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https://doi.org/10.5109/4794167

出版情報：Evergreen. 9 (2), pp.421-426, 2022-06. 九州大学グリーンテクノロジー研究教育センター
バージョン：

The Release of Hydrogen from $NaBH_4$ with Ni-Cu-B/Hydroxyapatite as The Catalyst

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(Received December 7, 2021; Revised June 1, 2022; accepted June 1, 2022).

Abstract: The environmentally friendly combustion of hydrogen makes hydrogen an ideal fuel. Research on the ideal hydrogen storage is still being carried out. one candidate for hydrogen storage is $NaBH_4$. $NaBH_4$ is hydrolyzed to release hydrogen. This work concerns the hydrolysis reaction of $NaBH_4$ to release hydrogen with a catalyst Ni-Cu-B deposited on hydroxyapatite. The research went through 2 stages, namely catalyst synthesis and $NaBH_4$ hydrolysis reaction. The catalyst synthesis was carried out electrochemically using a 2-compartment electrochemical cell at the certain current density and reaction time. The hydrolysis reaction was observed in a batch reactor at a constant temperature. The results showed that the most significant hydrogen release at room temperature occurred with a catalyst made at 160 mA/cm^2 for 90 minutes. The hydrogen release rate ranged from 435 to 1600 mL H_2/g catalyst/min. The resulting equation for the reaction rate constant as a function of temperature is $k = 3.567 \times 10^{10} \exp(8624.245/T)$.

Keywords: $NaBH_4$, Hydroxyapatite, Catalyst, Hydrolysis, Hydrogen

1. Introduction

Substitution of fossil fuels with more environmentally friendly fuels continues to be pursued[1,2)]. Hydrogen fuel is a potential candidate as a substitute for fossil fuels. Various studies have been carried out to make hydrogen an ideal fuel in the future[3)]. One of the challenges of using hydrogen fuel is hydrogen storage[4,5,6)]. One of the promising hydrogen storage is sodium borohydride ($NaBH_4$)[7,8,9,10)]. The important thing in the storage of hydrogen as $NaBH_4$ is the release of hydrogen from $NaBH_4$[11)]. A hydrogen release catalyst from $NaBH_4$ has been developed[12,13,14,15)].

The catalyst synthesis carried out in this study was carried out electrochemically. Electrosynthesis with bipolar membranes has been successfully developed[17,18,19)]. The production of Ni-B in hydroxyapatite (Ni-B/HA) and Cu-B in hydroxyapatite (Cu-B/HA) catalysts has also been carried out[20, 21)]. The rate of hydrogen release is 230 to 860 mL/g/min for the Ni-B in hydroxyapatite catalyst. With Cu-B in hydroxyapatite catalyst, the hydrogen release rate was 240 mL/g/minute to 924.44 mL/g/minute. This rate of hydrogen released is approximately equal to the rate of hydrogen released with a Ni catalyst, 600 mL/g/min[15)]. The release of hydrogen is slower with the Co catalyst[22)]. Some catalysts are more complex and produce hydrogen more rapidly[12,13,14,23)].

In this paper, the development of transition metal-based catalysts supported by hydroxyapatite catalysts is developed by combining Ni, Cu, and B catalysts. Ni and Cu catalysts were chosen based on their relatively low prices compared to other transition metals. As a sole catalyst, Ni is also quite effective as a catalyst for the reaction of hydrogen release from $NaBH_4$. There is no research on the use of Cu as a catalyst for this reaction. The novelty of this paper is the synthesis of Ni-Cu-B catalyst with hydroxyapatite as catalyst support by in situ electrolysis method and see its effect on the hydrogen release reaction from $NaBH_4$. In this study, efforts to increase the effectiveness of the hydrogen release catalyst were carried out by determining the catalyst production conditions. The objective of this study was to determine the effect of catalyst synthesis conditions (the electrolysis time and the current density) of Ni-Cu-B in hydroxyapatite on the release of hydrogen.

