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Synthesis of Ni/CaO-γ-Al_2O_3@Ru Core Shell via Micro-Emulsion Method for Bio-oil Steam Reforming of Empty Fruit Bunch

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Hydrogen production from bio-oil steam reforming plays an important role in the development of renewable hydrogen from biomass to produce the cleanest fuel. However, the existence of coke and low carbon conversion are problems that have been found in some studies. The purpose of this study was to reduce coke formation and to enhance carbon conversion by using core shell nanoparticle catalysts that could increase of surface area, support interaction and its catalytic activity for hydrogen production from bio-oil steam reforming of empty fruit bunch (EFB). Ni/CaO-γ-Al_2O_3@Ru core shells were prepared by CTAB/n-hexanol/n-hexane/water micro-emulsion system. The catalysts were characterized by means XRD, BET, FESEM-EDS and TEM. Bio-oil aqueous fraction was analyzed by using GC-MS. Carbon conversion and hydrogen yield by using Ni/CaO-γ-Al_2O_3@Ru core shell are resulted more 68.4 % and 18.6% than using Ni/CaO-γ-Al_2O_3 catalyst, respectively. The highest hydrogen yield by using Ni/CaO-γ-Al_2O_3@Ru core shell for steam reforming bio-oil is 5.6% in minute 10 with 0.07 g of coke deposit. The study concludes that the effect of Ni/CaO-γ-Al_2O_3@Ru core shell is more efficient in hydrogen production, carbon conversion and coke deposit compared to Ni/CaO-γ-Al_2O_3 catalyst.

Keywords : bio-oil, core shell, hydrogen, micro-emulsion, Ni/CaO-γ-Al_2O_3@Ru, steam reforming

INTRODUCTION

Fossil fuel feedstock is a limited stock that slowly moving depletion. The dependence on fossil fuel energy should be eliminated. Hydrogen is an alternative fuel to replace fossil fuels (Mohanti et al, 2012). However, hydrogen is still widely produced by steam reforming process from methane, naphtha, oil partial oxidation and coal gasification (Takanabe et al, 2004; Pefia et al, 1996). The researchers began to look for other ways in hydrogen production by using bio-oil as alternative source.

In general, biomass consists of three main components of cellulose, hemicellulose and lignin (Hamelinck et al, 2005; Hames et al, 2003). The cellulose, hemicellulose and lignin composition of empty fruit bunch were 59.7%, 22.1%, and 18.1% in dry weight percentages, respectively (Abdullah and Gerhauser, 2008). The highest content of cellulose and hemi-cellulose in biomass are used as feedstock for hydrogen production. Biomass can be converted into bio-oil by pyrolysis (Xiu and Ahahbazi, 2012).

Various catalysts have been developed to improve the hydrogen yield and carbon conversion for bio-oil steam reforming. The nickel catalyst that was used in steam reforming for hydrogen production, had been carried out by the researchers (Meibod, 2013; Vagia, 2008; Valle, 2013). Nickel was used as an active metal but it could produce high carbon deposit. The addition of MgO as support catalyst would enhance the activity of core dispersion on Al_2O_3 support and adsorb CO_2 (Koo et al, 2008). Steam reforming of the bio-oil aqueous fraction was examined and developed for ruthenium metal as a catalyst promotor and reported hydrogen yield of about 7 % was achieved by modifying its support (Meibod, 2013). But, ruthenium has high price and limited amount. One of the ways to anticipate this problem is to create a nanoparticle core shell. When precious metals are used as shell materials, their catalytic activity will enhance because surface area and the proximity of interface between core and shell increased. The core shell can be synthesized by micro-emulsion that is an effective catalyst preparation for forming nanoparticle size catalyst at room temperature and pressure (Gyger et al, 2014).

The objective of this study was to enhance carbon conversion of bio-oil steam reforming reaction of EFB over Ni/CaO-γ-Al_2O_3@Ru core shell because core shell form can increase of surface area, support interaction and its catalytic activity.

