Research Article

Journal of Applied Material Science & Engineering Research

Microwave Treatment on Co–B–P Catalyst to Enhance Catalytic Activity for Hydrogen Production by Hydrolysis of Nabh$_4$

Mehmet SAİT İZGİ[1]*, Ömer ŞAHİN[1], Ömer ÖDEMİŞ[2] and Sabit HOROZ[3]

[1]Siirt University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 56100 Siirt, Turkey

[2]Bitlis Eren University, Institute of Science, 13100 Bitlis, Turkey

[3]Siirt University, Faculty of Engineering and Architecture, Department of Electrical & Electronic Engineering, 56100 Siirt, Turkey

[*]Corresponding author
Mehmet Sait İZGİ, Siirt University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 56100 Siirt, Turkey. E-mail: saitizgi@siirt.edu.tr

Submitted: 06 Mar 2018; **Accepted**: 15 Mar 2018; **Published**: 26 Mar 2018

Abstract
*In this study, a microwave treatment was chosen as an alternative method to synthesize Co-B-P catalyst for hydrogen production from hydrolysis of sodium borohydride ($NaBH_4$) for the first time. The effect of gas, treatment time, and microwave power, amount of catalyst and temperature on the catalytic activity of Co-B-P catalyst was investigated under microwave treatment. The synthesized Co-B-P catalyst was characterized by XRD, SEM, EDX, BET and FTIR measurements. In the presence of Co-B-P catalyst, hydrolysis of $NaBH_4$ under microwave treatment was completed in 9 minutes whereas it was completed in 16 minutes under normal condition. It was found that the value of activation energy is 16.211 kJ*mol^{-1}.*

Keywords: Catalyst, Co-B-P, hydrogen, microwave, $NaBH_4$, production

Introduction
It is predicted that the hydrogen can be considered the main energy source in the near future and recently since it has been extensively utilized in different industrial areas. Nowadays, the hydrogen is produced from various sources and stored in different ways [1]. It is necessary to make good use of technology to protect the environment and improve the life quality. There is a need for a versatile technology for cars, homes and power plants [2]. There is a need for clean technologies to reverse the harm done to the environment [3-6]. One of these is the hydrogen production from sodium borohydride [7]. It showed that the hydrolysis of $NaBH_4$ with water is indicated in reaction 1.

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 + \text{heat}\ \Delta H = -212\ \text{kJ*mol}^{-1} \quad (1)$$

Many metals and compounds have been tested as catalyst for this important reaction. The process of $NaBH_4$ is usually carried out using heterogeneous and homogeneous catalysts in conditions which close to room temperature. The hydrogen production from $NaBH_4$ hydrolysis was achieved by using suitable catalysts such as Ni, Co, Co-B, Co-B/SiO_2, Co-B-Cr, Co-Cu-B, Co-Ni-P-B, Co-B-P and Co-B-F [8-16].

The heterogeneous catalysts used in the process of $NaBH_4$ hydrolysis have some advantages compare to homogeneous catalysts. These are; (1) longer operation of catalyst, (2) easy separation of catalyst from the sodium meta-borate ($NaBO_2$) solution which occurs as a byproduct in the hydrolysis reaction, (3) in the hydrolysis reaction process, there is no formation of other byproducts apart from $NaBO_2$. These by products may result in contamination in the hydrogen is produced [17].

Some properties such as high surface are, unaffected by reaction conditions and reusability are required for catalysts which increase the catalytic activity. Numerous studies have been conducted on the heterogeneous catalysts to obtain pure hydrogen from $NaBH_4$ hydrolysis and continue to increase the catalytic activity of these catalysts. In recent years, microwave techniques have been attracted considerable attention in the field of preparing effective catalysts with higher activity due to the reinforcing effect from microwave modification of surface [18]. The previous studies have been based on the synthesis of effective catalyst for the hydrolysis reaction to take place quickly and efficiently [19-21]. In our previous studies, we studied to obtain the best reaction efficiency in the presence of different catalysts. Therefore, we tried to irritate catalyst such as Co-B-TiO_2 and Co-B with plasma and microwave, respectively [5,22]. We observed that the microwave and plasma treatment play an important role to enhance catalytic activity of the catalysts. As can be seen, there is no report on the effect of microwave treatment on the Co-B-P catalyst.

