenth use.

Article Info

Received: 17 Dec 2024
Accepted: 23 Apr 2025

Keywords

Sodium Borohydride
Hydrogen
Catalyst
ELP (Electroless plating)

Abstract

In this study, catalyst synthesis with a long service life and high activity by hydrolysis was aimed at using $NaBH_4$, which is used as a hydrogen storage. Commercial alumina is used as a catalyst support, and Co-P and Ni-P loadings were done using the electroless plating method. The characterization was done using XRD and SEM/EDS analyses. In Co-P catalyst, the ratio of metal/P /P (weight) was determined as 2.5, whilst that of Ni-P was 1.2. Both synthesized catalysts had P and metallic forms as well as metal-P alloy structures. Co-P-based catalysts showed higher activity than Ni-P catalysts in hydrogen production from $NaBH_4$ via hydrolysis. The high Co/P ratio explained high activity in the Co-P/alumina catalyst, and more Pd (9.36% by mass) was detected on the catalyst surface. Regarding Co-P/alumina catalyst, the effects of NaBH4 concentration, NaOH concentration and reaction temperature on the amount of hydrogen produced and the production rate were examined. The hydrogen production rate increased with increasing $NaBH_4$ concentration up to a specific value (0.3 M), after that, no significant change was observed, which is explained by the increase in viscosity caused by the by-product $NaBO_2$, its strong adsorption to the catalyst surface, hence the closure of active centers. NaOH concentration had not significantly affected the hydrogen production amount and rate for the selected operating conditions. As the temperature was increased from 20°C to 60°C, the hydrogen production rate increased approximately three times, and the activation energy was calculated as 25 kJ/mol. In repeat experiments, 74% of the initial performance was preserved after the tenth use.

1. INTRODUCTION

There is much research done on renewable energy nowadays. Within this concept, the tendency towards alternative energy sources like solar panels, wind turbines, hydroelectric energy, hydrogen, and biomass is increasing. Hydrogen, being the most abundant element in nature, is seen as the most promising energy carrier as it consists of very high energy per unit mass and does not contain carbon or sulfur. One of the problems about energy is the storage and transportation of it. Hydrogen can be stored as gas or liquid as well as chemically in several components. Considering the reliability and lightness, it is preferred to be stored chemically. High recyclable storage levels and low release temperatures are desired properties in compounds used in the chemical storage of hydrogen. Metal hydrides attract attention as compounds with these properties [1].

---

*Corresponding author, e-mail: duysal@gazi.edu.tr

The formation reaction of metal hydrides is reversible and can change direction depending on temperature and pressure. Depending on the metal used, the reaction may be endothermic or exothermic. It is desired that the number of hydrogen atoms per atom of the selected metal is high, and it has a low molecular weight. Li, Be, Na, Mg, B and Al are metals that can be used for this purpose. Mg in this group can store approximately 7.6% hydrogen by mass. However, since the hydrogen absorption and desorption kinetics of Mg-containing compounds are slow, various modifications must be made in the systems in which they are used [1, 2]. Borohydride compounds of metals such as Li and Na contain high amounts of hydrogen. Borohydrides are compounds defined as reducing agents and used as hydrogen sources in many chemical reactions [3].

Sodium borohydride is one of the most researched compounds in hydrogen production, with its properties such as theoretically containing 10.6% hydrogen by mass, its aqueous solution being able to react at low temperatures, and the formation of recyclable sodium metaborate as a result of the reaction. Thus, sodium borohydride has become a renewable resource. While it reacts very slowly in a humid environment, it maintains its stable structure in dry air. No noticeable deterioration in its structure is observed at temperatures above 400°C. Aqueous alkaline solutions of sodium borohydride release the stored hydrogen using a catalyst. Sodium borohydride solution, whose alkaline solution is quite stable, is not flammable or explosive. The reaction rate during hydrogen production can be easily controlled with a catalyst. The reaction in the presence of the catalyst stops if contact with the catalyst is interrupted. Obtaining hydrogen with this method is simple and inexpensive compared to other methods. Prepared catalysts can be used more than once [4]. In addition to sodium borohydride, alanates such as sodium tetrahydroaluminate ($NaAlH_4$) and trisodiumhexahydroaluminate (Na_3AlH_6) are also suitable for hydrogen storage. Their use has been limited because the release of hydrogen from these compounds occurs very slowly and the process is irreversible [4].

It is seen that Pt, Ru, Pd and their alloys in various proportions are used as catalysts in the production of hydrogen from sodium borohydride. Dai et al. (2019), Pt was loaded onto alumina-modified cordierite monolith by the impregnation method, and the prepared catalysts were tested in NaBH4 hydrolysis [5]. Hydrogen production was achieved continuously and at a constant rate after the 5th minute on these catalysts. Wang et al. (2019), Ru-Ni/Ni-foam catalysts were prepared according to the electroless plating method [6]. The hydrogen production rate on the catalyst was determined as 360 mL/min.g. Noble metal-based catalysts appear to show high activity and stability in reaction applications [7].

The fact that noble metals are expensive forms the basis for developing alternative catalyst preparation studies. For this purpose, transition metals such as Co and Ni in catalyst preparation studies are becoming widespread [4, 8]. Zhang et al. (2019) used graphe3ne oxide as support, and Co-based catalysts were synthesized according to the carbothermic reduction method [9]. Hydrogen production of 5955 mL/min.g was observed in the catalytic hydrolysis of NaBH4 at room temperature. Kilinc et al. (2018) determined a hydrogen production rate of 62535 mL/min.g with catalysts prepared by impregnating 1% Ni by mass on alumina support [10]. The catalyst has been shown to maintain its activity after 5 uses. Chen et al. (2018), Co was loaded onto iron oxide loaded activated carbon supports using the wet impregnation method [11]. The hydrogen production rate in the prepared catalyst was determined as 1403 mL/min.g. Bozkurt et al. (2018), Co and Ni-based catalysts were prepared by microwave irradiation technique using Co_3O_4 supports [12]. Higher activity was determined in Co catalysts. The highest hydrogen production rate was 2823 mL/min.g at 10% NaOH concentration. Ni-Co/graphene oxide catalysts were prepared by Chou et al. (2015) using the electroless plating method [13]. In the preparation of the catalyst, two different syntheses were carried out by loading Ni and Co simultaneously, first Ni and then Co. Higher hydrogen production rates were observed in the catalyst prepared by sequential addition of metals. The study also showed that high NaBH4 concentrations do not guarantee high hydrogen production. It has been shown that the presence of Ni and Co in the catalyst structure used in NaBH4 hydrolysis increases the electrochemically active surfaces [14]. Support selection is important in preventing structural degradation of catalysts due to corrosion in alkaline environments. In recent studies, it has been shown that using carbon, carbon nanotubes, and titanate nanotubes as supports in the preparation of Co and Ni-based catalysts increases the resistance to corrosion [15].

The catalytic activity of the catalysts used in the catalytic hydrolysis of boron hydrides has a strong relationship with the electronic structure of the metal regions (M) in the structure. For this reason, adding boron or phosphorus next to metal sites contributes greatly to the electronic properties of metal active sites [16]. Liang et al. (2016) used Ni-B and Ni-B/$NiFe_2O_4$ catalysts [17]. When the hydrogen production rates released by the hydrolysis of $NaBH_4$ solution were compared, Ni-B and Ni-B/$NiFe_2O_4$ catalysts showed approximately the same performance in the first 2.5 minutes, while after this minute, the Ni-B/$NiFe_2O_4$ catalyst showed better performance than Ni-B. The Ni-B/$NiFe_2O_4$ catalyst retained 83.3% of its initial performance after the fifth use. It was emphasized that $NiFe_2O_4$ support improved the Ni-B alloy's catalytic activity and reusable life. Wang et al. (2019) Co-Mo-B alloy catalysts were prepared by the electroless plating method on copper foil [18]. In the preparation of the catalysts, the lowest particle size (4.3nm) was determined if the pH value of the bath was 11. The highest hydrogen production rate was also observed in this catalyst (5818 mL/min.g). Wang et al. (2018) Co-P catalysts were prepared using CNTs-Ni supports using the CVD (Chemical Vapor Deposition) method [19]. The maximum hydrogen production rate at 25°C was determined as 2430 mL/min.g. It has been shown that adding W as well as B or P to the structure of Co-based catalysts increases the lifetime of the catalyst [20, 21]. Pornea et al. (2019), Ni-Co-P catalysts were prepared by hydrothermal synthesis method using nickel foam as support [22]. The highest hydrogen production rate (3986 mL/min.g) was observed in the catalyst with a Ni/Co ratio of approximately 0.7. The results obtained are comparable to those obtained with noble metals. Co-P catalysts were prepared using the hydrothermal synthesis method by Huang et al. (2017) and the hydrogen production rate was determined to be 4028 mL/min.g [23]. The positive effects of CoB and Ni_4B_3 crystal phases formed in the structure due to the addition of boron to the catalyst structure, where Co and Ni metals are present, have been shown to have positive effects on catalytic activity [24].

