CHARACTERISTIC OF HYDROXYAPATITE-SUPPORTED Ni, Ce, Cu CATALYST PREPARED BY DEPOSITION-PRECIPITATION AND IMPREGNATION METHOD FOR GLYCEROL-AQUEOUS PHASE REFORMING PROCESS

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ABSTRACT

The need and development of cleaner and greener alternative technologies using the heterogeneous catalytic are very important in fuel synthesis. Hydroxyapatite-supported Ni-Ce-Cu as biomaterial catalysts were synthesized and characteristic to study their potential to be used for glycerol reforming to hydrogen production. The catalysts have been prepared by deposition-precipitation and impregnation method for hydrogen production via aqueous phase reforming (APR) with varying the amount of nickel, cerium and copper. The catalysts were characterized by BET surface area, X-ray diffraction, and SEM-EDX techniques. It is found that the difference percent weight of Ni, Ce, Cu loading prepared via deposition-precipitation method shows a significant effect for the surface area, distribution of metals and crystallization of catalysts. The highest BET surface (61,11 m²/gr) and uniformly metals distribution on the surface Hydroxyapatite (HAP) area was noticed for catalysts composition containing much more Ce and Cu.

Keywords: Hydroxyapatite, Glycerol, Aqueous-phase-reforming, Catalyst, Deposition-precipitation, Impregnation

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INTRODUCTION

The effect of climate change is immense, such as the increase in the earth's temperature and the rise in sea level, considerable attention was focused on the development of the technology utilizing biomass as an energy resource attracts much attention. At present, air pollution of fossil-based fuels is a serious concern; therefore, developing environmentally friendly fuels is a necessity. Besides that, due to the shortage of resources and price of the hydrocarbon fuels become more expensive, this is a strong reason to find and develop renewable fuel resources.

During biodiesel production by mean of transesterification of triglycerides, glycerol is formed as a by-product. This quantity of glycerin is huge if we consider that biodiesel production is increasing to get a more significant role in the next energy scheme. With the increased production of biodiesel, a glut of glycerol is expected in the world market and therefore, it is essential to find useful applications for glycerol. One possibility of using glycerol (C₃H₈O₃) from the by-product biodiesel industry is as a promising renewable source to produce hydrogen by reforming method. The overall reaction of glycerol aqueous phase reforming (APR) is as following ¹.

The reforming method is usually used for hydrogen production from glycerol by using some catalyst. In this work, we have focused on the investigation related to the use of noble metal catalysts supported on biomaterial Hydroxyapatite for the APR process. The idea of choosing Ni, Ce, Cu catalysts with another noble metal-based catalyst because of Ni, Ce, and Cu relatively cheaper than Pd and Pt catalyst for

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hydrogen production via reforming method.² A few studies have been carried out on hydrogen production from glycerol by the APR method process.³ Catalysts for glycerol APR are mainly based on nickel as an active component supported on various metal oxide with high thermal stability and porous solid. The nickel-based catalyst has some problems with the catalyst deactivation caused by carbon deposition and the sintering of the catalyst particle during the preparation and operating conditions. The sintering of metal active such as nickel not only reduces active component but also can obstruct the reaction of the catalysts due to the reduced active area. In order to achieve high metal active dispersion, many researchers have focused on the development of high surface area metal activated by a variety of preparation methods such as impregnation and deposition-precipitation and impregnation method with different support. The important thing, nickel and copper as an active component can be highly dispersed on support if metal active is incorporated into spinel structure of support to form the catalyst.

The current industrial processes used to produce hydrogen involve the reforming of hydrocarbons, resulting in high CO_x emissions and adding to the depletion of fossil fuel reserves.^{4,5} The production of hydrogen, couple with liquid-phase products, through aqueous phase reforming (APR) of glycerol is one possible route.

Aqueous phase reforming of glycerol, shown in Eq.(1), was reported in 2002 by Dumesic⁶ as a promising method for hydrogen production. The process can be done at relatively low temperature 250-350 °C, it minimizes undesirable side reaction and facilitates the water gas shift reaction (WGS) (Eq.-2), limiting the production of CO, knows to poison hydrogen fuel stream.⁷

In the effort to minimize wastes generated in the manufacturing of chemical products, a catalytic method one of the most promising solutions, which renews synthetic processes with low atom efficiencies using toxic and/or hazardous stoichiometric reagents. The use of homogeneous transition metal catalysts on an industrial scale, however, is faced with a number of disadvantages including the loss of expensive metals, difficulties associated with corrosion, and plating out on the reactor wall. Alternatively, heterogeneous catalysts have the advantages of being operationally simple well as enabling unprecedented functions based on specific surface ensemble sites in a regular arrangement. Precise control of active metal species on solid surfaces is one of the most important challenges in designing highly-functionalized heterogeneous catalysts.

