DOI: http://dx.doi.org/10.32571/ijct.785497 E-ISSN: 2602-277X

International Journal of Chemistry and Technology

http://dergipark.org.tr/ijct

Research Article

Effect of nano-multimetallic catalyst on hydrogen production by hydrolysis of ammonia borohydride

Erhan Onat[1], Mehmet Sait İZGİ[1,*]

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

Received: 26 August 2020; Final revised: 09 October 2020; Accepted: 10 October 2020

***Corresponding author e-mail: saitizgi@gmail.com**

Citation: Onat, E.; İzgi, M.S. *Int. J. Chem. Technol.* **2021**, 5 (1), 1-5.

ABSTRACT

This study focuses on the hydrolysis of hydrogen production parameters through the synthesized catalyst Co-Cr-B from ammonia borane using the low cost of cobalt (Co) and chromium (Cr). The synthesized Co-Cr-B catalyst was interacted with the ammonia borane solution. Later, optimum conditions for the hydrolysis of ammonia borane were determined at different catalyst amounts, NaOH concentrations, catalytic activities, and temperatures. Reaction kinetics was examined using the data obtained, and the activation energy of the reaction was determined as 22.30 $kJ.mol^{-1}$. The degree of reaction was in agreement with the 1st degree.

Keywords: Ammonia borane, Co-Cr-B, hydrogen, nanocatalyst, hydrolysis.

Nano boyutlu multi metalik katalizörünün Amonyok boran hidroliziyle hidrojen üretimine etkisi

ÖZ

Bu çalışma, düşük maliyetli kobalt (Co) ve krom (Cr) kullanılarak amonyak borandan sentezlenmiş katalizör Co-Cr B aracılığıyla hidrojen üretim parametrelerinin hidrolizine odaklanmaktadır. Sentezlenen Co-Cr-B katalizörü, amonyak boran çözeltisi ile etkileştirildi. Daha sonra amonyak boranın hidrolizi için optimum koşullar, farklı katalizör miktarlarında, NaOH konsantrasyonlarında, katalitik aktivitelerde ve sıcaklıklarda belirlendi. Reaksiyon kinetiği elde edilen veriler kullanılarak incelendi ve reaksiyonun aktivasyon enerjisi 22.30 kJ mol^{-1} olarak belirlendi. Reaksiyonun derecesi 1. derece ile uyumluydu.

Anahtar Kelimeler: Amonyum boran, Co-Cr-B, hidrojen, nanokatalizör, hidroliz.

1. INTRODUCTION

Rather than the decrease of fossil fuels over time, they spread to the environment because of using these fuels; toxic wastes such as unburned hydrocarbon, soot, odor, carbon monoxide (CO) and carbon dioxide (CO_2) with greenhouse effect disrupt the ecological balance and harm human health. Alternative clean energy sources that will overcome the environmental and environmental energy problems in the future are among the most researched topics by researchers. Hydrogen (H_2) comes to the fore as one of the most important of these energy sources researched today.[1] Systems that enable the use of hydrogen as an energy source are defined as Proton Exchange Membrane (PEM) fuel cells. In these cells, electricity is produced by taking hydrogen into the system. The basic requirement of using hydrogen as an energy source is that hydrogen is obtained from many sources. These resources can be listed as follows; electrolysis,[3] hydrolysis,[4] etc. from water by thermochemical methods from fossil sources.[5] Methods, photoelectrochemical methods from solar energy,[6] photobiological methods from green algae and plant tissue[7] and chemical methods from boron-derived compounds.[8] While considering the conditions of using hydrogen as an energy source, there is a fundamental problem of gas storage and transportation of hydrogen due to the high cost of hydrogen fuel technology. With the chemical storage of hydrogen in boron compounds, transportation and storage problems are largely eliminated.[8, 9-11] Ammonia borane is one of the boron-sourced compounds used in hydrogen storage. Besides

DOI: http://dx.doi.org/10.32571/ijct.732677 E-ISSN: 2602-277X

being capable of storing high hydrogen (16.6% by mass), ammonia boron allows hydrolysis to be separated from water by hydrolysis as well as the hydrogen it contains in its structure and enables high yield of hydrogen. The hydrogen decomposition reaction is given in Eq. (1).