Sodium borohydride solution reacts with the catalyst at pH>9 values. In the literature, NaOH is widely used to increase the pH value of sodium borohydride solution. The amount of NaOH in the hydrolysis solution not only ensures stability, but also affects the hydrogen production rate since OH- ion is involved in the reaction mechanism. However, large amounts of NaOH increases the formation of $NaBO_2$, and $NaBO_2$, which has low solubility, begins to precipitate on the catalyst after a certain concentration. Thus, $NaBO_2$ closes the active sites on the catalyst, causing profound decreases in hydrogen production performance [25, 26]. Wang et al. (2015) synthesized Co-Ni-Mo-P/alumina catalyst by electroless plating method [27]. The study observed that the particle sizes on the catalyst surface increased as the waiting time in the loading bath increased. It was observed that when the NaOH concentration was increased from 4% to 10% by mass, the hydrogen production rate increased from 6583 to 8083 L/min.g, and when the NaOH concentration was 12% by mass, the hydrogen production rate decreased by approximately 25%. The study also stated that molybdenum acts as an atomic barrier and prevents the growth of relevant particles. The synthesized catalyst retained 80% of its initial performance after the 5th use. Co-P was loaded onto a copper plate by electroless plating method by Wang et al. (2015) [27]. Co-P microstructure was obtained when the bath temperature was 50°C. The catalyst with microstructure showed an excellent hydrogen production rate of 2275 ml/min.g in the hydrolysis of NaBH4. It has also been shown that Co and P are distributed homogeneously in the catalyst structure. Li et al. (2014) used Ni-Co-P/alumina catalyst prepared by electroless plating method [26]. It was observed that when the reaction time was increased from 50 s to 360 s, the hydrogen production rate decreased from 5180 ml/min.g to 1409 ml/min.g. This decrease was explained by the decrease in specific surface area. As the NaOH concentration increased, the reaction rate increased and the maximum hydrogen production rate was reached at 10% NaOH. After this rate, the hydrogen production rate gradually decreased. It has been shown that the reason for this is the accumulation of $NaBO_2$ on the catalyst surface. Higher hydrogen production rates were observed as the Co/Ni ratio increased. Wang et al. (2016) Co-P/Cu catalysts were prepared by the electroless plating method [28]. The hydrogen production rate on the catalysts was 2275.1 mL/min.g. After 5 uses, catalyst activity decreased by approximately 30%. In another study by the same research group, fishbone-like Co-B nanoparticles were prepared by the electroless plating method. The hydrogen production rate was determined as 10089.1 mL/min.g. After 5 cycles, a 20% decrease in activity of the catalyst was observed. Kim et al. (2019), Co-Ni-Fe-P alloy catalysts were synthesized by the electroless plating method [29]. The highest hydrogen production rate (1128 mL/min.g) was determined with the catalyst containing 7.6% Fe by mass in the catalyst structure. In addition to catalysts using noble metals and transition metals as active ingredients, bio-catalysts prepared using Fe_2O_3 and Ag-Pt nanoparticles as support are also seen to be promising in the hydrolysis of $NaBH_4$ [30, 31].

As can be seen from the literature research summarized above, different synthesis methods are used in the preparation of catalysts used in $NaBH_4$ catalytic hydrolysis. Among these methods, the abundance of electroless plating method attracts attention. This method stands out due to its advantages, such as being applicable to materials of any shape or structure, the simplicity of the equipment used, providing homogeneous metal distribution, and being an inexpensive method. The method, which is based on the principle of autocatalytic reduction of metal ions on the support surface with the help of a reducer and loading of the metal onto the surface, basically consists of three steps. These steps include surface cleaning, activation and metal loading in the bath. Loading baths basically consist of pH regulator, reducer, metal salts and complexing agent. In the electroless plating method, temperature, pH, composition and loading time can be listed as parameters affecting the catalyst structure [32].

This study aimed to prepare catalysts with high activity and long lifetime by electroless plating method to obtain hydrogen by hydrolysis of sodium borohydride. Using the electroless plating method, two different catalysts were synthesized by loading Co-P and Ni-P onto alumina supports. Characterization studies of the prepared catalysts were carried out by XRD and SEM/EDS analyses. The activities of catalysts prepared with two different metals in obtaining hydrogen by hydrolysis of sodium borohydride were compared, and the highest activity was determined in Co-P/alumina. The effects of $NaBH_4$ and NaOH concentrations, operating temperature and solution feeding rate on the hydrogen production amounts on this selected catalyst were examined. The study also investigated the change in performance of the catalyst with reuse.

2. MATERIAL METHOD

2.1. Catalyst Synthesis and Characterization

Alumina spheres obtained from BASF were used as support in the catalyst preparation studies. The physical and chemical properties of the support material are given in Table 1.

Table 1. *Physical and chemical properties of the catalyst support material*

Physical Properties	
Diameter (mm)	3.2
Surface Area (m^2/g)	350
Total pore volume (cm^3/g)	0.5
Apparent density (kg/m^3)	769
Chemical Composition (mass %)	
Al_2O_3	92.7
SiO_2	0.02
Fe_2O_3	0.02
Na_2O	0.30
LOI (250-1100° C)	0.70

In the study conducted, it was decided to keep the component amounts (metal salt, NH_4Cl and reductant) in the Co and Ni loading baths at the same rate. The bath composition was determined by conducting preliminary experiments to determine the bath composition and characterization studies of the catalysts obtained as a result of these experiments. In the preliminary experiments, studies were conducted by increasing the amount of metal salt (the amount of reductant was also increased in proportion to the increasing amount of salt). For example, the results of the studies where the metal salt concentration was 5g/L (preliminary experiment-1) are presented below in Table 2.

Table 2. *Bath composition used in preliminary experiment-1*

Co-P Loading Bath		Ni-P Loading Bath	
Components	Amount	Components	Amount
$CoCl_2$	5 g/L	$NiCl_2$	5 g/L
NH_4Cl	30 g/L	NH_4Cl	30 g/L
$NaH_2PO_2.H_2O$	12 g/L	$NaH_2PO_2.H_2O$	12 g/L
pH = 10-11, T =35 – 40 C			

In the catalyst structure obtained with the bath composition specified above (all other steps followed in the catalyst preparation were applied as is), very low concentrations (0.33% by mass) were determined, especially for Co. As a result of the ongoing preliminary experiments, the bath composition providing concentrations of over 10% by mass for Co and Ni on the surface was selected among the obtained catalysts, and the study was carried out with this bath composition.

In the catalyst preparation studies, the ELP (electroless plating) method was used, in which metal loading can be carried out using simple equipment on supports of all kinds and shapes. Catalysts were prepared by loading Co-P and Ni-P onto the alumina support material. First of all, the alumina supports were subjected to a cleaning process to remove any contamination that may be present on them. The supports were respectively boiled in 0.1 N NaOH solution, 0.1 N HCl solution and finally in pure water for 30 minutes and dried at room temperature. In the ELP method, the metal loaded onto the surface through the activation process acts as a catalyst in subsequent loading processes. The activation step is necessary to initiate the reaction chain. In the activation step, the supports were first sensitized with acidic $SnCl_2$ (2.38 g $SnCl_2$ + 1L 0.2 N HCl) solution and then activated with acidic $PdCl_2$ (0.15 g $PdCl_2$ + 1 L 0.2 N HCl) solution. Then, the supports were kept in pure water for 10 minutes. The activation process was completed by repeating the above steps 10 times in a row. Co-P and Ni-P loadings were applied to the activated supports in ELP baths. The bath compositions and working conditions in which the studies were carried out are given in Table 3.

Table 3. *ELP bath compositions and operating conditions used in catalyst preparation studies*

Co-P Loading Bath		**Ni-P Loading Bath**	
Component	**Amount**	**Component**	**Amount**
$CoCl_2$	20 g/L	$NiCl_2$	20 g/L
NH_4Cl	30 g/L	NH_4Cl	30 g/L
$NaH_2PO_2.H_2O$	40 g/L	$NaH_2PO_2.H_2O$	40 g/L
pH : 10-11 Temperature: 35°C			

In preparing the metal loading bath, the metal salt and NH_4Cl were first dissolved in 25% NH_4OH solution by mass. Activated supports were added to the solution placed in the water bath, and the temperature was allowed to reach 35°C. One-third of NaH_2PO_2, used as a reducing agent and also as a phosphorus (P) source, was added to the bath when the bath temperature reached 35°C and the reaction was started. Then, the other third of NaH_2PO_2 was added to the bath at the 5th minute, and the last remaining amount was added to the bath at the 10th minute. The reaction initiated by adding NaH_2PO_2 continued for a total of 30 minutes. Then, the supports were removed from the bath and washed with pure water and left to dry at room temperature. This process was repeated three times in total with renewed baths. In all coating studies, the support mass/bath volume ratio was kept constant at 0.12 g/mL. Characterization studies of the prepared Co-P/alumina and Ni-P/alumina catalysts were carried out by XRD (40 MA 40kv D8 Advance Bruker) and SEM/EDS (FEI brand Nova Nanosem 430 model) analysis.

