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HYDROXYAPATITE-SUPPORTED TRI-METALLIC CATALYST FOR HYDROGEN PRODUCTION FROM STEAM REFORMING OF GLYCEROL

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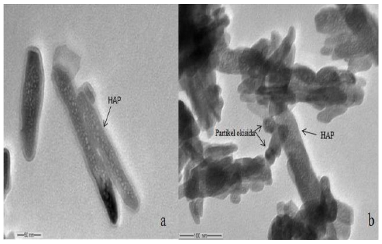
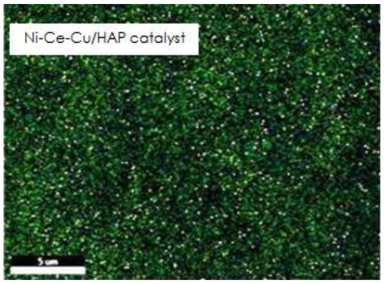
Graphical abstract





Abstract

Glycerol is a byproduct of biodiesel industry that has high economic value to produce hydrogen as an energy source. The selection of catalyst support for active metal catalyst in hydrogen production is a major concern since it affects the activity of metal catalyst during the steam reforming process of glycerol. Besides that, bio-based material as catalyst support provides attractive choice as it is more environmentally friendly. In this study, hydroxyapatite (HAP) as support material for tri-metallic catalyst Ni-Ce-Cu was prepared using deposition-precipitation method and used in steam reforming reaction of glycerol to produce hydrogen. The catalyst prepared was characterized by BET, FE-SEM, EDX, and TEM. The catalytic activity tests were conducted at atmospheric pressure and temperatures between 400 – 600 °C in a tubular micro-reactor. Glycerol-water ratios used were 1:4, 1:8, and 1:16. It was found that the highest hydrogen yield (55.0%) was obtained at temperature of 600 °C and glycerol-water ratio of 1: 8 with glycerol conversion of 94.0%.

Keywords: Catalyst support, H_2 production, hydroxyapatite

Abstrak

Gliserol merupakan produk sampingan dari industri biodiesel yang mempunyai nilai ekonomi yang tinggi untuk menghasilkan hidrogen sebagai sumber tenaga. Pemilihan penyokong mangkin sebagai pencantum logam aktif untuk penghasilan hidrogen menjadi perhatian utama dalam mengurangkan kelemahan logam aktif semasa proses pembentukan semula stim gliserol. Selain itu, bahan berasaskan bio sebagai penyokong mangkin ialah pilihan yang menarik kerana ianya lebih mesra alam. Dalam kajian ini, hidroksiapatit (HAP) sebagai bahan sokongan untuk logam pemangkin Ni-Ce-Cu telah disediakan menggunakan kaedah mendakan-endapan dan digunakan dalam tindakbalas pembentukan semula stim-gliserol untuk menghasilkan hidrogen. Pemangkin yang telah disediakan dicirikan menggunakan BET, FE-SEM, EDX, dan TEM. Ujian aktiviti pemangkinan telah dijalankan pada tekanan atmosfera dan suhu antara 400 – 600 °C dalam tiub mikro-reaktor. Nisbah gliserol-air yang digunakan ialah 1:4, 1:8, dan 1:16. Hasil ujikaji mendapati bahawa hasil hidrogen yang paling tinggi (55.0%) diperolehi pada suhu 600 °C dan nisbah gliserol-air 1: 8 dengan penukaran gliserol ialah 94.0%.

Kata kunci: Penyokong pemangkin, pengeluaran H_2, hidroksiapatit

1.0 INTRODUCTION

Hydrogen is an environmentally friendly fuel and has been widely used in fuel cell applications. Fuel cells can generate energy for transportation purposes. Investigation on hydrogen production as fuel substitute is still subject of interest in order to find energy sources that are more efficient and cost-effective as alternative fuel source in the future.

The abundant availability of glycerol from the byproduct of biodiesel industry causes the low price of glycerol in the market. Furthermore, the use of glycerol in industry is still limited to food and pharmaceutical industries. Low price and abundant availability of glycerol become major factors for converting glycerol into a high-value material such as fuel which may increase the selling price of glycerol in the market.