$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$ (1)

The reaction rate given in Eq. (1) can be adjusted with the catalyst. This provides great advantages in the use of hydrogen as an energy carrier, eliminating the problem of transport and storage.

1.1. Catalyst in hydrogen production

Catalysts are generally defined as substances that increase the reaction rate. It is possible to summarize hydrogen production from boron-borne compounds as in Equality 1 in general. Hydrolysis reactions are generally catalyst controlled. Considering that the hydrogen requirement is obtained from the reaction and the reaction is catalyst controlled, it is understood that the catalyst is important for hydrogen production. Metals used as catalysts are usually precious metals such as Rh, Ru, Pd and P.[12-16] Although they have high hydrocatalytic activities, the cost of these metals is quite high. Recently, catalyst production is obtained from non-precious metals (such as Co, Cu, Ni, Mn) and metal alloys, whose efficiency can be increased with multimetallic systems.[17-19] In this work, we report the synthesis, characterization and application of H_2 release of multimetallic-based CoCrB catalyst. Co and Cr were selected because they are highly reactive metals in the hydrolysis of boron based metal hydrides and B was coupled with $NaBH_4$ reduction method during synthesis which showed superior catalytic performance with a high rate of maximum hydrogen production rate 6071 ml $g^{-1}min^{-1}$

2. MATERIALS AND METHODS

Within the scope of the study, the catalyst was synthesized according to the literatüre.[14,15] The chemical was weighed at the ratios determined for the synthesis process[10] and mixed in the magnetic stirrer for 30 minutes at 500 rpm and then reduced with sodium borohydride at the specified rates. The catalyst obtained after reduction was filtered by vacuum filtration and left to dry in an oven at 60ºC for 6 h under nitrogen gas. Hydrolysis reactions of ammonia borane were carried out using the catalyst observed to be completely dry. The experimental set up for H_2 generation by the hydrogenetion of ammonia borane is illustrated in Figure 1. Hydrolysis test system consists of circulating water bath, magnetic stirrer, jacketed tube, graduated burette and connecting hoses used for temperature control. The jacketed tube in the figure provides the test environment. Graded burette was used to measure the released H_2 gas.

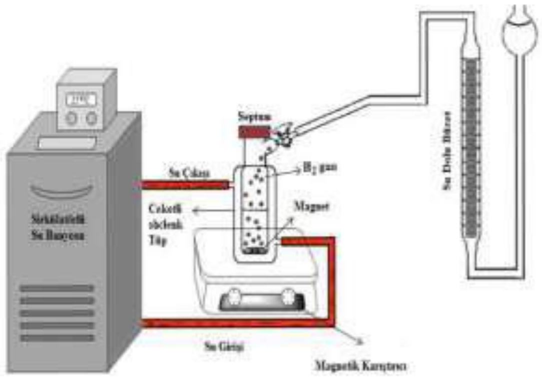

Figure 1. Hydrolysis reaction apparatus.

3. RESULTS AND DISCUSSION

3.1. NaOH Effect in solution medium

In this study, the first parameter measured for the ammonia borane catalytic reaction is the sodium hydroxide effect, which contains common ions and provides a positive effect on decomposition. The analyzed sodium hydroxide parameters are in the range of 1% and 7.5% by mass. The graph of the values showing hydrogen production of these environments were given in Figure 2. As seen in Figure 2, The most effective solution medium for hydrogen production is the environment with 5% (wt) NaOH solution.