EXPERIMENTAL METHODS

Catalysts Preparation and Characterizations

Preparation of CaO-γ-Al_2O_3 Supports and Ni Based Catalyst as Core Particles

The CaO-γ-Al_2O_3 support ($W_{(CaO)}$=20%; $W_{(γ\text{-}Al2O3)}$ =80%) was prepared by sol-gel method. The γ-Al_2O_3 and $Ca(NO_3)_2.4H_2O$ were mixed and added distillated water by stirring for 1 h at room temperature. Cetyltrimethylammonium bromide (CTAB) was added NH_4OH until 10 pH. Molar ratio for $Ca(NO_3)_2.4H_2O$ and CTAB was 1:1,4. The $Ca(NO_3)_2.4H_2O$ was added drop wise in to CTAB solution and stirred for 3 h at 60°C. The support was washed using distillated water and ethanol mixture, dried overnight at 60°C and calcined for 4 h at 600°C. The Ni based catalysts were prepared by wet impregnation method. The $Ni(NO_3)_2.6H_2O$ as Ni precursor was made as an aqueous solution. The Ni loading was 15wt% in the sample. After impregnation, the promoted support was dried overnight at 60°C and calcined for 3 h at 500°C.

Ruthenium Coating on Ni/CaO-γ-Al_2O_3 Particles

The Ni/CaO-γ-Al_2O_3@Ru core shell was prepared by micro-emulsion. To prepare the micro-emulsions; n-hexane, CTAB and n-hexanol were used as the oil phase, surfactant and co-surfactant, respectively. Then, the oil phase, surfactant and the co-surfactant were mixed with weight ratio 5:2:3 by magnetically stirring (MS). The micro-emulsions were prepared as follows: 5 g of MS was mixed by 2 g of Ni/CaO-γ-Al_2O_3 (MS1), 5 g of MS was mixed by 0.01 g of $RuCl_3.x.H_2O$ (MS2) and 2 g of MS was mixed by 2 g of 0.2 M NH_4OH solution (MS3). MS1 was added to MS3 and stirred for 30 minutes at room temperature. The MS2 was added dropwise in to the mixture of MS1 and MS3 under stirring condition for 30 minutes. The precipitates were washed using ethanol and dried overnight at 60°C and calcined for 1 h at 500°C.

Characterization of Catalysts

X-Ray diffraction (XRD) analyses were performed by using an X-Ray smart lab diffractometer with a C-K_β monochromatized radiation source. The nickel and ruthenium filter to examine the sample crystallinity in 2θ between 10° to 90°. Energy Dispersive Spectroscopy (EDS) analysis was performed with JEOL type JIB 4610F that was operated at 15 kV with 80000 times magnification. Transmission electron microscopy (TEM) images were taken to examine the morphology and dimension of nanoparticles. Surface area, pore volume and pore radian of samples were determined by Brunauer-Emmett-Teller (BET) analysis by Quantachrome Nova with BJH pore size distribution.

Bio-oil Steam Reforming

The reactor that used for steam reforming bio-oil was made of stainless steel. A furnace was used to provide heat for system and excess steam was recovered by glass condenser. The analysis system consisted of an online GC-TCD (Varian, model C-R6A). In the experiment; the initial weight of reactor, condenser and inlet bio-oil were calculated. A 0.1 g of 200 mesh catalyst was put in heating region reactor. The catalyst was reduced in situ using H_2 and N_2 mixture (50%) with 120 mL/min flow rate at 700°C for 1 h. Flushing with pure nitrogen was done using at flow rate of 120 mL/min at 700°C for 1 h. Water and bio-oil aqueous fraction (S/C = 2) were injected by using syringe pump to reactor at 0.1 mL/min flow rate.

During the experiment, steam reforming reaction would be held for 2 h at 700°C. A 1 mL of gas sample was taken and analyzed using GC every 10 minutes downstream of condenser. After each run, the catalyst bed was cooled to room temperature. The weight of reactor, inlets were calculated and considered as the amount of the carbon depositions. The weight of condenser was calculated by subtracting from the condenser initial weight.

