PRECIOUS METALS SUPPORTED ON ALUMINA AND THEIR APPLICATION FOR CATALYTIC AQUEOUS PHASE REFORMING OF GLYCEROL

Kiky Corneliasari Sembiring[*], Anis Kristiani, Fauzan Aulia, Luthfiana Nurul Hidayati, and Silvester Tursiloadi

Research Center for Chemistry, Indonesian Institute of Science
Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia

ABSTRACT

The high cost of Pt based catalyst for aqueous phase reforming (APR) reaction makes it advantageous to develop less cost of other metals for the same reaction. APR is hydrogen production process from biomass-derived source at mild condition near 500 K and firstly reported by Dumesic and co-worker. The use of hydrogen as environmentally friendly energy carrier has been massively encouraged over the last year. When hydrogen is used in fuel cell for power generation, it produces a little or no pollutants. The aim of this study is to study the effect of some precious metal catalysts for APR process. Due to investigation of metal catalysts for APR process, four precious metals (Cu, Co, Zn, Ni) supported on γ-Al_2O_3 with 20% feeding amount have been successfully prepared by impregnation method. Those precious metals were identified as promising catalysts for APR. The catalysts were characterized by N_2 physisorption at 77 K, X-Ray Diffraction (XRD) and Fourier Transform-Infra Red (FT-IR). The catalytic performance was investigated at 523 K and autogenous pressure in a batch reactor with glycerol concentration of 10%. The gaseous hydrogen product was observed over the prepared catalysts by GC. It was found that performance of catalysts to yield the hydrogen product was summarized as follow Cu/γ-Al_2O_3 > Co/γ-Al_2O_3 > Zn/γ-Al_2O_3 > Ni/γ-Al_2O_3.

Keywords: aqueous phase reforming; γ-Al_2O_3; hydrogen; metal catalyst

ABSTRAK

Penggunaan katalis heterogen berbasis logam Pt untuk reaksi reformasi fasa cair terbentur oleh mahalnya harga katalis jika diaplikasikan pada skala komersial, oleh karena itu diperlukan pengembangan sintesis katalis heterogen dengan logam yang lebih murah. Reaksi reformasi fasa cair adalah reaksi untuk menghasilkan gas hidrogen yang biasa dilangsungkan pada 500 K dan pertama kali diperkenalkan oleh Dumesic dkk. Hidrogen merupakan energi yang ramah lingkungan karena dalam penggunaannya sebagai pembangkit energi, hanya menghasilkan sedikit polusi. Dalam tulisan ini dibahas pengaruh katalis logam (Cu, Co, Zn, Ni) yang diembankan pada γ-Al_2O_3 terhadap proses reformasi fasa cair. Karakteristik katalis dianalisis dengan BET, XRD, dan FT-IR. Unjuk kerja katalis ditentukan dengan reaksi pada 523 K pada reaktor batch dengan konsentrasi gliserol 10%. Hasil yang didapatkan menunjukkan bahwa unjuk kerja katalis pada reaksi reformasi fasa cair dari produk hidrogen yang dihasilkan bisa diurutkan sebagai berikut Cu/γ-Al_2O_3 > Co/γ-Al_2O_3 > Zn/γ-Al_2O_3 > Ni/γ-Al_2O_3.

Kata Kunci: γ-Al_2O_3; hidrogen; katalis logam; reformasi fasa cair

INTRODUCTION

Due to the worldwide petroleum consumption has increased rapidly in the last decades, energy crisis and environmental pollution has become more and more serious. Therefore the use of renewable as a source for the production of fuel and chemicals has become important during the last few years [1]. As an alternative to industrial petroleum-based fuels, biodiesel has become one of the most common applications of biofuels from biomass [2]. Glycerol, as the main by-product of biodiesel production process, is increasing rapidly with the development of biodiesel industry [3]. One of some possibilities for efficient utilization of glycerol is the conversion to synthesis gas (CO/H_2) by reforming processes [4-6].