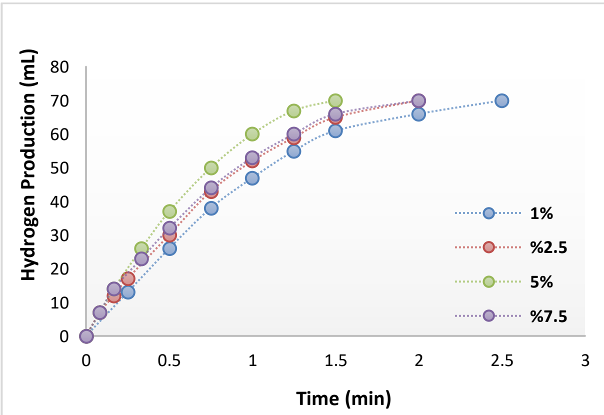

Figure 2. Effect of different NaOH concentrations on 30 º C, 25 mg Co_{96}-Cr_4-B catalyst, 1 mmole NH_3BH_3 solution

Depending on the change of NaOH concentration, that is, solution pH, it was determined that the hydrogen production rate, which was 2500 ml min^{-1} g^{-1} at 1% NaOH concentration, increased to 3478 ml min^{-1} g^{-1} at 5% NaOH concentration. In our study, we continued with 5% NaOH solution medium by mass as the solution medium in the next process.

DOI: http://dx.doi.org/10.32571/ijct.732677 E-ISSN: 2602-277X

3.2 Catalyst Amount

After determining the best NaOH (5% (wt) concentration value for the reaction medium, hydrogen production hydrolysis reactions based on catalyst amounts were carried out. The graph of the amount of hydrogen released due to catalyst amount was given in Figure 3. As seen in the graph, hydrogen production increased due to the increase of catalyst amount. This can be attributed to the increase in the amount of catalyst acting on ammonia borane.[20]

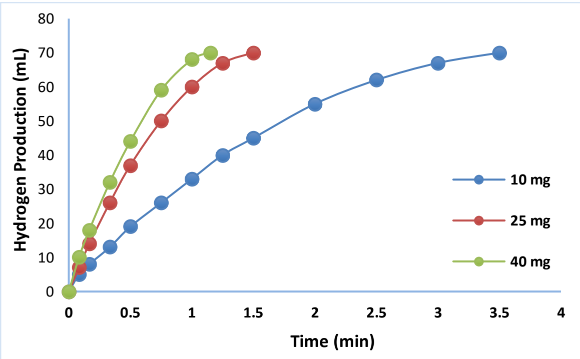

Figure 3. Hydrogen production in different catalyst amounts to 30 º C, Co_{96}-Cr_4-B catalyst, 1 mmole NH_3BH_3, 5% NaOH solution.

Considering the hydrogen production amount per catalyst, it was determined that the most effective hydrogen production rate was achieved with 10 mg of Co-Cr-B catalyst. As in the literature, subsequent experiments continued using 10 milligrams for the amount of catalyst, which is generally considered the lowest value.

3.3. Ammonia boran concentration

After determining the catalyst amount (10 mg) and NaOH 5%(wt) values of the solution, the substrate concentration having one of the most important effects on the hydrolysis reaction comes. At this stage of the study, hydrolysis reactions were performed with different NH_3BH_3 concentrations to determine the interaction between catalyst and substrate.

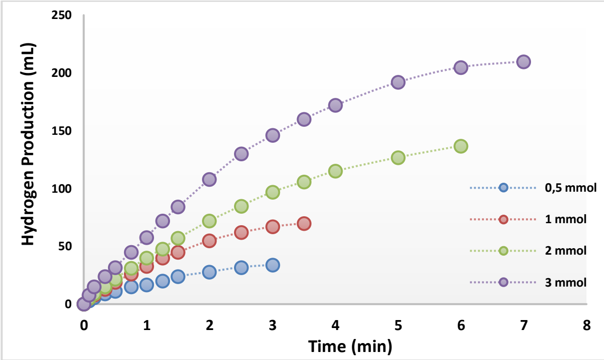

Figure 4. 30°C, 10 mg Co_{96}-Cr_4-B catalyst, hydrogen production at different concentrations of NH_3BH_3 to 5% NaOH solution.