2. Experimental

The arrangement of the experimental apparatus for synthesis of catalyst is shown in Fig. 1. The electrochemical cell made of an acrylic container containing 250 ml of electolyte solution. The composition of the electrolyte solution is 0.1M $NiCl_2$, 0.1M $CuCl_2$, 0.1M $NaBH_4$, 0.25M $CaCl_2$, 0,15M KH_2PO_4, and 0.25M $Na_2H_2EDTA.2H_2O$. All reagents were purchased from Merck as analytical grade reagents and used without further purification. The anode and cathode electrodes (from graphite) were carbon 5 x 2 x 0.4 cm. The bipolar membrane is from Fumatech BWT GmbH. The electrodes were connected to a power supply. The current density used was 40, 80, 160, and 240 mA/cm^2. Electrolysis of catalyst formation was carried out at 60, 90, and 120 minutes. These two parameters were varied to evaluate their effect on the reaction of $NaBH_4$ to release hydrogen. This solution was electrolyzed by flowing D.C. according to a predetermined variable. Furthermore, the resulting deposit was aged at 40ºC in an oven, separated between the solution and the deposit using filter paper, washed with water, then dried at 40ºC. The XRD analyzed the resulting particles. An analogous synthesis method was carried out for the synthesis of Ni-B/HA and Cu-B/HA with suitable electrolytic solutions.

Ni-Cu-B/HA, Ni-B/HA, and Cu-B/HA catalyst were tested on the reaction of $NaBH_4$ on the release of hydrogen at various temperatures. The hydrolysis reaction was observed in a batch reactor. The $NaBH_4$ solution was reacted with water at various conditions of specific temperatures and a particular type of catalyst. The hydrogen gas formed was flowed in a closed tube filled with water. The water was pushed to the next Erlenmeyer to be weighed and be measured (Fig. 2).

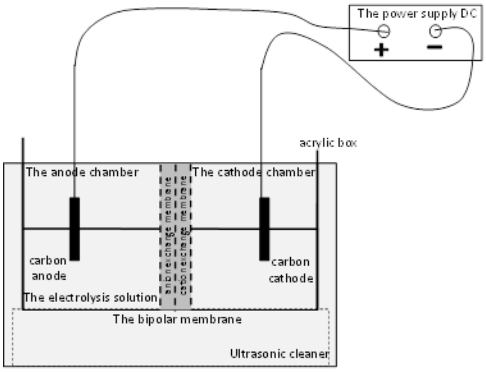

Fig. 1: The electrochemical catalyst synthesis equipment

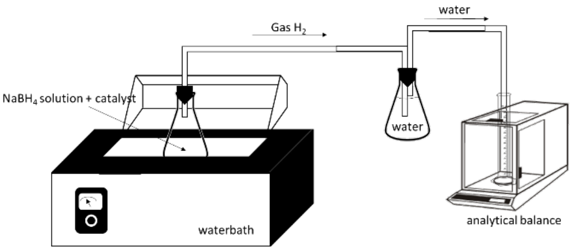

Fig. 2: The equipment for hydrogen release

3. Result and Discussion

The increase in the pH in the cathode compartment and the decrease in the pH in the anode compartment occur rapidly at higher current densities. The low pH of the solution cannot form hydroxyapatite$^{24)}$. Hydroxyapatite is formed at a pH of at least 7, although it still depends on the electrolysis time. During the electrolysis process, the solution in the cathode compartment showed an increase in pH, while the solution in the anode compartment showed a decrease in pH. The increase in pH in the cathode compartment is due to the reduction reaction of water during electrolysis which releases OH^- ions. The decrease in pH in the anode compartment is caused by water's oxidation reaction, which releases H^+. The presence of a bipolar membrane prevents OH^- ions and H^+ ions from moving to different compartments$^{16)}$.

The increase in the pH at the cathode compartment and the decrease in the pH at the anode compartment occur rapidly at higher current densities. The faster the current density, the faster the reduction reaction in the cathode compartment and the oxidation reaction in the anode compartment. The faster the formation of OH^- ions in the cathode compartment is characterized by the faster pH. The faster the formation of H^+ ions in the anode compartment, the faster the pH will decrease.

At 240 and 160 mA/cm^2, the solution pH was 10 at 60 minutes of electrolysis time. At 80 mA/cm^2, the solution pH was 8 at 90 minutes of electrolysis time. Hydroxyapatite begins to form at pH 8. At a current density of 40 mA/cm^2, no particles were created due to the low pH of the solution for 120 minutes of electrolysis.