It is worth to consider the production of hydrogen from glycerol. In this sense, biodiesel would be fully integrated in the renewable fuel concept as clean fuel for fuel cell devices [7]. Glycerol reforming for hydrogen production could be carried out by several available routes, such as aqueous phase reforming (APR), steam reforming, and autothermal reforming [8-11]. APR of oxygenated compounds derived from biomass,

* Corresponding author. Tel/Fax : +62-21-7560929/7560549
Email address : kiky001@lipi.go.id

first developed by Dumesic et al. It has several advantages, for instances it can be carried out at low temperatures, reducing the cost of the process because it is not necessary to vaporize water and minimizing undesirable decomposition reactions. Furthermore, it is possible to generate H_2 and CO_2 in a single step with low levels of CO, which is important for fuel cell applications [12-13].

The mechanism of hydrogen production by APR process involves the cleavage of C–C bonds as well as C–H bonds to form adsorbed species (especially CO) on the catalyst surface. Then CO is converted in H_2 and CO_2 by the water–gas shift reaction, as described by Dumesic group [9,13-14]. Several supported metal (Pt, Ru, Rh, Pd, Ir and Ni) catalysts have been tested in APR process and have shown good activity and selectivity for hydrogen production. Thus, a good catalyst for APR process has to be active in the cleavage of C–C bonds and water–gas shift reaction, but has to inhibit the cleavage of C–O bond and methanation reactions. However, the high cost of metal based catalyst for APR reaction makes it advantageous to develop less cost of other metals for the same reaction.

In this work, four precious metals (Cu, Co, Zn, Ni) supported on γ-Al_2O_3 with 20% feeding amount were prepared and evaluated for hydrogen production by APR of glycerol. The effect of the preparation methodology on the catalytic activity for reforming reaction and hydrogen selectivity was investigated, correlating with structural and morphological properties.

EXPERIMENTAL SECTION

Materials

Aluminium oxide (γ-Al_2O_3, > 99.5%), Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, > 99.5%), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 3H_2O$, > 99.5%), Zinc nitrate tetrahydrate ($Zn(NO_3)_2 \cdot 4H_2O$, > 99.5%), Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, > 98%) and glycerol ($C_3H_8O_3$, > 99.5%) were commercial products from Merck. All the catalyst precursors were reagent grade and were used as received.

Instrumentation

X-ray diffraction (XRD) patterns were obtained by Rigaku Smartlab diffractometer. BET surface areas were measured by N_2 physisorption using a Micromeritics TriStar II 3020 instrument. All the FTIR spectra were collected on an IR Prestige-21 Shimadzu spectrometer. The decomposition of catalysts was investigated by thermal gravimetric analysis (TGA) using Linseis STA

PT 1600 analyzer. The products were analyzed by gas chromatography, Shimadzu 8A GC.

Procedure

Catalyst preparation

Catalysts were prepared by impregnation methodology. Commercial γ-Al_2O_3 was used throughout the study. γ-Al_2O_3 and aqueous solutions of nitrate salts of metals nickel, cobalt, copper and zinc were prepared and soaked in distilled water. Feeding amount of the metal was 20% for all samples. The resulting slurry was stirred at 80 °C for 24 h, filtered, and washed with deionized water. The catalyst was subsequently dried overnight at 105 °C, and calcined in ambient air at 500 °C for 3 h.

Catalyst characterization

X-ray diffraction (XRD) analysis was carried out for crystallographic phases identification of the catalysts samples using a Rigaku Smartlab diffractometer, with Cu Kα radiation at 40 kV and 30 mA, and a secondary graphite monochromator in the 2θ range of 10–80°. The textural characteristics, such as BET specific area and pore volume (BJH method), were determined by N_2 adsorption–desorption on a Micromeritics TriStar II 3020 instrument. Prior to the analysis the samples were outgassed for 3 h at 250 °C. The chemical nature of adsorbed surface CO_2 species was determined by infrared (IR) spectroscopy after CO_2 adsorption at 298 K. Samples were pressed into small discs and placed in the IR cell. All infrared spectra were collected at resolution of 4 cm^{-1} in the 4000-400 cm^{-1} range. The decomposition of catalysts was investigated by thermal gravimetric analysis (TGA) using Linseis STA PT 1600 analyzer.