Many studies have been conducted on the process of converting glycerol to hydrogen such as steam reforming, partial oxidation and auto-thermal reforming. The most widely method for the production of hydrogen is catalytic steam reforming method since it is more cost-effective, efficient and produce product at high concentration [1]. Production of hydrogen from glycerol by this method can produce hydrogen gas higher than other sources such as methanol and ethanol whereby one mole of glycerol can produce seven moles of hydrogen. In addition, glycerol is not toxic and not volatile, therefore, its use for hydrogen production does not cause environmental problems.

The use of catalyst in the hydrogen production reaction from glycerol is essential to produce optimum product. In the preparation of catalyst, the most widely used component is catalyst support to support the active component so that it is more evenly dispersed and to prevent the inclusion between the active components, hence, better reaction will occur [2]. In general, the content of catalyst support exceeds 50% of the total catalyst and is usually use metal oxides which are very expensive and not environmentally friendly.

Currently, heterogeneous catalyst is often used in steam reforming method to produce hydrogen in order to produce more optimum hydrogen yield. The selection of active metal catalyst and catalyst support for producing hydrogen is the main problem faced by researchers. It becomes the major concern in reducing the activity of metal catalyst during steam reforming of glycerol [3]. Until now, research on catalyst support from bio-based materials is still rare. Catalyst support is an important component in the catalytic production of hydrogen. The selection of catalyst support material to support the active metal catalyst must meet the environmental criteria to produce an environmentally friendly fuel. The present use of metal oxide support for steam reforming process of glycerol is not yet fulfilled the environmental criteria. Therefore, the use of bio-based materials which are environmentally friendly is necessary. The most widely used catalyst support is metal oxide such as MgO, TiO, ZnO, ZrO, Al_2O_3 and others. Every metal oxide compounds are toxic and not inert. In addition, the side effects of these materials contribute to the pollution of water, soil and environment. This is inconsistent with the goal of producing clean energy to ensure the preservation of life and its surrounding nature. Hence, the selection of environmentally friendly materials as catalyst support material is necessary to achieve the goal of generating clean energy through chemical processes.

In this study, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), a non-toxic, bio-compatible and eco-friendly material was used as catalyst support for the production of hydrogen from steam reforming of glycerol.

2.0 METHODOLOGY

The experimental procedures for catalyst preparation and steam reforming of glycerol were following the procedures described elsewhere [4].

2.1 Catalyst Preparation

HAP-supported catalyst with Ni–Ce–Cu loading of 3 mass %–7.5 mass %–7.5 mass %/HAP was prepared by deposition–precipitation method. The precursors for Ni, Ce and Cu were $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 6H_2O$, respectively. All chemicals were purchased from Sigma–Aldrich. 15 g of HAP was dispersed in de-ionised water and heated to 70 °C under vigorous stirring. All the precursors were dissolved in de-ionised water at corresponding concentrations. Nickel, cerium, and copper solutions were added drop-wise to the HAP suspension at ambient temperature under vigorous stirring for 3 h and the suspension was precipitated by carefully adding an NH_4OH solution dropwise until the pH reached 8.5. The solid obtained was then filtered and washed with hot distilled water three times to remove excess ions. The resulting product was dried at 120 °C overnight and calcined at 500 °C for 5 h under atmospheric condition.

2.2 Catalyst Characterization

Surface area of the catalyst was measured using Altamira Instrument (AMI 200, Pittsburgh, PA, USA). The sample weighing 0.5 g was previously de-gassed at 120 °C for 1 h. N_2 adsorption–desorption isotherm was obtained at –196 °C and specific surface area was calculated from the isotherm using Brunauer–Emmett–Teller (BET) method. The size and dispersion of the catalyst was analyzed by transmission electron microscopy (TEM) using PHILIPS CM12 microscope (Eindhoven, The Netherlands). Field-emission scanning electron microscopic (FE-SEM) image for the catalyst was also obtained using SUPRA 55VP instrument (Carl Zeiss, Oberkochen, Germany).