In our present study, the microwave treatment was applied on the Co-B-P catalyst for the first time. The effect of different parameters such as gas, microwave power, treatment time, temperature and amounts of catalyst were investigated on the catalytic activity of

Co-B-P catalyst in microwave treatment and the optimum conditions were determined. It was found that N_2, 20 min, 500 W, 50 mg and 60°C are the most efficient gas, time, power, catalyst amount and temperature, respectively to improve the catalytic activity. The Co-B-P catalyst which shows the highest catalytic activity under the optimum conditions was characterized by XRD, SEM, EDX, BET and FTIR measurements. As a result, our results suggest that the microwave treatment with different conditions can be used as a promising technique to increase the catalytic activity of Co-B-P catalyst.

Materials and Method

Chemicals

The chemical reduction method was used to synthesize Co-B-P catalyst for hydrogen production from $NaBH_4$ solutions. Cobalt chloride hexahydrate ($CoCl_2.6H_2O$) as Co source, $NaBH_4$ as B source, and sodium hydrogenphosphate ($NaHPO_4$) as P source were utilized for Co-B-P catalyst preparation.

Synthesis

In typical the chemical reduction method, after 50 mL of $CoCl_2.6H_2O$ and $NaHPO_4$ solution was prepared, it was cooled to about 2-4°C and $NaBH_4$ solution was slowly added drop wise with vigorous stirring. Once a black precipitate was obtained, it was washed several times with absolute ethanol to remove foreign substances from the sample. The final product was dried under N_2 at 110 °C for 8 hours to obtain Co-B-P catalyst.

The microwave treatment was applied on the Co-B-P catalyst after the synthesis process was completed. The effect of different parameters such as gas (Ar, N_2 and CO_2), microwave power (250W, 500W and 750W), treatment time (5 min, 20 min and 30 min), temperature (30° C, 40° C and 60° C), and amount of catalyst (0.0125, 0.025 0.050 and 0.075g) were investigated on the catalytic activity of Co-B-P catalyst under microwave treatment and the optimum conditions were determined.

Characterizations

X-ray diffraction (XRD) (Bruker D8 Advance x-ray diffractometer with Cu Kα source) and scanning electron microscope (SEM) (JEOL JSM 5800) were used to analyze structural and morphological properties. The porous properties of catalyst were examined using N_2 adsorption studies. The surface area is calculated from the isotherms using the Brunauere Emmette Teller (BET) technique. FT-IR spectroscopy analyses were performed using a spectrometer Perkin Elmer 283.

Results and Discussions

The effects of different gases on catalysts suspended in microwave environment may indicate variability. Therefore, the effect of gases such as Argon (Ar), Nitrogen (N_2) and CO_2 on the catalytic activity of Co-B-P catalyst under microwave treatment was investigated. As shown in Fig.1a, the hydrolysis of $NaBH_4$ was completed in about 9 min in the presence of N_2 gas whereas it was only completed in 15 minutes when other gases (Ar and CO_2) were used. Experiments were carried out in the presence of N_2 in the subsequent stages of our present study after N_2 was determined as the most efficient gas.

The effect of microwave treatment time on $NaBH_4$ hydrolysis in the presence of Co-B-P catalyst is demonstrated in Fig.1b. As you can see, the most effective treatment time was determined as 20 min. Here, microwave and normal mediums were compared. The hydrolysis reaction was completed in approximately 7 min under microwave treatment while it was completed in 14 min in pure environment.