Catalytic performance test

Prior to catalytic performance test, the catalyst was reduced with H_2 at 350 °C for 3 h. The test on catalytic performance was carried out in a batch autoclave reactor. In each experiment, 1.125 g of catalyst and 10% glycerol solution were charged into a reactor. Before the reaction, the reactor was purged with N_2 to remove air. The catalytic tests were performed at 250 °C for 6 h, resulting in autogeneous pressures of about 42 bars. Gas products were collected in the end of the reaction time and analyzed by gas chromatography, equipped with a thermal conductivity detector (TCD). The products detected in the gas phase were H_2, CH_4, C_{2+}, CO_2, and CO. The molar fractions of these products were calculated without considering water. In the liquid phase only glycerol was quantified by GC/MS. Conversion was calculated based on the moles of glycerol in the feed.
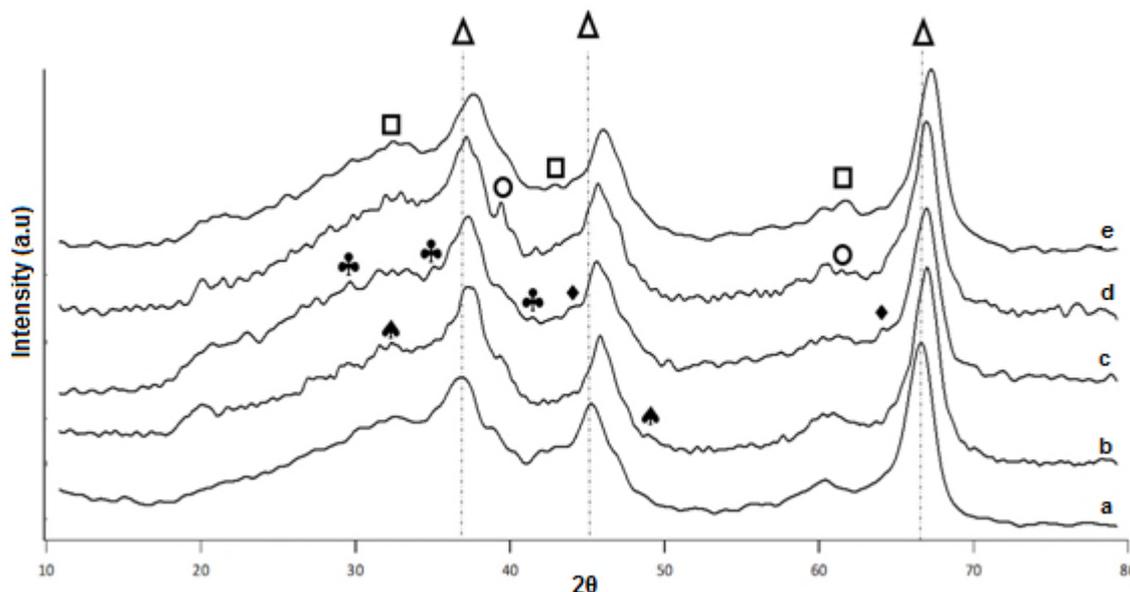
Fig 1. XRD patterns of γ-Al_2O_3 (a), Zn/γ-Al_2O_3 (b), Co/γ-Al_2O_3 (c), Ni/γ-Al_2O_3 (d), and Cu/γ-Al_2O_3 (e) after calcination with Δ γ-Al_2O_3 phase, $\square$ CuO phase, o NiO phase, $\clubsuit$ Co_3O_4 phase, $\blacklozenge$ CoO, $\spadesuit$ ZnO phase

Table 1. Physical properties of the catalysts calcined at 500 °C for 3 h

Catalyst M//γ-Al_2O_3	Metal content (% wt)	S_{BET} (m^2/g)	V_{PORE} (cm^3/g)	D_P (nm)
γ-Al_2O_3		131.05	0.0404	2.094
Co/γ-Al_2O_3	2.09	129.20	0.0389	2.101
Ni/γ-Al_2O_3	5.13	129.97	0.0395	2.099
Cu/γ-Al_2O_3	6.68	124.92	0.0378	2.104
Zn/γ-Al_2O_3	2.35	127.32	0.0385	2.102

RESULT AND DISCUSSION

Catalyst Characterization

In the catalysts preparation, the precursor metal loading of all samples is similar to the nominal value concentration of 20%. To confirm the successfulness of introducing the metal on the catalyst support, the metal content of the catalysts were measured by XRF. Table 1 shows the effect of metal loading on the specific surface area and pore volume of metal/alumina catalysts.