2.2. Testing of Prepared Catalysts in the Hydrolysis of Sodium Borohydride Solution

The prepared Co-P/alumina and Ni-P/alumina catalysts were tested in the hydrolysis of $NaBH_4$ solution. The weighed catalyst was placed in the glass reactor (ID: 0.8 mm; OD: 19.8 cm). The basic $NaBH_4$ solution taken from the beaker was sent to the reactor with the help of a peristaltic pump. The water displacement method measured the hydrogen released as a result of the reaction. As a result of the hydrolysis experiments carried out separately for Co-P/alumina and Ni-P/alumina catalysts, it was seen that the Co-P/Al_2O_3 catalyst showed better performance, and the effects of various parameters on the reaction of this catalyst were examined. The parameters examined in the studies of obtaining hydrogen from $NaBH_4$ solution with Co-P/alumina catalyst are, respectively, $NaBH_4$ concentration, NaOH concentration, and operating temperature. The operating conditions of the experiments in which these parameters were examined are summarized in Table 4.

Table 4. *Parameters and operating conditions examined in hydrogen production from $NaBH_4$ solution (Catalyst: Co-P/alumina)*

Investigated Paramete	**Operated values**	**Operating conditions that are kept constant**
$NaBH_4$ Concentration	0.1 M; 0.3 M; 0.5 M	NaOH concentration (by mass): 10% Operating temperature: 40°C Catalyst amount: 2 g Feed flow rate: 5mL/dk.
NaOH concentration (by mass)	5%; 10%; 15%	$NaBH_4$ concentration: 0.5M Operating temperature: 40°C Catalyst amount: 2 g Feed flow rate: 5mL/dk.
Operating temperature	20°C; 40°C; 60°C	NaOH concentration (by mass): 5% $NaBH_4$ concentration: 0.5M Catalyst amount: 2 g Feed flow rate: 5mL/dk.

The reuse performance of the catalyst was also investigated in the study. In these studies, the $NaBH_4$ concentration was 0.5 M, the NaOH concentration was 5% by mass, and the feed flow rate was kept constant at 5 mL/min. The studies were repeated 10 times at 40°C and with 2 g of catalyst.

3. THE RESEARCH FINDINGS AND DISCUSSION

3.1. Catalyst Synthesis and Characterization

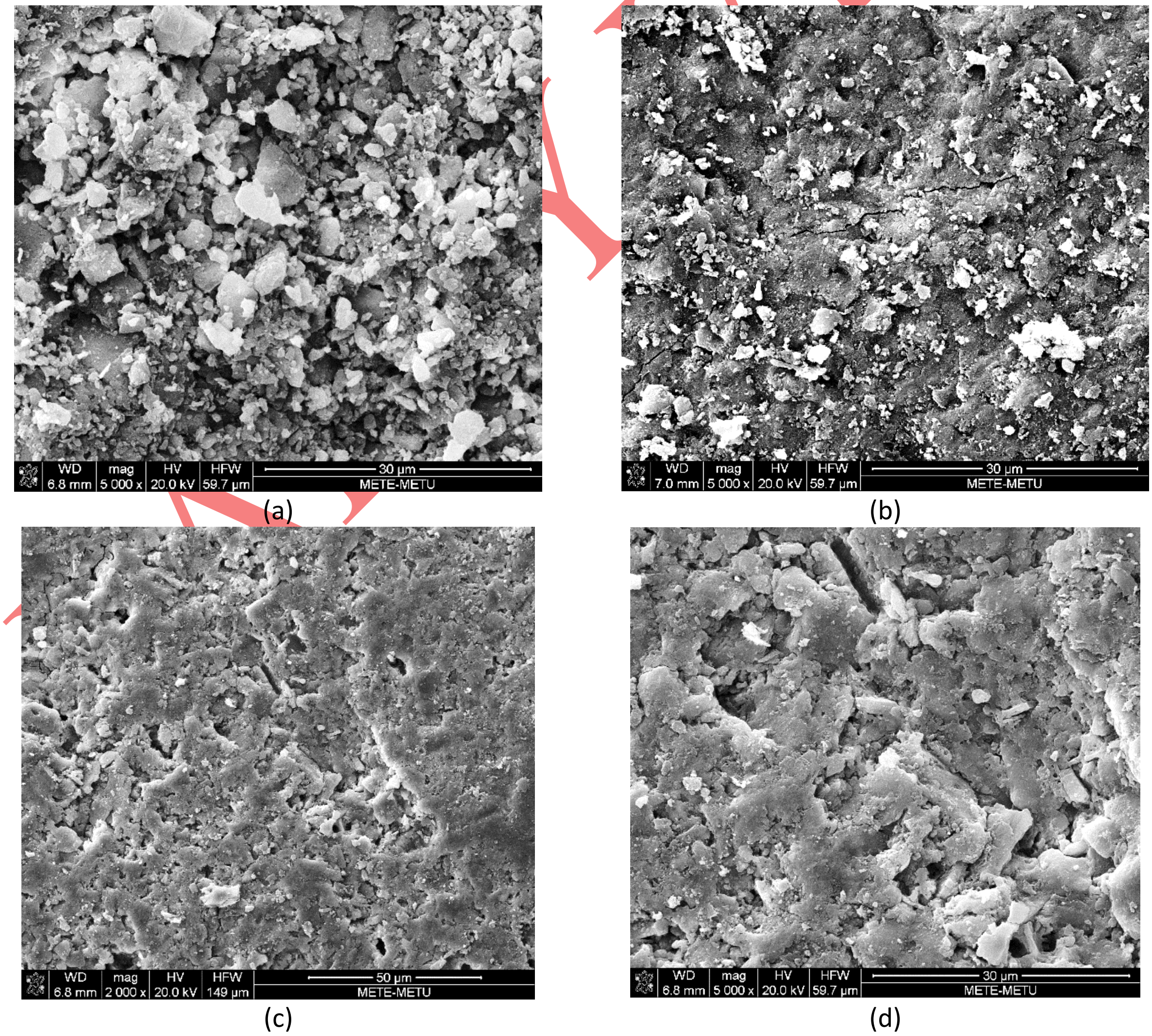
In the study conducted, XRD and SEM/EDS analyses were performed in order to evaluate the processes applied to the support. SEM analyses were conducted to determine the changes in surface morphology as a result of activation of alumina supports and Co-P and Ni-P loading. The surface composition of the prepared catalysts was determined by EDS analyses. Surface composition analyses were conducted at different points to obtain information on surface homogeneity. XRD analyses were conducted to evaluate the presence of Co, P, Ni, Co-P and Ni-P structures in the catalyst structure. The aim of the study was to alloy Co and Ni with P in the reductant structure. The characteristic peaks of Co-P and Ni-P alloys were observed in XRD analyses, and it was shown that the alloy formation was successfully achieved in the study.

In the catalyst preparation studies, commercially available alumina supports were sensitized, and after being cleaned with acidic $SnCl_2$ solution, were activated with acidic $PdCl_2$ solution. EDS analysis results of support before and after activation are given in Table 5.

Table 5. *Surface composition (EDS) of the support before and after activation*

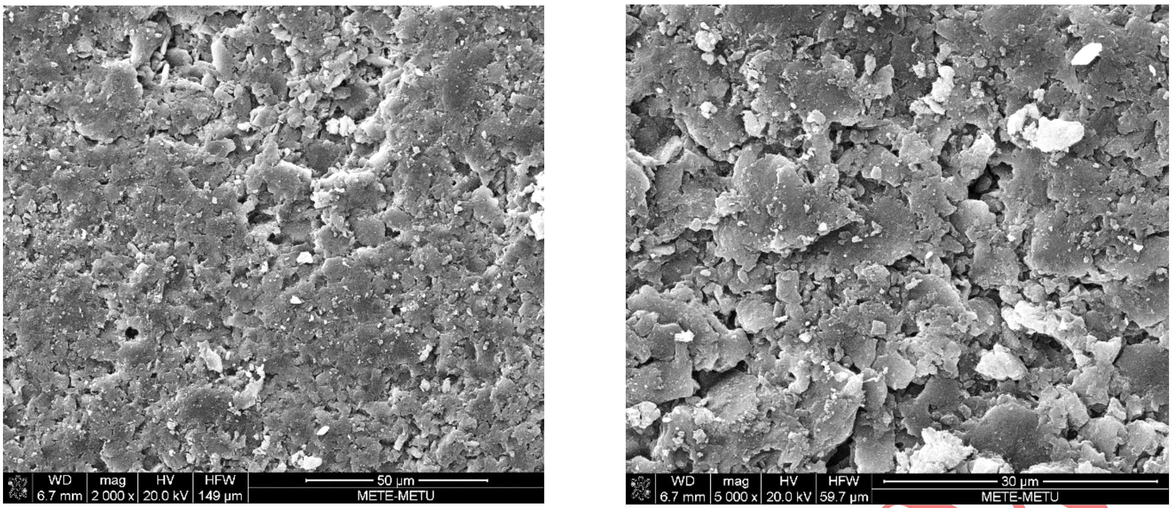
	Weight %	
Component	**Before Activation**	**After Activation**
Al	95.8	70.07
Na	4.2	-
Cl	-	5.62
Pd	-	1.54
Sn	-	22.77

The results in Table 5 show that Pd metal was loaded onto the surface during the activation process. It is also seen that there is a significant amount of Sn metal on the surface after activation. SEM photographs of the support before and after activation are given in Figure 1 (a,b).