HAP has potential to be developed as catalyst support because this biomaterial has a mesopores structure and particle size of 5 – 40 nm.^{8,9} Usage hydroxyapatite (HAP) as a substrate for the catalyst of hydrogen production from methane was first reported on 2007.¹⁰

Mesopores structure has particle size 2-50 nm, has a high surface area and high porosity.¹¹ as a result, HAP is an excellent high surface area support to make catalysts. HAP can be extracted from bone and tooth and exhibits good stability at high temperatures.^{11,12} Molecule structure of Ca₅(PO₄)₃(OH) consists of PO₄³⁻ tetrahedra, O-H group and calcium. Hydroxyapatite posses Ca²⁺ sites surrounded by PO₄ tetrahedra parallel to the hexagonal axis and are of considerable interest in many areas because of their ion-exchange ability, adsorption capacity, and acid-base properties.^{13,14} The objective of our study is to compare the effect of nickel, ceria and copper loading on the hydroxyapatite support by preparation deposition-precipitation and impregnation method. The presence of ceria and copper as a promoter in Ni-based catalysts has several favorable effects for hydrogen production by the reforming method. The addition of ceria to nickel-based catalysts particular led to significant inhibition of CO production and hindered the Ni and Cu sintering during the calcination process. Ceria has been effective for oxygen-storage capacity and beneficial for the elimination of coke species on the catalyst surface.^{13,15} Meanwhile, copper-based catalysts have long since been recognized to be active in reforming method with low-temperature activity and better resistance to poisons. Copper is more susceptible to thermal sintering at high temperatures but can display strong basic properties and high stability against sintering if copper is homogeneously dispersed on a support.¹⁶

EXPERIMENTAL

The experimental procedures for catalysts preparation for hydrogen production were following the procedure described in previous our report¹.

Catalyst Preparation

In our work for the four catalysts with different loading Ni-Ce-Cu on HAP and different preparation methods. The catalysts C1 (12%, 3%, 3% / HAP) and C2 (6%, 6%, 6% / HAP) prepared by deposition-precipitation method. The catalysts B1 (12%, 3%, 3% / HAP) and B2 (6%, 6%, 6% / HAP) were prepared by impregnation method. The catalysts with varying amounts nickel $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, cerium $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, and copper $[\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ loading on hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$ support purchased from Sigma-Aldrich. All the precursors were dissolved in deionized water with concentration variation. Nickel, cerium, and copper solution were added dropwise to the hydroxyapatite solution at room temperature under vigorous stirring for 3 h and the solution was precipitated by dropping NH_4OH solution until the pH is 8.5. The solid obtained was washed and filtered with hot distilled water three times to remove excess ions. Via impregnation method, all the precursors were dissolved in deionized water with concentration variation. Ni, Ce, and Cu aqueous solutions were loading on hydroxyapatite supported with continuous stirring for 3 hours. The resulting product was dried at 120°C overnight and calcinated at 500°C for 5 h in air atmosphere of on electric furnace.

Characterization

The catalysts are characterized by various techniques. The surface area of catalyst was measured by Braunauer-Emmet-Teller (BET) technique (Quantachrome Nova 4200e). The catalyst samples were treated at 120°C for 30 min to ensure a clean surface before the adsorption isotherm test. The specific surface area after the calcination process is calculated from the Nitrogen (N_2) adsorption-desorption data. Particle size, morphology, and the component ratio of catalyst were measured by Field Scanning Electron Microscopy (SEM-EDX) (JEOL Type JIB4610F). X-ray diffraction (XRD) patterns of the catalysts samples were obtained using RiGAKU-SMART LAB 3kV.

RESULTS AND DISCUSSION

Table-1 shows the surface area of the catalysts with a different preparation. The dispersion of the active metal on the surface of the catalysts is crucial in determining the reaction activity. Thus, the specific surface area (SA) is a very important property for catalysts. The surface of HAP was reduced after the incorporation of Ni, Ce and Cu. This indicates the introduction of metals into the pores of the HAP.