Fig.1c indicates the effect of microwave power on the Co-B-P catalyst for $NaBH_4$ hydrolysis. It clearly appears that the reaction was completed in shorter time when the power value was used as 500 W. Therefore, it could be said that the most effective power value is 500 W. Moreover, this result gives information about how the microwave is effective to enhance the catalytic activity of Co-B-P catalyst.

The effect of amount of catalyst on $NaBH_4$ hydrolysis in the presence of catalyst was revealed in Fig. 1d. Solution of 12.5, 25.0, 50.0 and 75.0 mg of catalyst were used for this analysis. It was observed that the hydrolysis reaction occurs more rapidly as the amount of catalyst increases. The optimum amount of catalyst was found as 25.0 mg because the highest hydrogen production value was obtained when that amount was used. On the other hand, the hydrogen production rate in the presence of 0.025g of catalyst in the microwave environment is 3022 (mL*min-1*g-1), whereas this value is 1712 (mL*min-1*g-1) in normal environment (Fig.1e). It is important to note that the microwave treatment increases the catalytic activity of the Co-B-P catalyst by about 75%.

When the effect of temperature on the hydrogen production shown in Fig. 2a was examined, an increase in hydrogen production was observed as the temperature increased.

Fig. 2b shows the nth order reaction kinetic of Co-B-P catalyst at different temperatures. The most appropriate value of n was found as 0.75. The fact that the reaction order is 0.75 instead of zero or first degree shows that the catalytic reaction does not occur in one step, that is, it runs under the lower steps.

The activation energy was calculated using relation is given in Equation 1.

$$nk = lnk_0 + \frac{E_a}{RT} \quad (1)$$

Where k0 is the rate constant ($mol*min^{-1}*g^{-1}$), Ea is activation energy (kJ*mol-1), R is gas constant (8.314 $J*mol^{-1}*K^{-1}$) and T is the reaction temperature (K). The linearity was calculated as ln k = -1949,87 1/T + 1,41847 (R^2 = 0.99341) and the activation energy was calculated as 16.211 $kJ*mol^{-1}$ from the slope of the line is shown in Fig.2c.

In the BET analysis, surface area of Co-B-P catalyst under microwave environment was determined as 43.7722 m^2*g^{-1} while the surface area was obtained as 78.6673 m^2*g^{-1} for Co-B-P catalyst under normal condition.

It can be clearly seen from the Fig. 3 (a-b) that the microwave treatment improves the activity of the Co-B-P catalyst. It can be said that the effect of the microwave treatment increases the spaces between the particles in the catalyst and the result is that the micro-pores are broken up into macro-pores, which reduces the BET surface area. Although the microwave treatment reduced the surface area, an increase in hydrogen production was observed owing the treatment. Fig. 3c and 3d indicate EDX spectrums of Co-B-P catalyst in normal and microwave environment, respectively. It is seen that the compositions of the structures obtained according to Fig. 3c and 3d are slightly different from each other and this shows that the structure differences can form different compositions in some regions of the produced Co-B-P catalyst, i.e. the structure is not completely homogeneous.

Fig.4a and Fig. 4b indicate XRD patterns of Co-B-P catalyst for normal and microwave environment, respectively. It can be clearly seen that the structure of the Co-B-P catalyst becomes amorphous when the microwave treatment is applied on the Co-B-P catalyst. As shown in Fig. 4c, there is no structural change between the microwave treatment state of the Co-B-P catalyst and without the microwave treatment state, indicating that there is no change in the chemical structure with the microwave catalysis applied.