Bio-oil steam reforming can be simplified as oxygenate organic compound $C_nH_mO_k$ by the following reaction:

$$C_nH_mO_k + (n-k)H_2O \leftrightarrows nCO + \left(n + \left(\frac{m}{2}\right) - k\right)H_2 \qquad (1)$$

This reaction is followed by water shift gas reaction. Therefore, The overall reaction can be represented as follows:

$$C_nH_mO_k + (2n-k)H_2O \leftrightarrows nCO + \left(2n + \left(\frac{m}{2}\right) - k\right)H_2 \qquad (2)$$

The hydrogen yield was defined as the number ratio of moles of produced

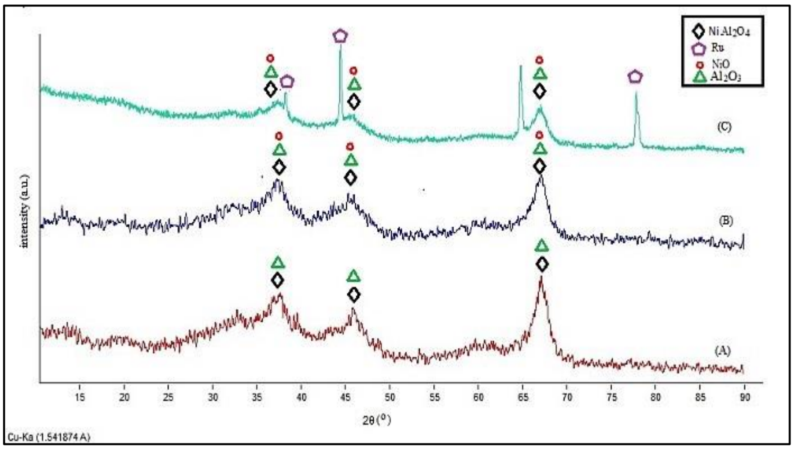

Fig. 1: (A) XRD patterns of CaO-γ-Al_2O_3; (B) Ni/CaO-γ-Al_2O_3; (C) Ni/CaO-γ-Al_2O_3@Ru

hydrogen to the theoretical quantity of the hydrogen obtained in complete reforming to CO_2 and H_2, took place and calculated form Eq. (3) (Salehi et al, 2011).

$$H_{2\ \mathrm{yield}}(\%) = \left(\frac{\mathrm{nH_2}}{2\mathrm{n} + (\frac{\mathrm{m}}{2}) - \mathrm{k}} \times n_{\mathrm{Ci\ feed}} \right) \times 100\% \quad (3)$$

n H_2 was the amount of hydrogen moles production; n, m, k were the atomic amount of oxygenated organic compound ($C_nH_mO_k$) of bio-oil and $n_{\mathrm{ci\ feed}}$ was amount of carbon moles in feed.

Each of the other gases yield (n_i) obtained to formula (Eq.(4)) over the amount of carbon moles feed ($n_{c,feed}$).

$$Y_i = \frac{nC_i}{n_{c,feed}} \times 100\% \quad (4)$$

Carbon conversion was defined as the amount of carbon deposited on catalyst over the amount of bio-oil, represented in Eq. (5).

$$\mathrm{X} = \frac{\mathrm{n_{Ci\ product}}}{\mathrm{n}_{\mathrm{Ci}\ bio-oil}} \times 100\% \quad (5)$$

n_{ci} products were amount of carbon in gas and $n_{\mathrm{ci\ bio\text{-}oi}}$l was amount of carbon in bio-oil.