Table 1 summarizes the textural characteristics of the catalysts. It can be seen that all the metal loading on the catalysts less than 10% with the highest is Cu with 6.68%. The lower loading of metal might be the result of intensive washing in the preparation, causing the loss of metal precipitate because the interaction of metal and support is physical interaction. From the specific surface area, it can be observed that the BET area of metal/γ-Al_2O_3 catalyst is slightly smaller than the area of γ-Al_2O_3 pure support (131 m^2/g). This reduction in area is possibly due to the partial blockage of the pores of support by metal oxide particles. Impregnation of the metals on the support slightly decreases the total pore volume of γ-Al_2O_3 pure support. However, the average pore diameter of all catalysts increase, it means that some of the impregnated metal species maybe locate on the inner surface of the alumina support. Therefore, it affected the pore volume and pore diameter.

The γ-Al_2O_3 is an amorphous matrix, therefore broad XRD patterns is observed in Fig. 1. The pure γ-Al_2O_3 pattern shows peaks at 36.78, 45.2, and 66.54° and the pattern is ascribed to an amorphous phase. There is no obvious peak of metal-containing species, indicating that the possible metal oxide may be in amorphous state or formed micro grain which was below the detection limit of XRD and overlapped with the XRD pattern of γ-Al_2O_3. The very broad diffraction peaks of metals in catalyst support could indicate a good dispersion of metal oxide crystallites in support matrix. Furthermore, a slight shift of γ-Al_2O_3 diffraction peaks demonstrating successfully incorporated of metal oxide into γ-Al_2O_3 lattice.

Furthermore, the metal/γ-Al_2O_3 samples were characterized by DSC/TGA to study the thermal decomposition behaviour, as shown in Fig. 2.