2.3 Catalyst Activity Test

Experiments for catalyst activity tests were conducted in a tubular fixed-bed micro-reactor. The tubular reactor was made of stainless steel (length: 390 mm, inner diameter: 6.35 mm, wall thickness: 0.9 mm) and the reactor was placed in an electric furnace equipped with K-type thermocouples located inside the reactor at the position of the catalyst bed.

To perform the catalytic activity test, 0.5 g of the catalyst powder was placed in the middle of micro-reactor tube and affixed with quartz wool. Prior to activation, each catalyst was heated at 120 °C for 30 min. The catalyst was activated in situ by reducing it in N_2 flow at 70 mL min⁻¹ with 10 vol.% H_2 at 300 °C for 1 h. The steam reforming experiment was carried out at temperatures of 400, 500 and 600 °C under atmospheric pressure. A solution with water-to-glycerol feed molar ratio of 8 : 1 was introduced into the fixed-bed micro-reactor at a constant flow-rate of 0.05 mL min⁻¹ using PHD 440 syringe pump into a vaporizer where it was heated to 320 °C and mixed in a static mixer. The gas outlet from the reactor was connected to a knockout drum to trap the gas-condensable products (water and glycerol) which were analyzed using HPLC (Agilent Technologies 1200 Series, Santa Clara, CA, USA) using C18 (25 cm × 4.6 mm) column with a refractive index detector (RID). The mobile phase was acetonitrile–water (ϕr = 60 : 40) pumped at a constant flow-rate of 1.0 mL min⁻¹ at 30 °C. The reaction was performed over a period of 4 h and the gas products were analyzed every 0.5 h using gas chromatograph (GC) (model Clarus 500, Perkin–Elmer, Waltham, MA, USA) equipped with a flame ionization detector (FID), a dual-channel thermal conductivity detector (TCD), a molecular sieve 13× column, a molecular sieve 5A column, and a Hayesep D column. Helium was used as carrier gas and nitrogen was used as internal standard for subsequent GC. The performance of the catalyst is reported in terms of H_2, CO_2, CO, and CH_4 yield and glycerol conversion.

Performance parameters [4] were calculated based on the following Eqs. (1) and (2):

$$\text{Glycerol conversion}/\% = \\ = \left[\frac{(\text{Glycerol in}) - (\text{Glycerol out})}{(\text{Glycerol in})}\right] \times 100 \qquad (1)$$

$$\text{H}_2\ \text{yield}/\% = \frac{\text{H}_2\ \text{product/mole}}{7\,(\text{Glycerol feed/mole})} \times 100 \qquad (2)$$

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

Surface area of the catalyst was determined using BET method. The test is based on how much nitrogen gas is adsorbed onto the pores of the catalyst. Results of BET analysis showed that the surface areas were 66.9 and 61.1 $m^2\ g^{-1}$ for pure HAP and Ni-Ce-Cu/HAP catalyst, respectively. The surface area of pure HAP was significantly reduced with the addition of active metals. This reduction is due to the addition of active metals on the surface of catalyst support which block the pores of HAP and thus reducing the surface area of the resulting catalyst.

Figure 1 shows the FE-SEM images of pure HAP powder and Ni-Ce-Cu/HAP catalyst. From Figure 1, the morphology of HAP did not change after the addition of active metals and during the catalyst calcination process. This means that the use of hydroxyapatite as catalyst support with high porosity can prevent sintering of Ni, Ce, Cu metals and produce good dispersion on the HAP surface.

The morphologies of pure HAP and Ni-Ce-Cu/HAP catalyst shown by the images of FE-SEM are similar each other that is elongated spheroid shape with equal size. This is the same shape as that by Teixeira *et al.* [5]. When compared with the morphological shape of pure HAP, morphology of the catalyst does not seem change much after the addition of Ni, Ce, and Cu. On the surface of the catalyst, there are no agglomerates. This indicates that sintering process was not occurred during calcination. No agglomeration and no shape changes indicated that the HAP catalyst support has important function in preventing sintering and can maintain its morphological shape. Catalyst which has large porosity and resistant to high temperatures will increase the active sites so that reaction will occur perfectly.