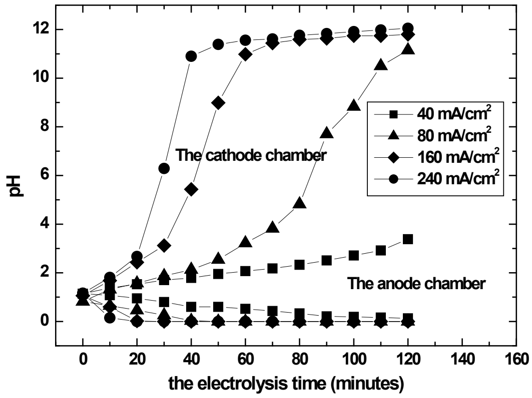

Fig. 3: The pH of the electrolyte solution during electrolysis.

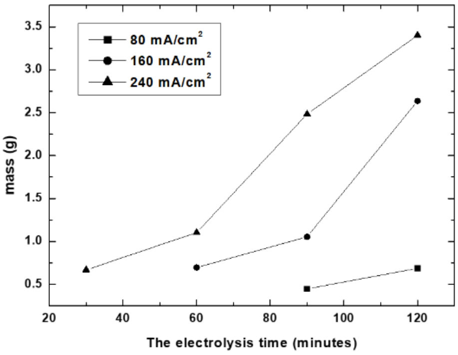

Fig. 4: The mass of particles formed at a certain current density.

Fig. 4 shows the mass of particles formed during electrolysis at various current densities. At a current density of 40 mA/cm^2, no particles were formed after 120 min. At a current density of 80 mA/cm^2, the particles formed were few and formed after 90 minutes. Particles formed at 60 minutes of electrolysis time (160 mA/cm^2) and 30 minutes of electrolysis time (240 mA/cm^2). The particles formed are getting bigger with increasing electrolysis time and current density.

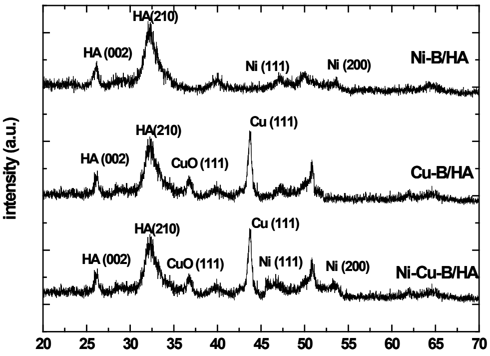

Fig. 5: The XRD analysis results of particles at 120 mA/cm^2 and 60 min electrolysis time

Fig. 5 shows the resulting particle diffraction pattern with a current density of 160 mA/cm^2 and an electrolysis time of 90 minutes. Peaks indicate the presence of Ni in the formed particles at 46° (111) and 52° (200)$^{25)}$. Peaks at 43° (111) and 50° (200) indicate the presence of Cu$^{26)}$. The hydroxyapatite particles were characterized by the presence of a peak at 26° (002). Particle B is characterized by peaks at 28° and 36° overlap with the peaks of the other particles.

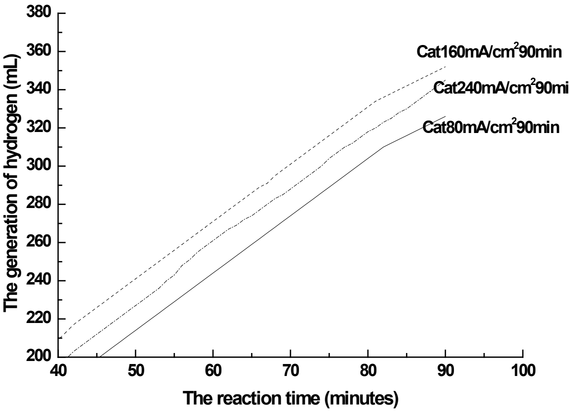

Fig. 6: The XRD analysis results of particles at 120 mA/cm^2 and 60 min electrolysis time