(a) (b)

(c) (d)



(e) (f)

Figure 1. *Surface SEM photographs of the support (a): Before activation (b): After activation; Surface SEM photograph of Co-P/alumina catalyst (c): mag 2000x (d): mag 5000x; Surface SEM photograph of Ni-P/alumina catalyst (e): mag 2000x (f): mag 5000x*

It can be seen from Figure 1 that the support surface becomes tighter/narrower after activation. EDS analysis shows that a significant amount of Sn remains on the surface after activation. The structure became narrower due to the filling of the spaces on the surface with Sn. The homogeneously distributed small bright spots in the structure originate from Pd metal.

After the activation process, studies were carried out to prepare catalysts by loading Co-P and Ni-P onto the alumina support. EDS analysis results of the catalysts are given in Table 6.

Table 6. *Surface composition (EDS) of Co-P/alumina and Ni-P/alumina catalysts*

	Weight %	
Component	**Co-P/alumina**	**Ni-P/alumina**
Na	1.24	1.19
Si	---	1.25
Al	54.9	59.97
P	6.73	12.69
Cl	1.35	1.22
Pd	9.36	-
Sn	8.51	8.83
Ca	1.24	-
Co	16.65	-
Ni	-	14.85

From Table 6, it can be seen that the ratios of Co and Ni metals on the support surface are close. When the metal/P ratios are examined, this ratio is around 2.5 in the Co-P/alumina catalyst and 1.2 in the Ni-P/alumina catalyst. Although supports with the same Pd loading rate were used in catalyst preparation studies, Pd (9.36%) was detected on the surface of the Co-P/alumina catalyst, which could not be detected in the Ni-P/alumina catalyst. XRD diffraction patterns of the prepared Co-P/alumina catalysts are seen in Figure 2.

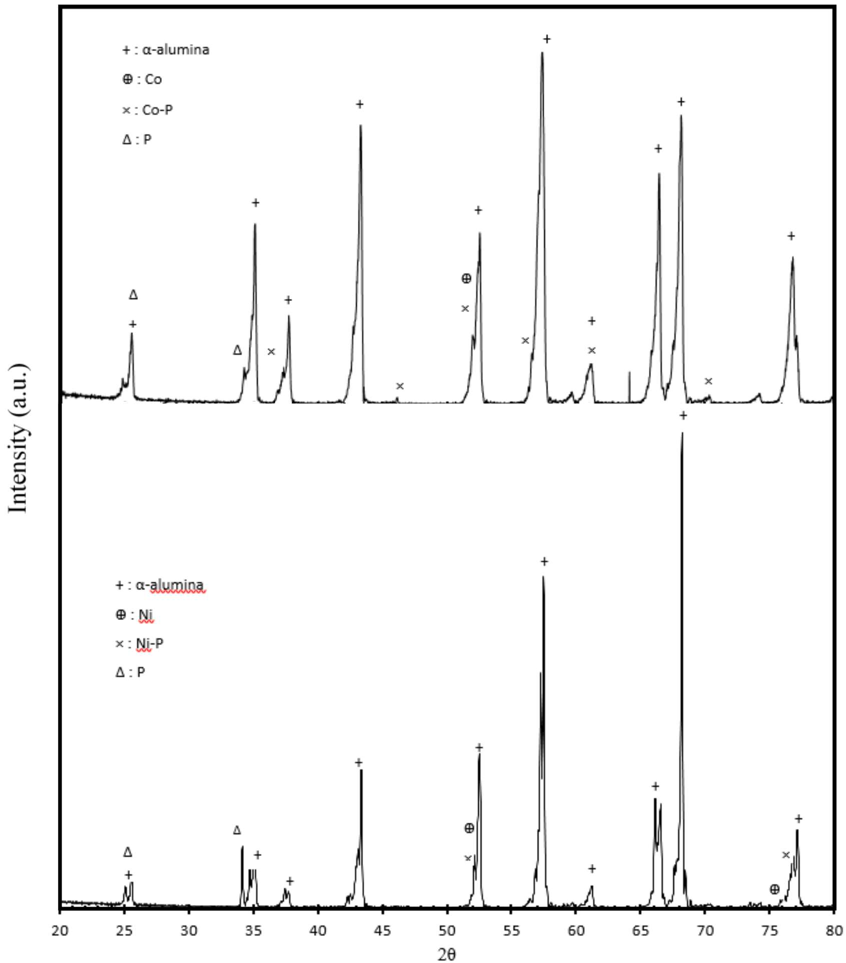


Figure 2. *XRD diffraction patterns of Co-P/alumina catalyst (above) and Ni-P/alumina catalyst (below)*

When Figure 2 is examined, the peaks of Co metal (JCPDS 15-0806) are observed to overlap with alumina peaks at 2ϴ values of 52 and 75.5°. The peaks characterizing P (JCPDS 34-0379) were detected in the XRD diffraction pattern at 25.5 and 34°. As with the peaks of Co metal, the P peaks also overlap with alumina peaks. The majority of the peaks (JCPDS 29-0497) characterizing the formation of Co-P in the catalyst structure were observed coincident with the alumina peaks (2ϴ:37°, 46.5°, 52°, 56.5°, 61°, 66°, 67.5°, 70.5°). Similar conflict situations have been reported in the literature [33]. The XRD diffraction pattern of the Ni-P/alumina catalyst is seen in Figure 2.

In Figure 2, the characteristic peaks of Ni metal (JCPDS 04-0850) were detected overlapped with the alumina peaks at 52° and 76°. Ni-P (JCPD589-2742) formation is also seen in the structure. Characteristic peaks of P metal are also seen at 25.5° and 34° (JCPDS 34-0379).

Surface SEM photographs of Co-P/alumina and Ni-P/alumina catalysts are shown in Figure 1 (c,d) and Figure 1 (e,f), respectively. When the surface morphologies of the catalysts seen in Figure 1 (c,d) and Figure 1 (e,f) are compared, it is seen that the Ni-P/alumina catalyst structure is narrower. This is due to P, which is found more in the catalyst structure than the other catalyst.

3.2. Comparison of Activities of Co-P/alumina and Ni-P/alumina Catalysts

The prepared Co-P/alumina and Ni-P/alumina catalysts were tested in the hydrolysis of sodium borohydride solution. The change in the amount of hydrogen produced for both catalysts over time is seen in Figure 3.

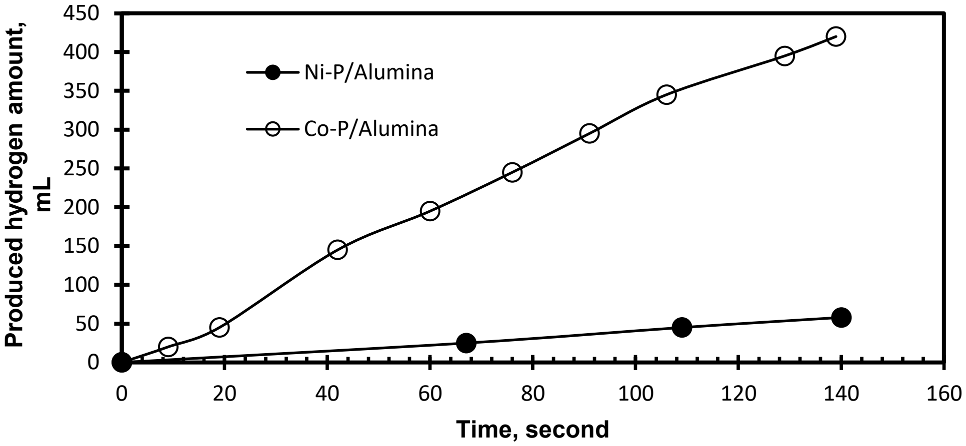


Figure 3. *Change over time in the amount of hydrogen produced for Ni-P/alumina and Co-P/alumina catalysts (T: 40°C, Feed flow rate: 15 ml/min, $NaBH_4$ concentration: 1 M, NaOH concentration (by mass): % 10, catalyst amount: 4g)*

As seen in Figure 3, the Co-P/alumina catalyst showed higher hydrogen production performance than the Ni-P/alumina catalyst. It is seen that the difference between the amounts of hydrogen produced by the catalysts widens over time. While 41 mL of hydrogen was produced on the Ni-P/alumina catalyst 100 s after the start of the reaction, this value was measured as 325 ml on the Co-P/alumina catalyst. In the literature [9, 17] although the high hydrogen production amount for both Co and Ni catalysts is noted, the difference between the performances is seen to be high in our study. One of the reasons for this situation might be the detection of 9.36% Pd by mass on the surface of the Co-P/alumina catalyst because Pd-based catalysts have high activity in hydrogen production by hydrolysis of $NaBH_4$ solution [34]. The high preparation cost of these catalysts is the biggest obstacle to their preference. Another reason for the high difference between the catalysts' hydrogen production amounts might be the surface component ratio. When Table 6 is examined, it can be seen that the amount of P is high in the Ni-P/alumina catalyst structure. When the studies on obtaining hydrogen from sodium borohydride are examined, it is stated that the ratios of the components loaded on the surface are essential. In the study conducted by Wang et al. [2018], the hydrogen production performances of catalysts synthesized at different Co/P ratios were compared [19]. The research found the highest activity in the catalyst with the highest Co/P ratio (approximately 19% by mass). When Table 6 is examined, it is seen that the amounts of loaded nickel and phosphorus are close to each other, and the Ni/P ratio is approximately 1.2. It is seen that this ratio is approximately 2.5 in the Co-P/alumina catalyst. For this reason, it is thought that the excessive amount of P in the Ni-P/alumina catalyst structure may have negatively affected the activity of Ni metal sites. In light of these results, the Co-P/alumina catalyst was used in the continuing parts of the study. The effects of $NaBH_4$ and NaOH concentration and reaction temperature on the amount of hydrogen production in the catalytic hydrolysis of $NaBH_4$ solution using Co-P/alumina catalyst were investigated. In addition, studies have been conducted on how much activity is preserved after repeated reactions on the same catalyst. The results obtained are presented in the following sections.