Conclusion

In our current study, the optimum parameters such as treatment time, gas and power were determined as 20 min, N_2 gas and 500 Watt, respectively. Moreover, it was observed that the hydrolysis reaction ends in 9 min under microwave treatment whereas it finishes in 17 min in normal condition. After the determinatin of the optimum parameters in microwave environment, the hdyrogen production rate was found as 3022 mL*min^{-1}*g^{-1}. The hydrolysis reactions carried out at different temperatures were also found to be in the 1st order of reaction rate. The activation energy of the Co-B-P catalyst was also determined as 16.2 kJ*mol^{-1} using Arhenius equation. The hydrogen production rate in the presence of Co-B-P catalyst based on the information given in the literature is 2120 mL*min^{-1}*g^{-1}. Based on the our results, the hydrogen production rates of Co-B-P catalyst were found as 3022 mL*min^{-1}*g^{-1}at 30 ^{o}C and 4733 mL*min^{-1}*g^{-1} at 60 ^{o}C. The most reliable and highest hydrogen capacity of borohydrides is the increasing importance of $NaBH_4$. In this study, it is appropriate to produce such high added value products in our country which has the biggest boron reserve in the world, especially in the energy sector.

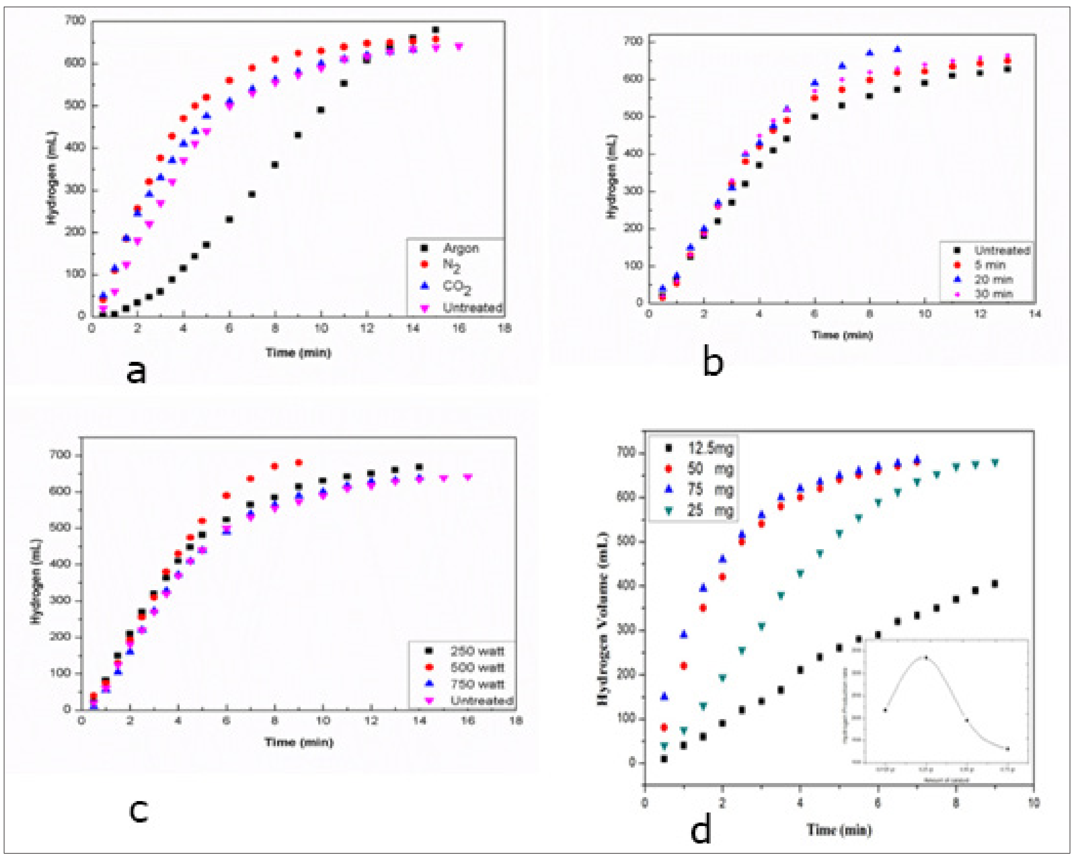

Figure 1: **(a)** Effect of different gases on hydrolysis of $NaBH_4$ in microwave environment **(b)** Effect of different microwave treatment time on hydrolysis of $NaBH_4$.**(c)** Effect of different microwave powers on hydrolysis of $NaBH_4$. **(d)** Effect of different amount of Co-B-P catalyst on hydrolysis of $NaBH_4$.