Analysis of the distribution of active metals is required to determine whether the active metal dispersion on the surface of HAP occurs uniformly or not. Uniform dispersion of the active metal will increase the active sites of the catalyst and can produce better reaction. Mapping method was used to determine the distribution of the active metals on the HAP surface. The distribution of active metals catalyst is shown in Figure 2. It can be concluded from Figure 2 that Ni, Ce, and Cu metals were uniformly dispersed on the surface of HAP and there were no agglomerations formed.

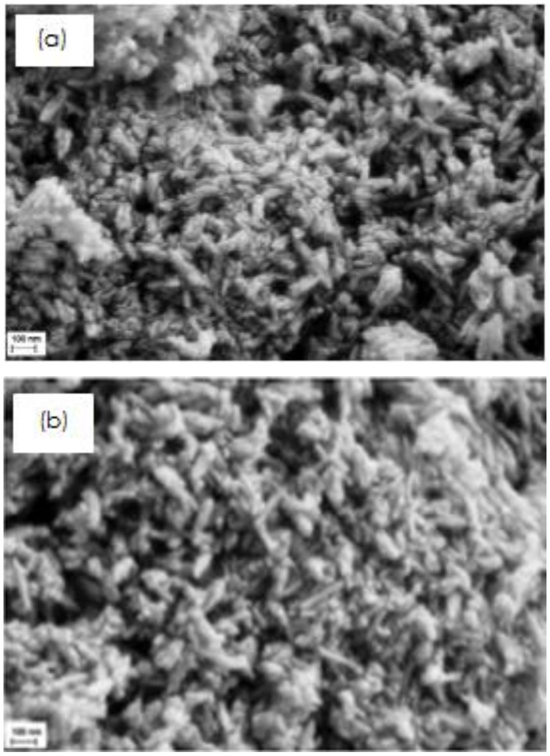


Figure 1 Morphology of: (a) pure HAP, (b) Ni-Ce-Cu/HAP catalyst

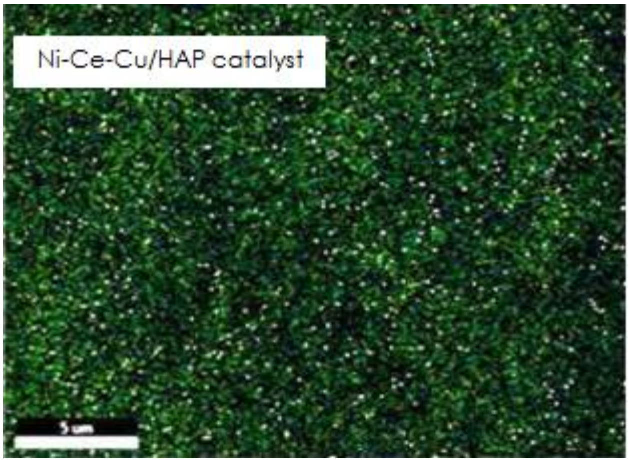


Figure 2 Dispersion of Ni, Ce and Cu metals on HAP

SEM-EDX technique was used to determine the content of Ni, Ce, and Cu on the surface of HAP as shown in Figure 3. Result from SEM-EDX analysis shows that P, Ca and O are major components in HAP depicted by the high peaks on the figure. It also shows the presence of Ni, Ce and Cu in the composite catalyst. These metals were well dispersed on the surface of HAP. This is due to the mesoporosity of HAP as well as its good ion exchange property that makes HAP suitable to be used as catalyst support.