3.3. Effect of $NaBH_4$ Concentration on Hydrogen Production Amount and Rate

To examine the effect of $NaBH_4$ concentration on the amount of hydrogen production, studies were carried out at 0.1 M, 0.3 M and 0.5 M concentrations. Figure 4 shows the change in hydrogen production amounts obtained at different $NaBH_4$ concentrations over time.

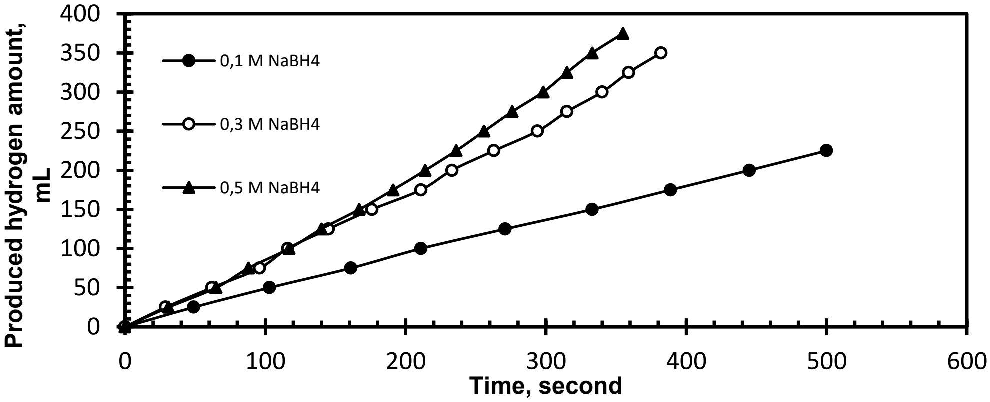


Figure 4. *Change over time of hydrogen production amounts measured at different $NaBH_4$ concentrations (T: 40°C, feed flow rate: 5 ml/min, NaOH concentration (by mass): 10%, catalyst: Co-P/alumina, catalyst amount: 2 g)*

When Figure 4 is examined, it can be seen that the amounts of hydrogen obtained from the hydrolysis of 0.3 M and 0.5 M solutions are very close to each other at the beginning of the experiment. Although the results for the 0.5 M solution were higher starting from the 140th second, there was no significant difference between the two concentrations. However, when the solution concentration increases from 0.1 M to 0.3 M, the significant difference in the amount of hydrogen produced is noteworthy. Figure 5 shows the hydrogen production rates obtained at different $NaBH_4$ concentrations (the hydrogen amounts determined at the end of the experiment were used to determine the production rates).

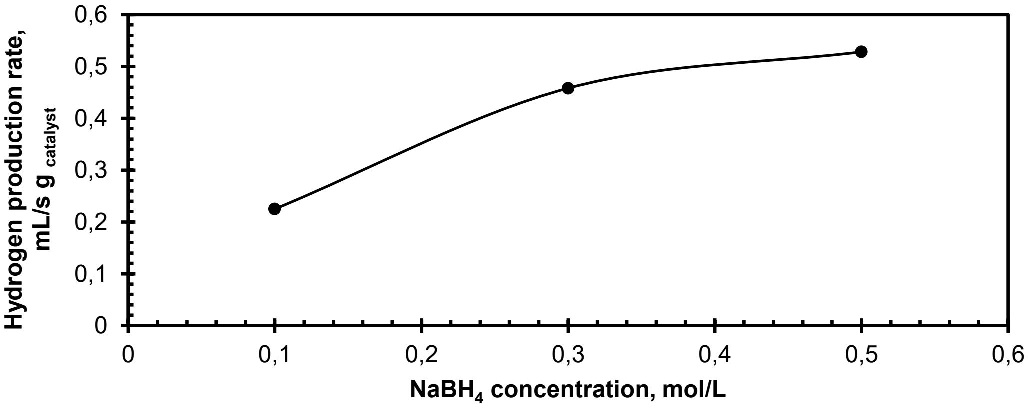


***Figure 5**. Measured hydrogen production rates at different $NaBH_4$ concentrations (T: 40°C, flow rate: 5 ml/min, NaOH concentration (by mass): % 10, catalyst amount: 2 g)*

When Figure 5 is examined, it is seen that the hydrogen production rate decreases with the increase in $NaBH_4$ concentration. The literature review states that the optimum $NaBH_4$ concentration should be determined for the operating conditions. It has been shown that the hydrogen production rate starts to decrease after the optimum value [35]. The reason for this is mass transfer limitations caused by the increase in viscosity due to the increasing amount of $NaBO_2$ in solution. Apart from the fact that the amount of $NaBO_2$ causes an increase in viscosity, it is also stated in the literature that the hydrogen production rate decreases due to its strong adsorption on Co [36].

3.4. Effect of NaOH Concentration on the Amount and Rate of Hydrogen Produced

NaOH concentration is an important parameter in hydrogen production by the hydrolysis of $NaBH_4$ solution. In the study, experiments were conducted with 5%, 10%, and 15% solutions by mass to observe the effect of NaOH concentration. The amounts of hydrogen obtained at different NaOH concentrations are given in Figure 6.

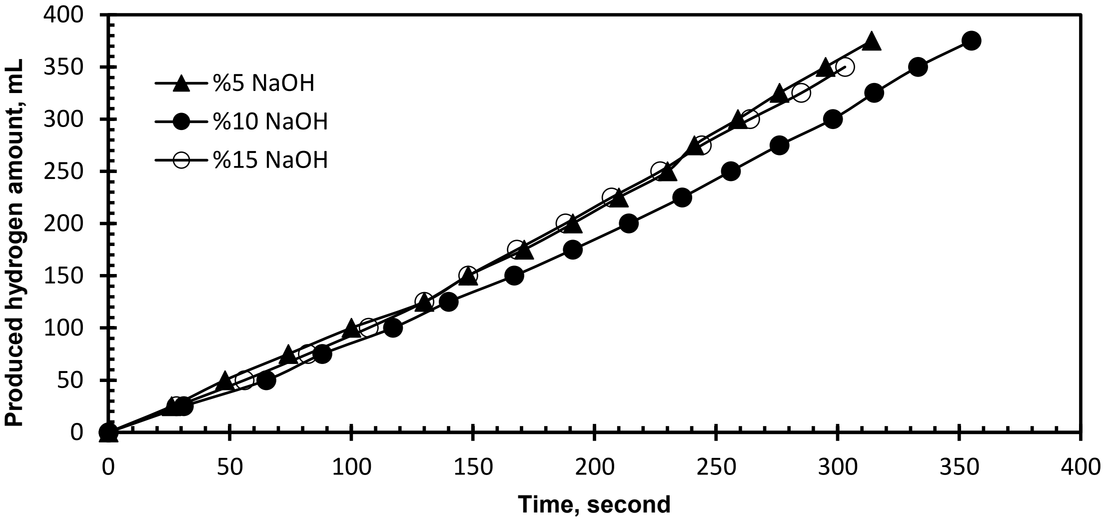


Figure 6. *Change in the amount of hydrogen produced over time at different NaOH concentrations (T: 40°C, feed flow rate: 5 mL/min, $NaBH_4$ concentration: 0.5 M, catalyst amount: 2 g)*

NaOH acts as a kind of catalyst in the hydrolysis of $NaBH_4$ solution. Since OH^- ion presents in the reaction step, increasing the amount of NaOH increases hydrogen production. However, increasing the NaOH concentration increases the pH value of the solution, causing OH^- ions to act as inhibitors in the hydrolysis reaction and reducing proton exchange. Slow ionization of $NaBH_4$ negatively affects catalytic activity [25]. Additionally, as the amount of NaOH increases, the solubility of $NaBO_2$ decreases and precipitated $NaBO_2$ can reduce the catalyst performance by closing the active sites of the catalysts. Therefore, the optimum NaOH concentration should be determined in studies on catalytic hydrogen production from $NaBH_4$ solution. When Figure 6 is examined, it can be seen that the amounts of hydrogen obtained from solutions containing different concentrations of NaOH are very close to each other, especially at the beginning. As the reaction progresses, solutions containing 5% and 15% NaOH show similar hydrogen production amounts throughout the experiment, while the solution containing 10% NaOH has relatively lower values. Figure 7 shows the hydrogen production rate values determined at different NaOH concentrations.