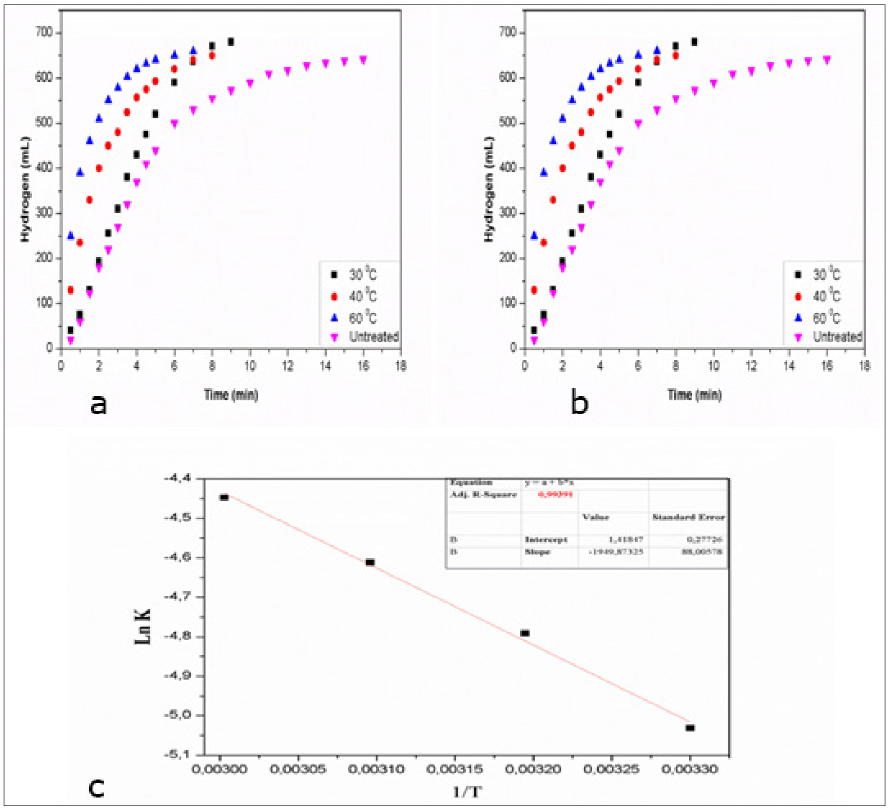

Figure 2 (a): Effect of different temperatures on hydrolysis of $NaBH_4$. **(b)** The nth order reaction kinetics of Co-B-P catalyst at different temperatures. **(c)** The first-order Arhenius equation of Co-B-P catalyst.