These values are in the range of 0.5, 1, 2 and 3 mmole NH_3BH_3. Hydrogen production related to hydrolysis reactions carried out at different concentrations were given in Figure 4.

Considering the hydrogen production rate at different NH_3BH_3 concentrations, it was determined that the hydrogen production rate increased depending on the increase in concentration. The hydrogen production rate at a concentration of 3 mmole NH_3BH_3 was determined as 6071 ml g^{-1} min^{-1}

3.4. Effect of temperature

One of the most important parameters studied for catalytic reactions is the temperature effect on the reaction. In this study, the graph of the examinations of the Co-Cr-B catalyst at different temperatures for the temperature effect of NH_3BH_3 hydrolysis was given in Figure 5. As seen in Figure 5, hydrogen production increases due to temperature increase. This is attributed to the effective collision theory that it is clear that particles with increasing temperature will interact more.

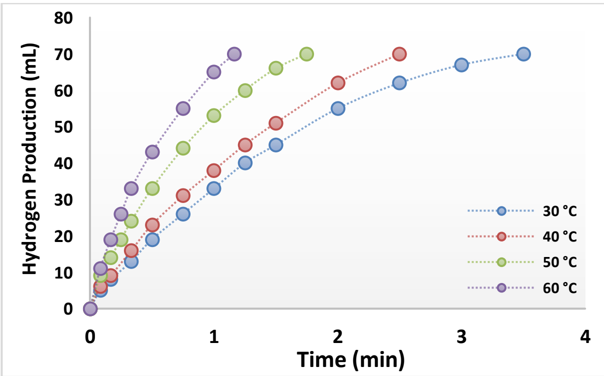

Figure 5. Hydrogen production in different concentrations of 258 NH_3BH_3 to 1 mmole NH_3BH_3, 10 mg Co_{96}-Cr_4-B catalyst, 5% (wt) NaOH solution.

3.5. Activation energy

The activation energy is one of the main parameters obtained from temperature experiments and is

DOI: http://dx.doi.org/10.32571/ijct.732677 E-ISSN: 2602-277X

determined according to the Arrhenius equation. The hydrogen production rate of ammonia borane hydrolysis catalyzed by the catalyst can be described by the Arrhenius equation (Eq. (2).

$ln\ k = ln\ A - Ea\ /\ RT$ (2)

Here, R is the universal gas constant (8.314 kJ K^{-1} mole^{-1}). *K* is the rate constant (min^{-1}). A is a constant known as the Arrhenius factor. *T* is absolute temperature (K). The values seen in Figure 5 are the data obtained from Figure 5. Based on the data obtained in Figure 5, when the 1/T graph is drawn against lnk as in Figure 6, the activation energy of the reaction (*Ea*) is 22.30 kJ mole-1 when the slope value obtained is replaced in the Arrhenius equation given in Eq. (2). Using the same values, the reaction was determined to be 1st degree.

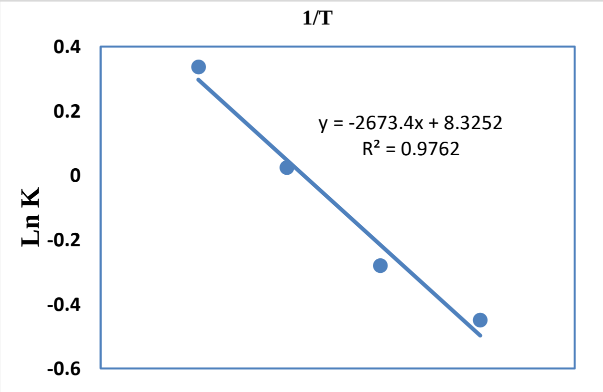

Figure 6. 1st order Arrhenius equation for the catalytic effect of Co_{96}-Cr_4-B catalyst to the NH_3BH_3 reaction