The initial exothermic peak at around 90 °C in the DSC curves for all samples can be attributed to moisture on the surface, correspond to the weight loss of 3% to 7%. The highest weight loss for this region was for pure support γ-Al_2O_3 which was 7%. Weight loss of up to 10% between 90 and 185 °C can be attributed to the removal of physically adsorbed water and organics, for example hydrated aluminium hydroxide,
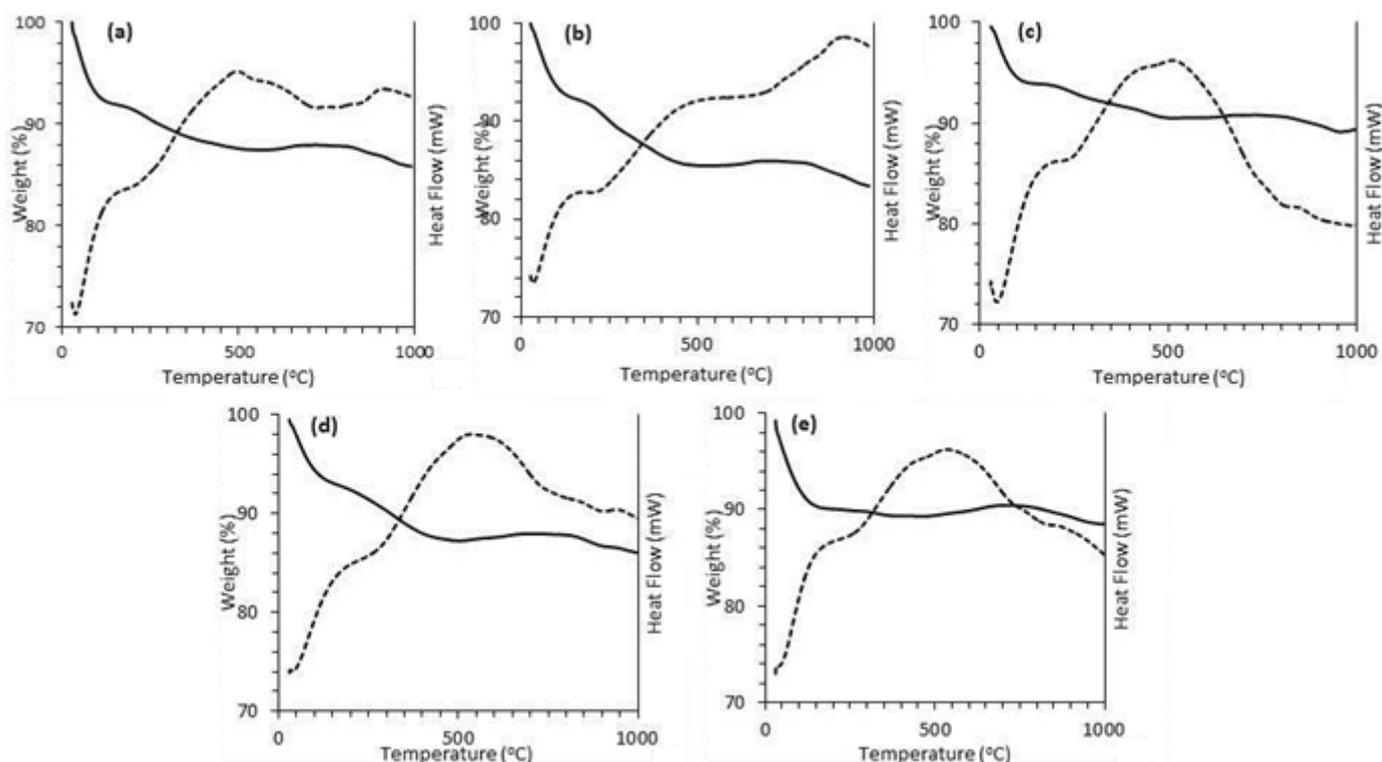
Fig 2. DSC/TGA curves for (a) Co/γ-Al$_2$O$_3$, (b) Cu/γ-Al$_2$O$_3$, (c) Zn/γ-Al$_2$O$_3$, (d) Ni/γ-Al$_2$O$_3$, (e) γ-Al$_2$O$_3$
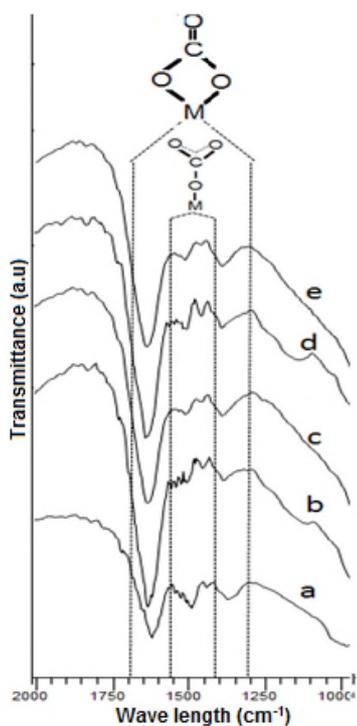
Fig 3. Infrared spectra of (a) γ-Al$_2$O$_3$ and CO$_2$ adsorbed on (b) Co/γ-Al$_2$O$_3$, (c) Cu/γ-Al$_2$O$_3$, (d) Zn/γ-Al$_2$O$_3$ and (e) Ni/γ-Al$_2$O$_3$ catalysts

which can possibly formed. For metal impregnated over γ-Al$_2$O$_3$ samples, the weight loss at temperature range of 200 to 500 °C were observed relating to the decomposition of chemically and strongly bound water molecules and organic groups, such as metal nitrate which entrapped in the pores support [15]. The total weight loss of the supported metal samples was more than the total weight loss of the support, as expected. This difference is related to the dissociation of metal nitrate presented in the supported metal samples. As it can be seen, there were no appreciable thermal changes and weight loss when the samples were heated above 500 °C and it was considered as calcination temperature of the catalysts.