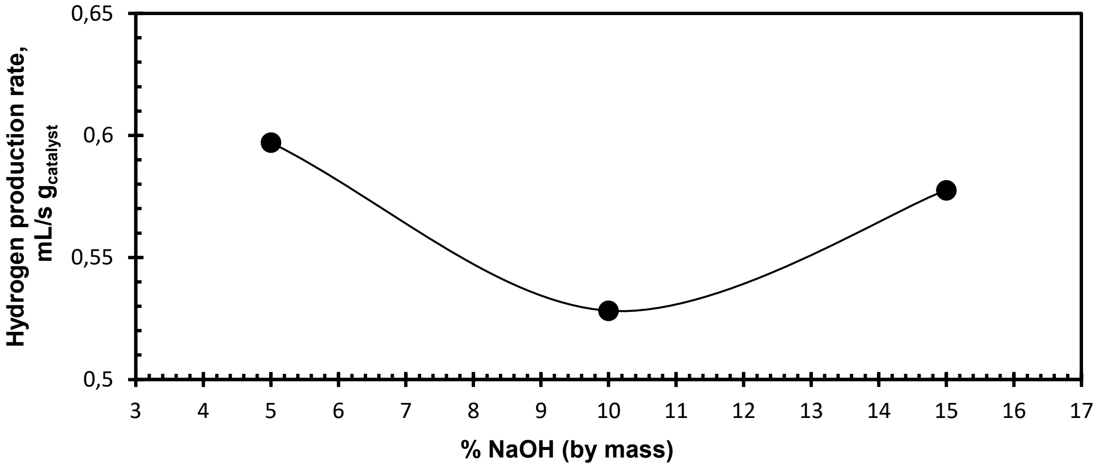


Figure 7. *Effect of NaOH concentration on hydrogen production rate (T: 40°C, feed flow rate: 5 ml/min, $NaBH_4$ concentration: 0.5 M, catalyst amount: 2 g)*

When Figure 7 is examined, it can be seen that although the hydrogen production rate decreases slightly at 10% NaOH concentration, there is no significant difference in all three values. At increasing concentrations of NaOH, the hydrogen production rate decreases as the free water ions needed for hydrolysis decrease due to the ions from NaOH forming a solid complex with water [36]. In the absence of NaOH, $NaBH_4$ solution undergoes continuous spontaneous hydrolysis. The reason for adding NaOH to the environment is to increase the usage time by preventing the continuous decomposition of $NaBH_4$. For this, NaOH concentration in the proper range is sufficient. In our study where the effect of NaOH concentration was examined, the $NaBH_4$ concentration was 0.5 M. These results showed that, in line with the literature, NaOH concentration was not an effective parameter on hydrogen production at low $NaBH_4$ concentrations [37].

3.5. Effect of Operating Temperature on Hydrogen Production Amount

To investigate the effect of operating temperature on hydrogen production, hydrogen production experiments were carried out from $NaBH_4$ solution at 20°C, 40°C, and 60°C. Figure 8 shows the amounts of hydrogen produced at different operating temperatures.

The temperatures to be investigated were selected regarding the competition between the catalytic reaction and the dissolution rate of the formed products. The increase in temperature results in increased hydrogen generation rate; yet the adsorption and/or desorption, and so the dissolution of reactant and/or product, have a limit regarding the mass transfer between the catalyst structure and the bulk [38,39]. Although the temperature, of course, is one of the key points in the reaction, the transport mechanism and the competition between them should be considered. Moreover, one of the aims of this study is to generate hydrogen more economically. Higher temperature requires more energy, which would end up in more cost in operation, as well as the rapid consumption of the reactant at higher temperatures. Considering these points, if assessed regarding a scale-up for such a system with all auxiliary units, higher temperature would decrease the efficiency of the hydrogen production in general. In addition to these, the deterioration of $NaBH_4$ at higher temperatures than 60°C was also considered; so the maximum temperature had been selected as 60°C, as in many research in literature [40, 41].

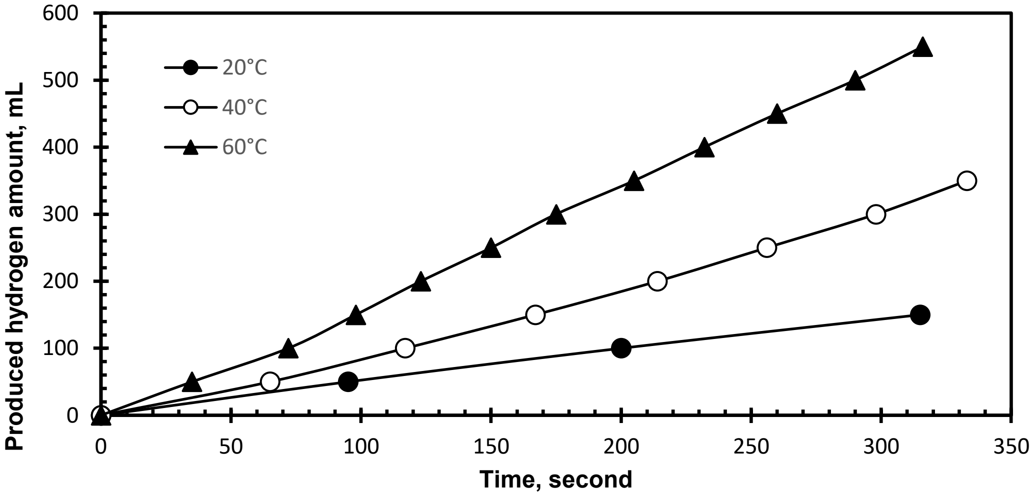


Figure 8. *Change of the amount of hydrogen produced at different temperatures over time (Feed flow rate: 5 ml/min, $NaBH_4$ concentration 0.5 M, NaOH concentration (by mass): 5%, catalyst amount: 2 g)*

When Figure 8 is examined, it is seen that, as expected, temperature is an important parameter affecting the amount of hydrogen production. Hydrogen production, which was quite low at 20°C, increased significantly with increasing temperature. 200 s after the start of the hydrolysis experiment, the amount of hydrogen production obtained at 20°C increased approximately 3.4 times by increasing the temperature to 60°C. Figure 9 shows the effect of temperature on the hydrogen production rate.

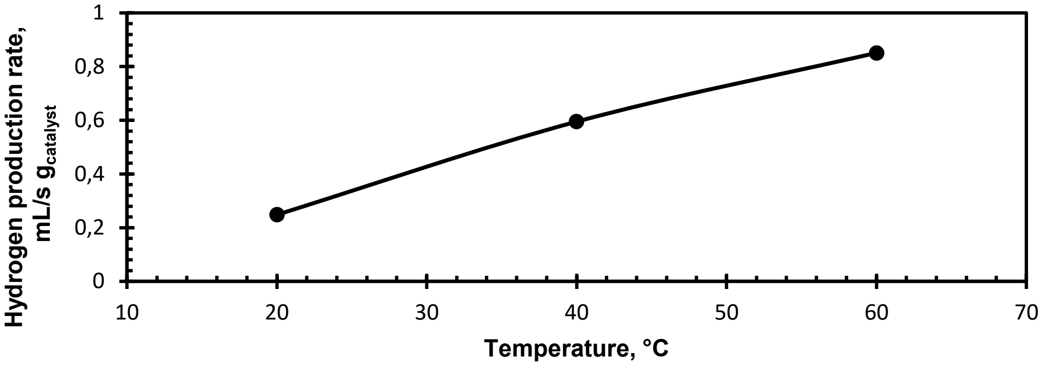


Figure 9. *Change of hydrogen production rate with temperature (feed flow rate: 5 ml/min, $NaBH_4$ concentration: 0.5 M, NaOH concentration (by mass): 5%, catalyst amount: 2 g)*

When Figure 9 is examined, it is seen that the hydrogen production rate increases approximately linearly with temperature. When the literature is examined, it is seen that the hydrogen production reaction by $NaBH_4$ hydrolysis is a zero-order reaction [42]. In this study, it was shown that there was no significant change in hydrogen production rates at $NaBH_4$ concentration values after 0.3 M. Assuming the reaction is zero order, the following expressions can be written

$$r = k = k_o exp\left(\frac{-E_A}{RT}\right) \tag{1}$$

$$lnr = lnk_o - \frac{E_A}{R}\frac{1}{T}\ . \tag{2}$$

By plotting the lnr values against 1/T, the activation energy was calculated as 25 kJ/mol. In the literature, it is seen that the activation energies determined on Co-supported catalysts are in the range of 20-60 kJ/mol [10, 43, 44, 45]. The observed low activation energy can be explained by the rapid reaction on the catalyst.

3.6. Performance Change in Catalyst Reuse

The change in performance of the Co-P/alumina catalyst was tested by reusing it in 10 repeated experiments. In repeat experiments, reaction studies were carried out with renewed $NaBH_4$ solution on the same catalyst, keeping the operating conditions constant. The hydrogen production rates obtained in each experiment conducted are shown in Figure 10.