3. CONCLUSIONS

In this study, in which the catalytic effect of Co-Cr-B catalyst on ammonia borane hydrolysis was measured, the catalytic effective NaOH concentration for the solution medium was determined as the solutio medium containing 5% NaOH by mass. In addition, it was positively evaluated that an effective hydrogen production rate was achieved by using only 10 mg of catalyst. The catalytic effective value, determined as the ammonia borane concentration, was determined as 3 mmole. As a result of the parameter evaluation of this study, the most effective hydrogen production conditions were achieved at 30°C in 5% NaOH solution by using 10 mg of catalyst at 3 mmole NH_3BH_3 hydrolysis value. At these values, the hydrogen production rate was determined as 6071 ml g^{-1} min.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. İzgi, M. S.; Şahin, Ö.; Onat, E; Saka, C., Int. J. Hydrog. Energy, 2020, 45 (43), 22638-22648

2. Kazici, H. C.; Salman, F.; Izgi, M. S.; Şahin, Ö., J. Electron Mater 2020, 1-11.

3. Zeng, K.; Zhang, D. *Prog. Energy Combust. Sci.* **2010**, 36 (3), 307-326.

4. Kazici, H. C.; Yilmaz, S.; Sahan, T.; Yildiz, F.; Er, O. F.; Kivrak, H. *Front. Energy Res.* **2020**, 14(3) 578-589.

5. Balat, M., A global perspective. *Energ. Source. Part B:* **2007**, 2 (1), 31-47.

6. Horoz, S.; Dai, Q.; Maloney, F.; Yakami, B.; Pikal, J.; Zhang, X.; Wang, J.; Wang, W.; Tang, J. *Phys. Rev. Appl.* **2015**, 3 (2), 11-24.

7. Gamborg, O. I.; Murashige, T.; Thorpe, T. A; Vasil, I. K. *In vitro* **1976,** 12 (7), 473-478.

8. İzgi, M. S.; Şahin, Ö.; Ödemiş Ö; Saka, C. Mater. Manuf. Processes 2018, 33 (2), 196-201.

9. Şahin, Ö.; İzgi, M. S.; Onat, E.; Saka, C. *Int. J. Hydrog. Energy*, **2016**, 41 (4), 2539-2546.

10. Fernandes, R.; Patel, N.; Miotello, A. *Appl. Catal. B: Env.* **2009**, 92 (1-2), 68-74.

11. Ding, X. L.; Yuan, X.; Jia, C.; Ma, Z. F. *Int. J. Hydrog. Energy* **2010**, 35 (20), 11077-11084.

12. Huynh, K.; Napolitano, K.; Wang, R.; Jessop, P. G.; Davis, B. R. *Int. J. Hydrog. Energy* **2013**, 38 (14), 5775-5782.

13. Su, C. C.; Lu, M. C.; Wang, S. L.; Huang, Y.H. *RSC Adv.* **2012**, 2 (5), 2073-2079.

14. İzgi, M. S.; Şahin, Ö.; Saka, C. *Int. J. Hydrog. Energy* **2016**, 41 (3), 1600-1608.

15. İzgi, M. S. *Energ. Source. Part A* **2016,** 38 (17), 2590-2597.

16. İzgi, M. S.; Şahin, Ö.; Saka, C. *Mater. Manuf. Processes* **2019**, 34 (14), 1620-1626.

17. Jeong, S.; Kim, R.; Cho, E.; Kim, H. J.; Nam, S.-W.; Oh, I. H.; Hong, S. A.; Kim, S. H. J. *Power Sour.* **2005**, 144 (1), 129-134.

18. Salinas-Torres, D.; Navlani-García, M.; Kuwahara, Y.; Mori, K.; Yamashita, H. *Catal. Today* **2019,** (324),90-96.

DOI: http://dx.doi.org/10.32571/ijct.732677 **E-ISSN: 2602-277X**

19. Jia, H.; Chen, X.; Song, X.; Zheng, X.; Guan, X.; Liu, P. *Int. J. Energ. Res.* **2019**, 43 (1), 535-543.

20. Li, Y.; Li, S. *Int. J. Hydrog. Energy* **2020**, 45 (17), 10433-10441.