The basic properties of metal/γ-Al$_2$O$_3$ samples were probed by CO$_2$ adsorption at room temperature and then analyzed by FTIR. Fig. 3 shows the IR spectra obtained from metal/γ-Al$_2$O$_3$ samples that reveal the presence of two different carbonates, which are unidentate carbonate formation and bidentate carbonate. Unidentate carbonate formation is low-coordination anions that exhibits a symmetric O-C-O stretching at 1360 to 1400 cm^{-1} and an asymmetric O-C-O stretching at 1510 to 1560 cm^{-1}. While bidentate carbonate forms on Lewis acid-Brønsted base pairs(Al^{3+} -O^{2-} pair site), and shows a symmetric O-C-O stretching at 1320 to 1340 cm^{-1} and an asymmetric O-C-O stretching at 1610 to 1630 cm^{-1} [14-16].

Table 2. The catalytic aqueous-phase reforming of glycerol over metal supported on γ-Al₂O₃ catalysts[a]

Entry	Catalyst	Conversion[b] (%)	Gas product [c] (%)				
			H₂	CH₄	C₂₊	CO	CO₂
1	γ-Al₂O₃	2.00	0.00	0.00	0.00	-	-
2	Ni/γ-Al₂O₃	>99.00	1.53	0.08	29.48	0.42	68.48
3	Cu/γ-Al₂O₃	>99.00	14.64	0.07	34.01	0.33	34.01
4	Co/γ-Al₂O₃	>99.00	6.83	0.08	26.48	0.39	66.22
5	Zn/γ-Al₂O₃	>99.00	2.89	0.08	3.00	0.41	93.62

[a] 10 wt% glycerol (7.5 g glycerol in 67.5 mL H₂O), 1.5 wt% metal/glycerol, 250 ºC, 6 h

From the spectra of Fig. 3, it can be observed that the basicity increased by impregnating metal on the support, it was confirmed by increasing the intensity of transmittance spectra.

Catalytic Tests

The catalytic activity of the metal supported on γ-Al₂O₃ catalysts for aqueous-phase reforming of glycerol concentration 10% glycerol at 250 °C are summarized in Table 2. GC-MS analysis of the remaining liquid after reaction showed trace glycerol concentration, so that the conversions of reaction are close to 100%.

The reaction data presented in Table 2 shows that glycerol aqueous phase reforming over all studied catalysts indeed leads to a synthetic gas phase with a quite low CO concentration. The Cu/γ-Al₂O₃ catalyst stands out in terms of having the highest selectivity toward hydrogen. While C₂₊ consists mostly of ethane and ethene. Higher concentration of C₂₊ than hydrogen in the gas product, indicate the capability of the catalyst for cleaveage of C-C bonds was still low. This could be due to deactivation of the catalysts happened during the reaction. With γ-Al₂O₃ as a support, the rate of hydrogen production decreased in the following order Cu/γ-Al₂O₃ > Co/γ-Al₂O₃ > Zn/γ-Al₂O₃ > Ni/γ-Al₂O₃. The study that was conducted by Guodong at al. showed Ni and Co catalysts performed low activity due to deactivation with time on stream [17]. Ni showed a good activity for C–C scission, but it exhibited high rates of methanation [12]. On the other hand, Cu performed medium activity for C–C bond cleavage but it had high activity for water-gas shift reaction, thus favoring the selectivity to hydrogen. Therefore, in this study Cu/γ-Al₂O₃ performs the highest selectivity with 14.6% hydrogen yield.

CONCLUSION

Four γ-Al₂O₃-supported metal catalysts with 20% feeding amount have been successfully prepared by impregnation method and characterized. Application of the prepared catalysts for APR reaction showed selectivity of γ-Al₂O₃-supported metal catalysts towards hydrogen decreased in the following order Cu/γ-Al₂O₃ >

Co/γ-Al₂O₃ > Zn/γ-Al₂O₃ > Ni/γ-Al₂O₃. The highest selectivity was Cu/γ-Al₂O₃ with 14.6% hydrogen yield.

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