The hydrogen released during the hydrolysis reaction with a catalyst prepared at various current densities is shown in Fig. 6. Catalysts prepared at a current density of 160 mA/cm^2 and 90 minutes showed the best results, although the difference with a current density of 80 and 240 mA/cm^2 was not significant. At the accurate current density, the formation of Ni-Cu-B catalyst with hydroxyapatite as catalyst support becomes effective as catalyst for the hydrogen release reaction$^{11,13)}$. If the current density is too high, the hydroxyapatite formation reaction is too fast and forms large particles so that the catalyst is not properly protected and causes the catalyst to be contaminated by hydrogen that is formed^{15}. If the current density is too low, the hydroxyapatite formation reaction is too slow so that it cannot protect the catalyst completely and causes the catalyst to be lost and contaminated by hydrogen.

The hydrogen released on the catalyst is prepared at the variation of the reaction time is shown in Fig. 7. It can be seen that the catalyst prepared at 160 mA/cm^2 for 120 minutes showed the best release rate. Under these catalyst-forming conditions, the catalyst is well deposited on the catalyst support but can react completely to accelerate the hydrogen release reaction.

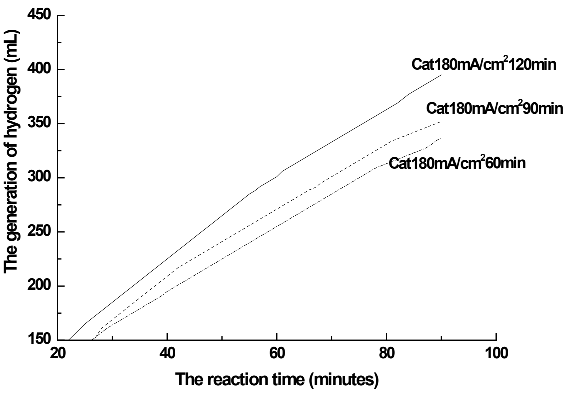

Fig. 7: The release of hydrogen on various catalysts prepared at various electrolysis times.

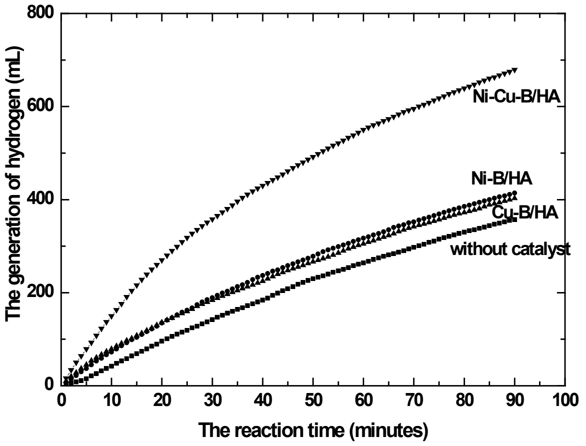

Fig. 8: The release of hydrogen on various types of catalysts.

Fig. 8 shows the comparison of hydrogen released on Ni-Cu-B/HA, Ni-B/HA, Cu-B/HA, and without catalysts with the same amount of catalyst. The results showed that Ni-Cu-B/HA increased the amount of hydrogen released significantly compared to Ni-B/HA and Cu-B/HA. The presence of a bimetal catalyst causes an excellent interaction to accelerate the hydrolysis reaction of $NaBH_4$.

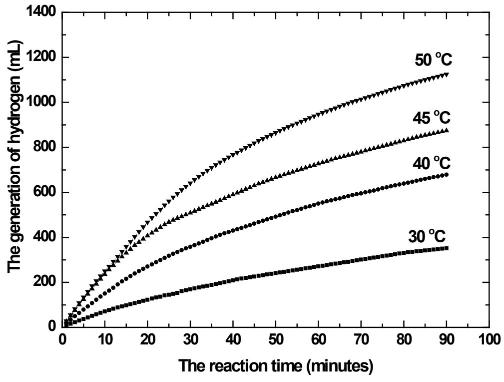

Fig. 9: The release of hydrogen on the various reaction temperature

Ni-Cu-B/HA catalyst was tested in the hydrolysis reaction at various reaction temperatures. The release of hydrogen at various temperatures is shown in Fig. 9. The release of hydrogen at high temperatures is faster than at low temperatures. An increase in temperature accelerates the reaction rate because an increase in temperature causes the particle to move faster, making it easier for the reaction to occur[10)]. At the beginning of the reaction, the hydrogen release rate ranged from 435 to 1600 mL H_2/g catalyst/min.