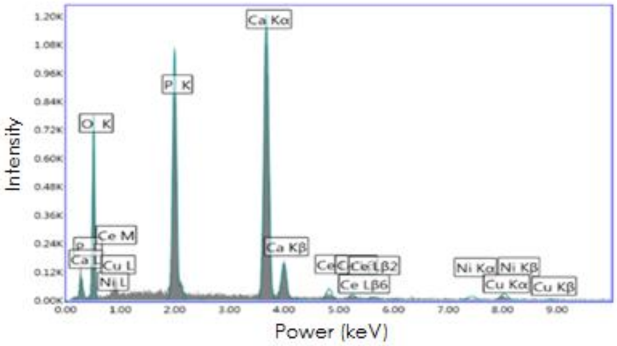


Figure 3 Result from SEM-EDX analysis of Ni-Ce-Cu/HAP catalyst

TEM tests were carried out on pure HAP and the composite catalyst to observe the structure as well as material shape. The internal structure test is also used to determine the actual shape of the material either having high porosity or otherwise. Figure 4 shows the internal structure of pure HAP and Ni-Ce-Cu/HAP catalyst. The internal structure of both figures shows the similar shape. Figure 4(a) shows that pure HAP has elongated spheroid shape with many pores. This is consistent with the result reported by Xia *et al*. [6]. It gives indication that HAP has high porosity and is suitable for metal dispersion in the preparation of a catalyst.

Figure 4(b) shows that there are dark spots on the surface of HAP. It is known that metal has high molecular weight density [7] compared to HAP and these spots are likely the metal oxides of Ni, Ce, and Cu that were formed during the calcination process. It is related and consistent with the results from FE-SEM and SEM-EDX that shows the uniform dispersion of Ni, Ce, and Cu and that the elongated spheroid shape of HAP did not change after the addition of Ni, Ce, and Cu through deposition-precipitation and calcination processes.

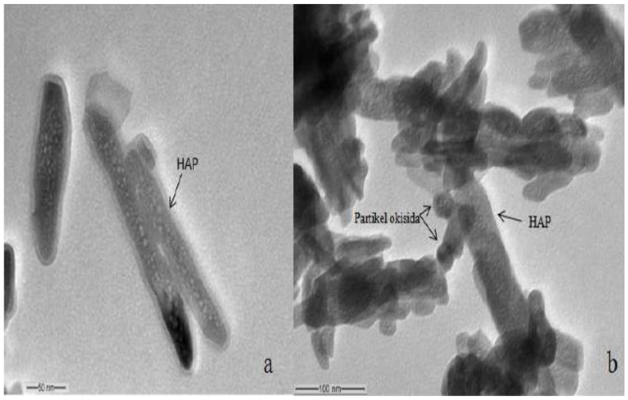


Figure 4 TEM images of: (a) pure HAP, (b) Ni-Ce-Cu/HAP catalyst

3.2 Catalytic Activity

Figure 5 shows glycerol conversion at different temperatures and glycerol-water ratios. It is depicted from Figure 5 that the glycerol conversions for all operating conditions tested are higher than 85%. This means that the catalyst used in the steam reforming reaction showed good effect to conversion of glycerol. At temperature of 600 °C for all glycerol-water ratios, the glycerol conversion is higher than at 400 °C and 500 °C as shown in Figure 5. This shows that the conversion of glycerol is related to the breakdown of C-C bond which easily occurs at high temperature as reported by Buffoni *et al*. [8]. In other words, temperature is a major factor affecting the rate of glycerol conversion.