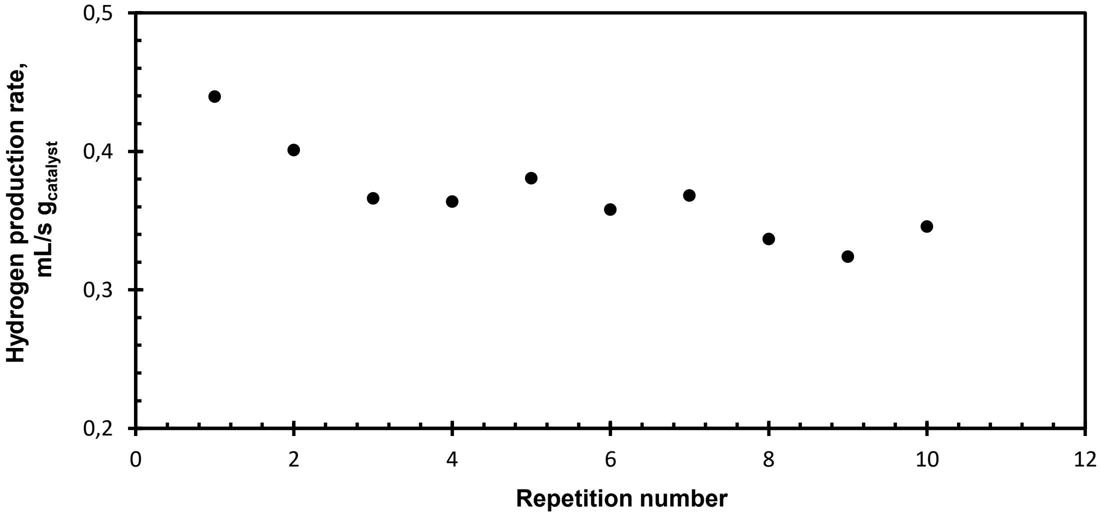


Figure 10. *Reuse performance of Co-P/alumina catalyst (T: 40°C, feed flow rate: 5 mL/min, $NaBH_4$ concentration: 0.5 M, NaOH concentration (by mass): 5%, catalyst amount: 2 g)*

When Figure 10 is examined, it is seen that the hydrogen production rate decreases as the number of repetitions increases. The Co-P/alumina catalyst showed approximately 74% of its initial performance after the 10th use. In a study in the literature, the Co-Ni-Mo-P/γ-alumina catalyst prepared with the ELP technique retained 80% of its initial performance after the 5th use [27]. The study showed that the prepared Co-P/alumina catalyst had promising results in hydrogen production by $NaBH_4$ hydrolysis.

4. RESULTS

In the study, Co-P/alumina and Ni-P/alumina catalysts were prepared for hydrogen production by the hydrolysis of $NaBH_4$ solution using the ELP technique. Since better results with Co-P/alumina catalyst were gathered, the parametric studies ($NaBH_4$ concentration, NaOH concentration, and temperature) on hydrogen production rate were carried out using this catalyst.

- It has been shown that high metal/P ratios positively affect catalyst activity. The high Co/P ratio explains the high activity values detected with Co-P/alumina catalysts and Pd detected on the surface.
- As the $NaBH_4$ concentration increased, the amount and rate of hydrogen production increased, but a significant increase was observed after a specific concentration value. This situation is explained by the mass transfer limitations and strong adsorption caused by the excess $NaBO_2$ formed at high $NaBH_4$ concentrations and the closure of the active centers in the catalyst.
- It has been shown that the amount and rate of hydrogen production are not significantly affected by the change of NaOH concentration. Consistent with the literature, it was determined that the NaOH concentration did not affect the reaction at low $NaBH_4$ concentrations (0.5 M).
- The relatively low activation energy determined for the reaction on Co-P/alumina catalysts is explained as evidence that the reaction can occur rapidly on the catalyst surface.
- The preservation of high activity levels in repeated experiments on the same catalyst showed that using the synthesized catalyst is promising.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

[1] Usman, M., "Hydrogen storage methods: Review and Current Status", Renewable and Sustainable Energy Reviews, 167: 112743, (2022).

[2] Yao, J., Wu, Z., Wang, H., Yang, F., Ren, J., and Zhang, Z., "Application-Oriented Hydrolysis Reaction System of Solid-State Hydrogen Storage Materials for High Energy Density Target: A Review", Journal of Energy Chemistry, 74: 218-238, (2022).

[3] Grinderslev, J.B., Amdisen, M.B., Skov, L.N., Moller, K.T., Kristensen, L.G., Polanski, M., Heere, M. and Jensen, T.R. "New Perspectives of Functional Metal Borohydrides", Journal of Alloys and Compounds, 896, 163014, (2022).

[4] Abdelhamid, H.M., "A Review on Hydrogen Generation from the Hydrolysis of Sodium Borohydride", International Journal of Hydrogen Energy, 46: 726-765, (2021).

[5] Dai, P, Zhao, X., Xu, D., Wang, C., Tao, X., Liu, X. and Gao, J., "Preparation,Characterization, and Properties of Pt/Al_2O_3/Cordierite Monolith Catalyst for Hydrogen Generation from Hydrolysis of Sodium Borohydride in a Flow Reactor", International Journal of Hydrogen Energy, 44: 28463-28470, (2019).

[6] Wang, F, Luo, Y. Wang, Y. and Zhu, H., "The Preparation and Performance of a Novel Spherical Spider Web-Like Structure Ru-Ni / Ni Foam Catalyst for $NaBH_4$ Methanolysis", International Journal of Hydrogen Energy, 44: 13185-13194, (2019).

[7] Huff, C., Biehler, E., Quach, Q., Long, J.M. and Abdel-Fattah, T.M., "Synthesis of highly dispersive platinum nanoparticles and their application in a hydrogen generation reaction", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 610: 125734, (2021).

[8] Jafarzadeh, H., Karaman, C., Güngör, A., Karaman, O., Show, P.L., Sami, P. and Mehrizi, A.A., "Hydrogen Production via Sodium Borohydride Hydrolysis Catalyzed by Cobalt Ferrite Anchored Nitrogen-and Sulfur Co-Doped Graphene Hybrid Nanocatalyst: Artificial Neural Network Modeling Approach", Chemical Engineering Research & Design, 183: 557-566, (2022).

[9] Zhang, H., Feng, X., Cheng, L., Hou, X., Li, Y. and Han, S., "Non-Noble Co Anchored on Nanoporous Graphene Oxide, as an Efficient and Long-Life Catalyst for Hydrogen Generation from Sodium Borohydride", Colloids and Surfaces A, 563: 112-119, (2019).

[10] Kilinc D., and Sahin, O., "Highly Active and Stable CeO_2 Supported Nickel Complex Catalyst in Hydrogen Generation", International Journal of Hydrogen Energy, 46: 499-507, (2021).

[11] Chen, B., Chen, S., Bandal, H.A., Appiah-Ntiamoah, R., Jadhav, A R. and Kim, H., "Cobalt Nanoparticles Supported on Magnetic Coreshell Structured Carbon as a Highly Efficient Catalyst for Hydrogen Generation from $NaBH_4$ Hydrolysis, International Journal of Hydrogen Energy, 43: 9296-9306, (2018).

[12] Bozkurt, G., Özer, A. and Bayrakçeken Yurtcan, A., "Hydrogen Generation from Sodium Borohydride with Ni and Co Based Catalysts Supported on Co_3O_4", International Journal of Hydrogen Energy, 43: 22205-22214, (2018).

[13] Chou, C.C., Hsieh, C.H. and Chen, B.H., "Hydrogen Generation from Catalytic Hydrolysis of Sodium Borohydride using Bimetallic Ni-Co Nanoparticles on Reduced Graphene Oxide as Catalysts", Energy, 90: 1973-1982, (2015).

[14] Karaman, O. "Three-dimensional graphene network supported nickel-cobalt bimetallic alloy nanocatalyst for hydrogen production by hydrolysis of sodium borohydride and developing of an artificial neural network modeling to forecast hydrogen production rate", Chemical Engineering Research and Design, 181: 321–330, (2022).

[15] Narasimharao, K., Abu-Zied, B.M. and Alfaifi, S.Y., "Cobalt Oxide Supported Multi Wall Carbon Nanotube Catalysts for Hydrogen Production via Sodium Borohydride Hydrolysis International Journal of Hydrogen Energy, 46: 6404-6418, (2021).

[16] Sun H., Meng J., Jiao L., Cheng F. and Chen J. "A review of transition-metal boride/phosphide-based materials for catalytic hydrogen generation from hydrolysis of boron hydrides", Inorganic Chemistry Frontiers, 5: 760-772, (2018).

[17] Liang, Z., Li, Q., Li, F., Zhao, S. and Xia, X., "Hydrogen Generation from Hydrolysis of $NaBH_4$ Based on High Stable NiB/NiFe2O4 Catalyst", International Journal of Hydrogen Energy, 42: 3971-3980, (2017).