The remaining $NaBH_4$ was tested with an equation of the zero-order reaction model and the first-order reaction model. The concentration of the remaining $NaBH_4$ was obtained from the stoichiometric equation of the reaction using the hydrogen formed. The assumption of the zero-order reaction is shown in Fig. 10, and the first-order reaction is shown in Fig. 11. The coefficient of determination of the two equations shows that the reaction is more suitable using the first-order reaction equation.

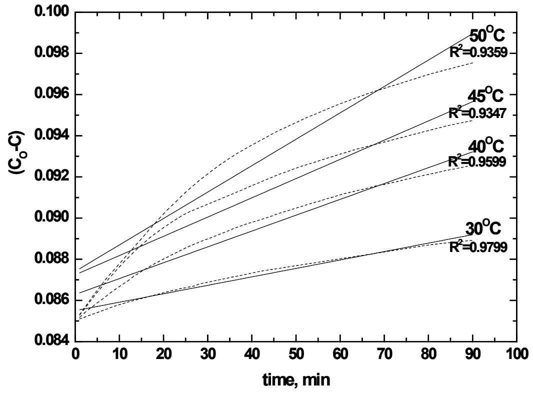

Fig. 10: The zero-order reaction model

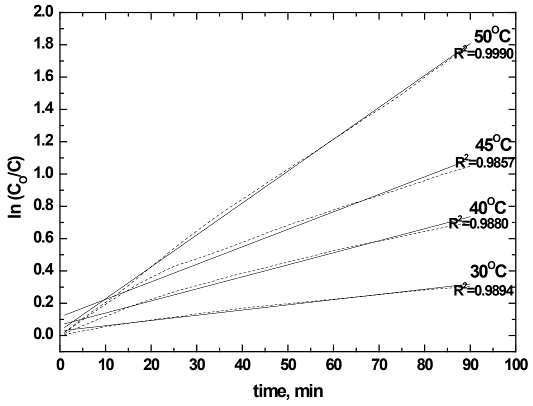

Fig. 11: The first-order reaction model.

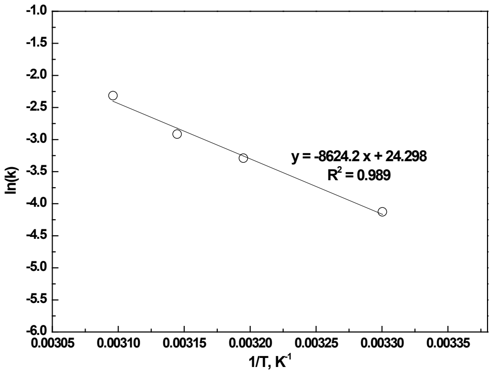

Fig. 12: The first-order reaction of $NaBH_4$.

The constant reaction rate for the first-order reaction was calculated at various temperatures[12)]. The linear regression equation to determine the Arrhenius equation is shown in Fig. 12. The resulting equation for the constant of reaction rate as a function of temperature is $k = 3.567 x 10^{10} \exp(8624.245/T)$.

4. Conclusion

During the electrolysis process, the solution in the cathode compartment showed an increase in pH, while the solution in the anode compartment showed a decrease in pH. The higher current density causes an accelerated increase in pH in the cathode compartment and accelerates the decrease in the anode compartment. The pH of the solution affects the amount of precipitate formed. The higher the pH, the greater the mass formed. The most significant hydrogen release at room temperature occurred with a catalyst prepared at 160 mA/cm^2 for 90 minutes. The hydrolysis reaction of $NaBH_4$ with Ni-Cu-B/HA catalyst follows the first-order reaction equation. The hydrogen release rate at the beginning of the reaction ranges from 435 to 1600 mL H_2/g catalyst/min. The resulting equation for the constant of the reaction rate is k = 3.567x10^{10} exp(8624.245/T).

Acknowledgements

We are extremely grateful to DIRJEN DIKTI (the Directorate General of Higher Education (DGHE)) and Universitas Sebelas Maret for research funding.

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