Table-1: The Surface Area, Pore Volume and Pore Size of the Catalyst

Catalyst Ni-Ce-Cu/HAP	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
HAP	66.92	0.512	117.03
C1 (12%, 3%, 3% /HAP)	56.89	0.347	124.01
C2 (6%, 6%, 6%/HAP)	46.65	0.290	129.61
B1 (12%, 3%, 3% /HAP)	36.15	0.278	154.75
B2 (6%, 6%, 6% /HAP)	34.61	0.230	130.11

The C1 and C2 catalysts preparation by deposition-precipitation exhibited higher surface area among the others. This is caused by different preparation methods. A slight decrease in the surface area was observed after impregnation with Ni, Ce, and Cu. This is mainly due to the penetration of the dispersed metal into the pores of blocking some of the micropores. As mentioned before, nickel-based catalysts cause sintering of the catalyst particle during the preparation and operating conditions that resulted in decrease surface area of catalysts. The higher loading of Ni with combined Ce and Cu helping to minimize of the catalyst sintering and have large surface area have shown in C1 catalyst. In addition, HAP as support, enable a better catalyst dispersion because it is hexagonal in shape with apatite structure. The apatite structure is very flexible and accepts various substitution and ions exchanges in its framework¹⁷. The morphology of all the catalysts was analyzed using scanning electron microscope (FE-SEM) test illustrated in Fig.-1. All the catalysts morphology exhibited similar textures with an elongated spheroid shape. The catalysts texture similar to that show by Teixeira and Hakim.^{1,16}

The initial texture of HAP does not change much after the addition Ni, Ce and Cu by deposition-precipitation and impregnation method¹⁸. It can be concluded that using HAP as support for Ni, Ce and

Cu by deposition-precipitation and impregnation method may prevent the occurrence of sintering and still have high porosity and better active metal dispersion.

Fig.-1: Morphology of HAP and Catalysts: (a-b) Deposition-Precipitation Method, (c-d) Impregnation Method.

Fig.-2: Dispersion of Active Metals on HAP Via Deposition-Precipitation: (a) Catalyst, (b) Ni, (c) Cu, (d) Ce

Analysis of the distribution of Ni, Ce, and Cu is required to determine whether the metal dispersion on the HAP occurs uniformly or not. Uniform dispersion of the Ni, Ce, and Cu as active metals will increase the active site of catalyst and can produce a better reaction. The mapping method was used to determine the distribution of metals on HAP. The distribution of active metals by the impregnation method for the

preparation of catalysts is shown in Fig.-2 and the distribution of metal by deposition-precipitation method is shown in Fig.-3.

Fig.-3: Dispersion of Active Metals on HAP Via Impregnation: (a) Catalyst, (b) Ni, (c) Cu, (d) Ce.

In both of Fig.-2 and 3, it can be concluded that by deposition-precipitation the Ni, Ce, and Cu were more uniformly dispersed or homogeneous distribution than by the impregnation method. Distribution of the active metals (Ni, Ce, Cu) by impregnation method not uniformly due to occurred agglomeration or aggregated crystals as illustrated in Fig.-2 (b,c,d) so that the surface of the catalysts will decrease. The active metals agglomeration occurs when the calcination process at 500°C.

Investigation of the crystalline phase present in the as calcinated catalysts was performed by X-ray diffraction analysis. The XRD patterns of the catalysts are presented in Fig.-4 (a,b,c,d) with a scanning angle (2θ) range 10-90°.

Fig.-4: XRD Patterns of Ni-Ce-Cu/HAP Catalysts (a,b) by Impregnation and (c,d) Deposition- Precipitation Method with Different Active Metal Loading on HAP

Figure-4 shows that are all the catalysts were similar and their typical diffraction peaks showed no substantial change intensity.¹⁹ This accrued because a molecule of hydroxyapatite is crystallized in the hexagonal axis, has the ion-exchange ability and adsorption capacity therefore the crystal structure does not change after calcination process¹⁹. Meanwhile that a part of active metals may incorporate into the phosphate structure (PO_4 tetrahedra) by taking the position of Ca^{2+} .¹² Therefore, hydroxyapatite has been considered a suitable catalyst supports.

CONCLUSION

The study on catalysts preparation by impregnation and deposition-precipitation method with different active metal loading on HAP for aqueous phase reforming (APR) of glycerol showed quite promising as catalysts for hydrogen production. On the basis of the above experimental observations and discussions regarding the Ni, Ce, Cu/HAP catalysts prepared by the deposition-precipitation method gives rise to a catalyst with superior catalytic activity for glycerol APR reaction then impregnation method. This is indicated by the surface area of the C1 and C2 catalysts higher than B1 and B2 catalysts (56.89 & 46.65 m²/g). The results of the mapping method show that catalysts preparation by deposition-precipitation method more agglomeration or aggregated crystals so that the deposition-precipitation method is better for preparation of heterogeneous catalysts.

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