[18] Wang, Y, Meng, W., Wang, D., Wang, Z., Zou, K., Cao, Z., Zhang, K., Wu, S. and Li, G., "Ultrafine Cobalt-Molybdenum-Boron Nanocatalyst for Enhanced Hydrogen Generation Property from the Hydrolysis of Ammonia Borane", International Journal of Hydrogen Energy, 44: 23267-23276, (2019).

[19] Wang, F., Zhang, Y., Wang, Y., Luo, Y., Chen, Y. and Zhu, H., "Co-P Nanoparticles Supported on Dandelion-Like CNTs-Ni Foam Composite Carrier as a Novel Catalyst for Hydrogen Generation from $NaBH_4$ Methanolysis", International Journal of Hydrogen Energy, 43: 8805-8814, (2018).

[20] Wang, L., Li, Z., Zhang, Y., Zhang, T. and Xie, G., "Hydrogen Generation from Alkaline $NaBH_4$ Solution using Electroless-Deposited Co-Ni-W-P/γ-Al_2O_3 as Catalysts", Journal of Alloys and Compounds, 702: 649-658, (2017).

[21] Baydaroğlu, F.O., Özdemir, E. and Gürek, A.G., "Polypyrrole Supported Co-W-B Nanoparticles as an Efficient Catalyst for Improved Hydrogen Generation from Hydrolysis of Sodium Borohydride", International Journal of Hydrogen Energy, 47: 9643-9652, (2022).

[22] Pornea, A.M., Abebe, M.W. and Kim, H., "Ternary NiCoP Urchin Like 3D Nanostructure Supported on Nickel Foam as a Catalyst for Hydrogen Generation of Alkaline $NaBH_4$", Chemical Physics, 516: 152-159, (2019).

[23] Huang, X., Wu, D. and Cheng, D.. "Porous Co_2P Nanowires as High Efficient Bifunctional Catalysts for 4-Nitrophenol Reduction and Sodium Borohydride Hydrolysis", Journal of Colloid and Interface Science, 507: 429-436, (2017).

[24] Paksoy, A., Kurtoğlu, S.F., Dizaji, A.K., Altıntaş, Z., Khoshsima, S., Uzun, A. and Balcı, Ö., "Nanocrystalline Cobalt-Nickel-Boron (Metal Boride) Catalysts for Efficient Hydrogen Production from the Hydrolysis of Sodium Borohydride", International Journal of Hydrogen Energy, 46: 7974-7988, (2021).

[25] İzgi, M.S., Ödemiş, Ö., Şahin, Ö. And Saka, S., "Co-B-F ve Co-B-P Katalizörleri Kullanılarak NaBH4'den Hidrojen Üretimine NaOH'in Etkisi", Selçuk Üniveritesi Mühendislik, Bilim ve Teknoloji Dergisi, 4: 55-64, (2016).

[26] Li, Z., Li, H., Wang, L., Liu, T., Zhang, T. and Wang, G., "Hydrogen Generation from Catalytic Hydrolysis of Sodium Borohydride Solution using Supported Amorphous alloy Catalysts (Ni-Co-P/γ-Al_2O_3)", International Journal of Hydrogen Energy, 39: 14935-14941, (2014).

[27] Wang Y, Qi K, Wu S, Cao Z, Zhang K, Lu Y, and Li H., "Preparation, characterization and catalytic sodium borohydride hydrolysis of nanostructured cobalt-phosphorous catalysts", Journal of Power Sources, 284: 130-1377, (2015).

[28] Wang, Y., Shen, Y., Qi, K., Cao, Z., Zhang, K. and Wu, S., "Nanostructured Cobalt-Phosphorous Catalysts for Hydrogen Generation from Hydrolysis of Sodium Borohydride Solution", Renewable Energy, 89: 285-294, (2016).

[29] Kim, D.H., Jo, S., Kwon, J.H. and Lee, S., "Effect of Iron Content on the Hydrogen Production Kinetics of Electroless-Deposited Co-Ni-Fe-P Alloy Catalysts from the Hydrolysis of Sodium Borohydride, and a Study of Its Feasibility in a New Hydrolysis using Magnesium and Calcium Borohyrides", International Journal of Hydrogen Energy, 44: 15228-15238, (2019).

[30] Tiri, R.N.E., Gulbagca, F., Aygun, A., Cherif, A. and Sen, F., "Biosynthesis of Ag–Pt Bimetallic Nanoparticles using Propolis Extract: Antibacterial Effects and Catalytic Activity on $NaBH_4$ Hydrolysis", Environmental Research, 206: 112622, (2022).

[31] Duman, S., Kaya, B., Caf, F., Enez, B. and Fincan, S.A., "Innovative hydrogen release from sodium borohydride hydrolysis using biocatalyst-like Fe2O3 nanoparticles impregnated on Bacillus simplex bacteria", International Journal of Hydrogen Energy, 4: 15410-15430, (2021).

[32] Vitry, V., Hastir, J., Megret, A., Yazdani, S. and Yunacti, M., "Recent Advances in Electroless Nickel-Boron Coatings", Surface & Coatings Technology, 429: 127937, (2022).

[33] Wei Y., Fu, J., Song, H., Zhang, B., Pi, C., Xia, L., Zhang, X., Gao, B., Zheng, Y. and Chu, P. "N-doped TiO_2 nanotube arrays with uniformly embedded Co_xP nanoparticles for high- efficiency hydrogen evolution reaction", Royal Society of Chemistry, 9: 11676-11682, (2019).

[34] Al-shaikh, H., Lasri, J., Knight, J.G. and Al-Goul, S.T., "Palladium Mesoporous Nanoparticles Pd NPs@[KIT-6] and Pd NPs@[KIT-6]-PEG-Imid as Efficient Heterogeneous Catalysts for H_2 Production from $NaBH_4$ Hydrolysis", Fuel, 325: 124962, (2022).

[35] Hosgun, S., Özdemir, M. and Sahin, Y.B., "Optimization of Hydrogen Generation by Catalytic Hydrolysis of $NaBH_4$ with Halloysite-Supported CoB Catalyst using Response Surface Methodology*",* Clay and Clay Minerals, 69: 128-141, (2021).

[36] Bu, Y, Liu, J., Chu, H., Wei, S., Yin, Q., Kang, I., Luo, X., Sun, L., Xu, F., Huang, P., Rosei, F., Pimerzin, A.A., Seifert, H.J., Du, Y. and Wang, J., "Catalytic Hydrogen Evolution of $NaBH_4$ Hydrolysis by Cobalt Nanoparticles Supported on Bagasse-Derived Porous Carbon", Nanomaterials, 11: 3259, (2021).

[37] Amendola, S.C., Sharp-Goldman, S.L., Janjua, M.S., Kelly, M.T., Petillo, P.J. and Binder, M., "An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst", Journal of Power Sources, 85: 186-189, (2000).

[38] Hunga, A., Tsaib, S., Hsub, Y., Kub, J., Chenc, Y., Yua, C., "Kinetics of sodium borohydride hydrolysis reaction for hydrogen generation", International Journal of Hydrogen Energy, 33: 6205–6215, (2008).

[39] Chen, J., Wu, Z., Zheng, J., Shi, Y., Xie, L., Yang, F., Wang, Y., Zhang, Z., "Novel solid-state hydrolysis kinetics of $NaBH_4$ for stable and high-capacity on-line hydrogen production", Chemical Engineering Journal, 486: 150062, (2024).

[40] Andrieux, J., Laversenne, L., Krol, O., Chiriac, R., Bouajila, Z., Tenu, R., Counioux, J.J., Goutaudier, C., "Revision of the $NaBO_2$-H_2O phase diagram for optimized yield in the H_2 generation through $NaBH_4$ hydrolysis", International Journal of Hydrogen Energy, 37: 5798-5810, (2012).

[41] Xu, F., Ren J., Ma J., Wang Y., Zhang, K., Cao, Z., Sun, Q., Wu, S., Li, G., Bai, S., "A review of hydrogen production kinetics from the hydrolysis of NaBH4 solution catalyzed by Co-based catalysts", International Journal of Hydrogen Energy, 50: 827-844, (2024).

[42] Andrieux, J., Demirci, U.B., Hannauer, J., Gervais, C., Goutaudier, C. and Miele, P., "Spontaneous hydrolysis of sodium borohydride in harsh conditions", International Journal of Hydrogen Energy, 36: 224-233, (2011).

[43] Chou, C., Hsieh, C. and Chen, B., "Hydrogen generation from catalytic hydrolysis of sodium borohydride using bimetallic Ni-Co nanoparticles on reduced graphene oxide as catalysts", Energy, 90: 1973-1982, (2015).

[44] Kaya M., and Bekiroğulları, M., "Investigation of Hydrogen Production from Sodium Borohydride Methanolysis in the Presence of Al_2O_3/Spirulina Platensis Supported Co Catalyst", European Journal of Science and Technology, 16: 69-76, (2019).

[45] da Silva, B.S.L., Amorim, M.K.M., Souza, E.S., de Oliveira, M.A., da Costa, O.M.M.M., Barros, B.S., Kulesza, J., "Sodium borohydride hydrolysis for hydrogen generation over Mn-BDC and

MnCo-BDC (BDC – 1,4-benzene-dicarboxylate) coordination polymers", Polyhedron, 273: 117493, (2025).