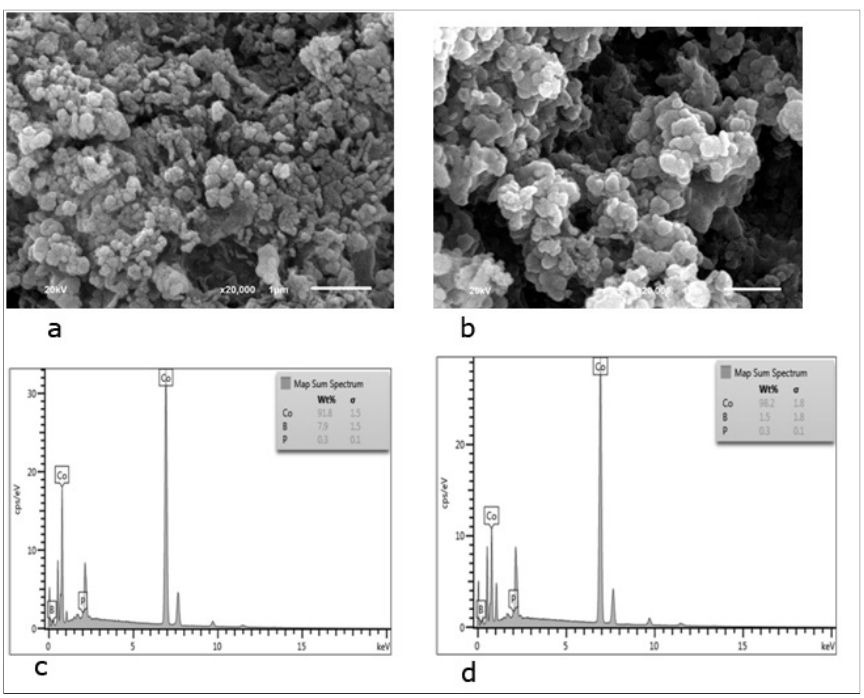

Figure 3: (a) A SEM image of Co-B-P catalyst; without microwave treatment. **(b)** A SEM image of Co-B-P catalyst; with microwave treatment. **(c)** EDX chart of Co-B-P catalyst in normal environment. **(d)** EDX chart of Co-B-P catalyst in microwave environment.

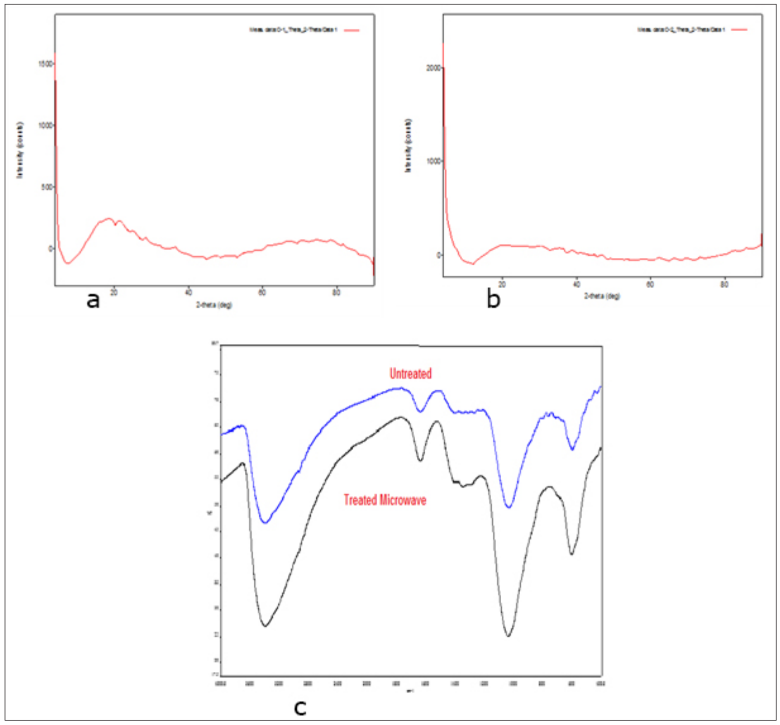

Figure 4: **(a)** XRD of Co-B-P catalyst in normal environment. **(b)** XRD of Co-B-P catalyst in microwave environment. **(c)** FTIR spectra of Co-B-P catalyst in normal and microwave environments.