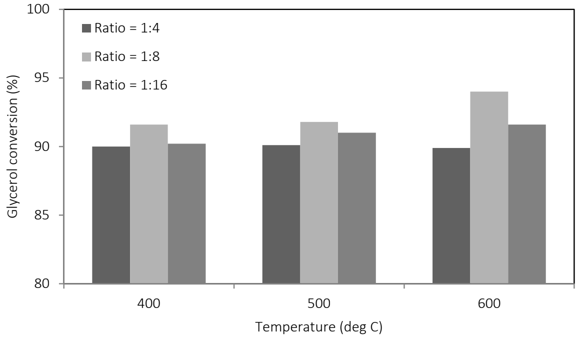


Figure 5 Glycerol conversion at different temperatures and glycerol-water ratios

Glycerol conversion was also influenced by variations in the ratio of glycerol-water as shown in Figure 5. The conversion of glycerol was high at glycerol-water ratio of 1: 8 with glycerol conversion reached 94.0% at operating temperature of 600 °C. The high glycerol conversion was due to the presence of Ni, Ce and Cu metals as catalyst. It is known that metals such as Ni and Cu have high activity in the steam reforming process of glycerol. Ni has the activity and ability to break the C-C and O-H bonds from glycerol, while Cu has the activity and ability in the water gas shift process for the formation of hydrogen from carbon monoxide and steam [9, 10]. The metal activity is related to the ability of HAP as catalyst support and active metal dispersing agent. Good metal dispersion in HAP support prevents the sintering process at high temperatures so that the activity of metal catalyst in the process can be maintained.

At 600 °C, a high glycerol conversion was obtained at glycerol-water ratio of 1:8. This is because the excess steam in the glycerol steam reforming process improved the conversion of glycerol into gaseous products through water gas shift process. The excess steam will reduce the formation and accumulation of CO on the catalyst surface by converting it into CO_2 and H_2 [11]. To prevent the accumulation of CO on the catalyst surface, the water gas shift process can reduce the poisoning of active sites, hence, the activity of the catalyst remains high for the steam reforming process of glycerol. But at a ratio of glycerol-water of 1:16, the glycerol conversion was found to decrease due to the high excess quantity of steam that will interfere the reaction in which the steam can condense and thus the conversion of glycerol is not optimal [12]. The glycerol conversions at glycerol-water ratio of 1:4 are lower than the others. This is due to the insufficient quantity of steam to produce more hydrogen through water gas shift process. At high temperature, the presence of steam will assist the migration of OH group on the active metal surface thus facilitates the reaction [10].

The hydrogen yield from steam reforming of glycerol at different temperatures of 400, 500 and 600 °C is shown in Figure 6. Among the three temperatures used, 600 °C shows a high hydrogen production of over 50%. This is because at high temperature, the process of breaking C-C and O-H bonds from glycerol is easy to achieve. Moreover, the presence of Ni can facilitate the breaking of the bonds and thus the H atoms are easier to form H_2 molecules [10, 13]. The presence of steam at high temperature can also assist the movement of OH groups towards the catalyst surface and hence simplifying the reaction process.

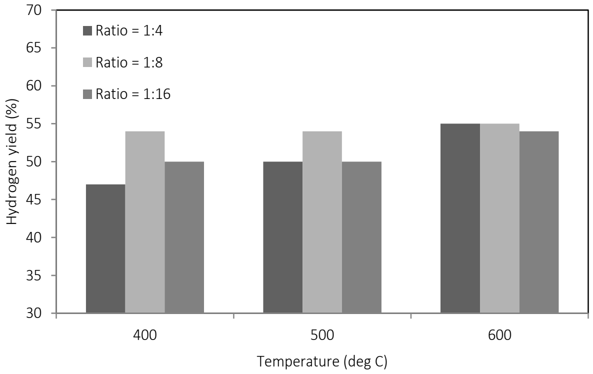


Figure 6 Hydrogen yield at different temperatures and glycerol-water ratios

4.0 CONCLUSION

The application of hydroxyapatite (HAP) which is a bio-based material is the first step to create an environmentally friendly catalyst. Preparation of the tri-metallic catalyst by deposition-precipitation method resulted in the uniform dispersion Ni, Ce, and Cu on the surface of HAP. The addition of Ni, Ce, and Cu onto the HAP support did not change the morphology of HAP, indicating that the sintering process did not occur during calcination. However, the surface area was reduced after the addition of the metals as a result of the incorporation of the active metals with HAP. The incorporation of active metals catalyst created active sites that play a key role in the steam reforming reaction of glycerol. Glycerol conversion at temperature of 600 °C with glycerol-water ratio of 1: 8 was as high as 94.0%. The yield of hydrogen from steam reforming reaction of glycerol at all operating conditions is about 52.1%. This indicated that the Ni-Ce-Cu/HAP catalyst composite was effective towards steam reforming reaction of glycerol.

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