Electrosynthesis of Cu/hydroxyapatite as the catalyst for hydrogen production via NaBH₄ hydrolysis

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Abstract. Synthesis of Cu/hydroxyapatite by electrochemical was studied. These particles used as the catalyst for hydrogen production via NaBH₄ hydrolysis. The work aimed to study how the current density and the electrolysis time during catalyst synthesis affect the generation of hydrogen via the hydrolysis kinetics of NaBH₄. Catalyst synthesis was carried out in an electrochemical cell separated by the membrane bipolar. Electrolysis was carried out at various current densities (67, 133 and 200 mA/cm²) and various electrolysis times (30, 60, and 90 minutes). This research shows that at high current density and electrolysis time, the peak intensity of the XRD Cu and CuO patterns was low and the peak intensity of the hydroxyapatite pattern was high. Hydrogen production by hydrolysis of NaBH₄ is better for catalysts that are synthesized at high current density and electrolysis time.

1. Introduction

Hydrogen as an environmentally friendly and sustainable fuel has been used in various fields such as transportation, industry and power generation. The challenge that must be overcome immediately is the problem of hydrogen storage [1, 2]. The most recognized hydrogen storage system is metal hydride. The use of metal hydrides as hydrogen storage still has problems, namely the inability to store large amounts of hydrogen and the slow release of hydrogen at low temperatures [3]. Sodium borohydride (NaBH₄) is one of the candidates for hydrogen storage [4, 5]. In this work, the generation of hydrogen from the NaBH₄ hydrolysis was catalyzed by a Cu catalyst. Cu catalyst was synthesized simultaneously with hydroxyapatite formation using electrochemical methods. The formation of metal-hydroxyapatite catalysts has been largely carried out electrochemically [6, 7]. The electrolysis reaction was carried out on an electrochemical cell separated by a bipolar membrane [8, 9]. The work aimed to study how the current density and the electrolysis time during catalyst synthesis affect the generation of hydrogen via the hydrolysis kinetics of NaBH₄.

2. Experimental
Catalyst synthesis was carried out in an electrochemical cell consisting of a carbon cathode, a carbon anode, a DC power supply, an acrylic box (3 x 10 x 10 cm) and a bipolar membrane. Catalyst synthesis is carried out in an electrochemical cell consisting of a carbon cathode (5 x 2.5 cm), a carbon anode (5 x 2.5 cm), a DC power supply, an acrylic box (3 x 10 x 10 cm) and a bipolar membrane (Fumatech BWT GmbH). The cathode and anode spacing is set 3 cm with a bipolar membrane placed between them. Cation exchange membrane is installed facing the carbon cathode while the anion exchange membrane is installed facing carbon anode. The electrochemical cell was placed in an ultrasonic cleaner. The set of equipment was shown in Figure 1. The 250 mL electrolyte solution consisted of 0.25 M CaCl$_2$, 0.25 M Na$_2$H$_2$EDTA, 0.15 M KH$_2$PO$_4$ and 0.1 M CuCl$_2$. Electrolysis was carried out at various current densities (67, 133 and 200 mA/cm$^2$) and various electrolysis times (30, 60, and 90 minutes). During electrolysis, the pH of the solution in the anode and cathode chambers is measured by a portable pH meter (Ohaus ST300). The resulting particles were filtered, washed and dried overnight. The XRD patterns of the particles were obtained from the mini X-Ray diffractometer (EQ-MD-10-LD MTI Corp). The particles were tested as a hydrogen generation catalyst for the hydrolysis of NaBH$_4$. The catalyst (0.5 g) was added to 150 mL 0.1 M NaBH$_4$. The gas produced was recorded at every time interval. The set of equipment for the catalyst performance test was shown in Figure 2.

![Figure 1. The set equipment for the synthesis of catalyst.](image1)

![Figure 2. The set of equipment for the catalyst performance test.](image2)
3. Result and Discussion

The pH of the solution in the anode chamber and cathode chamber during electrolysis is shown in Figure 3. The pH of the solution in the cathode chamber increases while the pH of the solution in the anode chamber decreases with increasing electrolysis time. The increase in pH of the solution in the cathode chamber is due to the release of OH\(^{-}\) ions as the result of reducing water around the carbon cathode, while the decrease in the pH of the solution in the anode chamber is due to the release of H\(^{+}\) ions as the result of water oxidation around the carbon anode. The reduction of Cu\(^{2+}\) ions occurs in the cathode chamber. The bipolar membrane prevents OH\(^{-}\) ions in the cathode chamber to the anode chamber and H\(^{+}\) ions in the anode to the cathode chamber. The oxidation of Cu\(^{2+}\) ions occurs in the anode chamber.

In the cathode chamber, the higher the current density the faster the pH of the solution increases. The increase in current density causes the release of OH\(^{-}\) faster so that the pH of the solution rises more rapidly. In the anode chamber, the higher the current density the faster the pH of the solution decreases. The decrease in current density causes the release of OH\(^{-}\) faster so that the pH of the solution downs more rapidly.

![Figure 3. pH of the solution in the anode and cathode chambers during electrolysis.](image)

The XRD patterns of the resulting particles at various current densities are shown in Figure 4. The XRD pattern shows that the particles formed contain Cu, CuO and hydroxyapatite. The presence of Cu is indicated by peaks around 43° (111) and 50° (200). The presence of CuO is indicated by the presence of peaks around 32° (110), 36° (111) and 61° (113). The peaks around 26° indicate the presence of hydroxyapatite. The greater the current density the lower the peak intensity of Cu and CuO and the greater the peaks of the hydroxyapatite. Hydroxyapatite is formed faster at large current densities.
Figure 4. XRD patterns at various current densities at 60 minutes electrolysis.

Figure 5. XRD patterns at various time electrolysis at 133 mA/cm$^2$.

Figure 5 shows the XRD patterns of the particles at various electrolysis times. At the electrolysis time of 30 minutes, the XRD pattern showed the presence of Cu and CuO with very high intensity. The intensity of peaks decreases with increasing electrolysis time. The peak intensity of hydroxyapatite increases with increasing electrolysis time.
Figure 6. Hydrogen generated on the catalyst which was synthesized with a variety of current density.

The catalyst that was synthesized at various current densities was tested to generate hydrogen via the hydrolysis of NaBH₄. The test results are shown in Figure 6. Hydrogen is produced mostly with a catalyst that is synthesized at a current density of 200 mA/cm². The XRD pattern of the synthesized catalyst at a current density of 200 mA/cm² (Figure 4) shows that the intensity of Cu and CuO particles is not high but the intensity of the hydroxyapatite particles is high.

Figure 7. Hydrogen generated on the catalyst which was synthesized with a variation of time electrolysis.
The hydrogen generated on the catalyst synthesized at various electrolysis time is shown in Figure 7. The XRD pattern for the synthesized catalyst at the current density of 133 mA/cm² and the electrolysis time of 90 minutes (Figure 5) shows that the correct composition of Cu, CuO, and hydroxyapatite particles is needed.

4. Conclusion

Current density and electrolysis time in the synthesis of Cu / Hydroxyapatite catalyst affect the performance of the catalyst to generate hydrogen by hydrolysis of NaBH₄. The peak intensity of the XRD patterns of Cu and CuO was high at the low current density and electrolysis time. This condition does not support the catalyst to produce hydrogen. At high current density and electrolysis time, the peak intensity of the XRD Cu and CuO patterns was low and the peak intensity of the hydroxyapatite pattern was high. Hydrogen production by hydrolysis of NaBH₄ is better for catalysts that are synthesized at high current density and electrolysis time.

5. References

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