References

1. Liu J, Choi HJ, Meng LY, A review of approaches for the design of high-performance metal/graphene electrocatalysts for fuel cell applications. Journal of Industrial and Engineering Chemistry.
2. Homayouni F, Roshandel R, Hamidi AA (2017) Sizing and performance analysis of standalone hybrid photovoltaic/battery/hydrogen storage technology power generation systems based on the energy hub concept. International journal of green energy 14: 121-134.
3. Schlapbach L, Züttel A (2011) Hydrogen-storage materials for mobile applications, in Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group World Scientific 265-270.
4. Fakioğlu E, Yürüm Y, Veziroğlu TN (2004) A review of hydrogen storage systems based on boron and its compounds. International journal of hydrogen energy 29: 1371-1376.
5. İzgi MS, et al. (2018) Microwave treatment and fluorine addition on Co-B catalyst to improve the hydrogen production rate. Materials and Manufacturing Processes 33: 196-201.
6. Minkina V, Kalinin V, Shabunya S (2016) Producing hydrogen from sodium borohydride using mesh nickel catalyst. Theoretical Foundations of Chemical Engineering 50: 536-541.
7. Schlesinger HI, et al. (1953) Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen1. Journal of the American Chemical Society 75: 215-219.
8. Ingersoll J, et al. (2007) Catalytic hydrolysis of sodium borohydride by a novel nickel–cobalt–boride catalyst. Journal of Power Sources 173: 450-457.
9. Fernandes R, Patel N, Miotello A (2009) Hydrogen generation by hydrolysis of alkaline $NaBH_4$ solution with Cr-promoted Co–B amorphous catalyst. Applied Catalysis B: Environmental 92: 68-74.
10. Şahin Ö, et al. (2015) The effect of microwave irradiation on a Co-b-based catalyst for hydrogen generation by hydrolysis of $NaBH_4$ solution. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 37: 462-467.
11. Yang CC, Chen MS, Chen YW (2011) Hydrogen generation by hydrolysis of sodium borohydride on CoB/SiO_2 catalyst. international journal of hydrogen energy 36: 1418-1423.
12. İzgi MS (2016) Effect of microwave irritated Co-B-Cr catalyst on the hydrolysis of sodium borohydride. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 38: 2590-2597.
13. İzgi MS, Şahin Ö, Saka C (2016) Hydrogen production from $NaBH_4$ using Co–Cu–B catalysts prepared in methanol: Effect of plasma treatment. International Journal of Hydrogen Energy 41: 1600-1608.
14. Fernandes R, Patel N, Miotello A (2009) Efficient catalytic properties of Co–Ni–P–B catalyst powders for hydrogen generation by hydrolysis of alkaline solution of $NaBH_4$. international journal of hydrogen energy 34: 2893-2900.
15. Şahin Ö, et al. (2017) The effects of plasma treatment on electrochemical activity of Co–B–P catalyst for hydrogen production by hydrolysis of $NaBH_4$. Journal of the Energy Institute 90: 466-475.
16. İZGİ MS, et al. (2016) Effect Of NaoH In Hydrogen Production From $NaBH_4$ By Using Co-BF And Co-BP Catalysts. Selçuk Üniversitesi Mühendislik, Bilim ve Teknoloji Dergisi 4: 55-64.
17. Cho KW, Kwon HS (2007) Effects of electrodeposited Co and Co–P catalysts on the hydrogen generation properties from hydrolysis of alkaline sodium borohydride solution. Catalysis Today 120: 298-304.
18. Lee JH, Hong SK, Ko WB (2010) Synthesis of cuprous oxide using sodium borohydride under microwave irradiation

and catalytic effects. Journal of Industrial and Engineering Chemistry 16: 564-566.
19. Singh S, et al. (2015) Microwave processing of materials and applications in manufacturing industries: A review. Materials and Manufacturing Processes 30: 1-29.
20. Mandal AK, Sen R (2017) An overview on microwave processing of material: A special emphasis on glass melting. Materials and Manufacturing Processes 32: 1-20.
21. Lü H, et al. (2013) Synthesis and Characterization of MgFe x Cr2-x O4 by a Microwave Method. Materials and Manufacturing Processes 28: 621-625.
21. Şahin Ö, et al. (2016) Influence of the using of methanol instead of water in the preparation of Co–B–TiO_2 catalyst for hydrogen production by $NaBH_4$ hydrolysis and plasma treatment effect on the Co–B–TiO_2 catalyst. International Journal of Hydrogen Energy 41: 2539-2546.