RESULTS AND DISCUSSION

Characterization of Ni/CaO-γ-Al_2O_3 and Ni/CaO-γ-Al_2O_3@Ru Core Shell

The surface area, pore size and pore volume for Ni/CaO-γ-Al_2O_3 and Ni/CaO-γ-Al_2O_3@Ru core shell are summarized in **Table 1**. BET result shows that adding Ru can contribute to increase the surface area and pore volume after micro-emulsion process for Ni/CaO-γ-Al_2O_3. The Cao-γ-Al_2O_3 pores offer some spaces for active Ni access. Surface area of Al_2O_3 support that mainly is contributed by effect plays the dominating role during the impregnation process (Zhang et al, 2016).

Table 1. BET surface and pore size result by using BJH desorption data

Catalyst	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radian (Å)
Ni/CaO-γ-Al_2O_3	117.087	0.241	38.762
Ni/CaO-γ-Al_2O_3@Ru	127.566	0.435	38.177

Figure 1 shows three peaks with high intensity that are related to γ-AL_2O_3 at 2θ = 46°, 38° and 66.6° (JCPDS 96-110-1169). A peak at 2θ = 37.8° is indicated as NiO

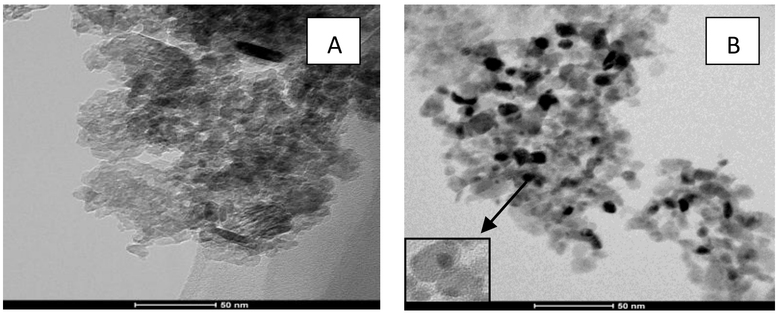

Fig. 2: TEM morphology of (A) Ni/CaO-γ-Al_2O_3, (B) Ni/CaO-γ-Al_2O_3@Ru core-shell in 50 nm scale

(JCPDS 21-0155). Peaks of CaO are assigned at 2θ = 37.5° and 67.2°. The obtained Ni/CaO-γ-Al_2O_3@Ru core shell sample showed sharp peaks at 2θ = 37.02°, 44.22°, and 77.82°, indicating the presence of RuO_2 and Ru metals (Valle et al, 2013). The diffraction peaks ascribed to $NiAl_2O_4$ indicated that the NiO reacted with Al_2O_3.

Table 2 shows that the element compositions composed of Ni, Ca, O, Al and Ru by using point analysis for ten points. The reduction average weight ratio of Ni and Ca is probably due to well dispersion of these particles on to the support.

Table 2. EDS analysis result of Ni/CaO-γ-Al_2O_3 and Ni/CaO-γ-Al_2O_3@Ru core shell

Catalyst	**Average weight ratio (%)**				
	Ni	**Ca**	**O**	**Al**	**Ru**
Ni/CaO-γ-Al_2O_3	5.30	1.69	47.21	45.76	-
Ni/CaO-γ-Al_2O_3@Ru	5.15	1.40	49.68	43.68	0.10

The TEM morphology of catalyst structures before and after micro-emulsion is shown in **Figure 2**. The core-shell morphology keeps well after loaded with Ru. The core and shell can be clearly seen on Figure 2B. The core is shown by black circle spot that is indicated by Ni particle. Ru is indicated as a shell that covers Ni/CaO-γ-Al_2O_3. Ru is one of the noble metal that used as promotor to enhance hydrogen yield (Majewski and Bujalski, 2013).

Performance of Steam Reforming of Bio-Oil Aqueous Fraction

The Ni/CaO-γ-Al_2O_3@Ru core shell prepared by micro-emulsion gave higher carbon conversion, hydrogen yield and lower coke deposit, compare to Ni/CaO-γ-Al_2O_3 catalyst. Carbon conversion can be calculated based on Eq. (5) according to the amount of converted carbon in to gas products such as CO, CO_2 and CH_4. Ni/CaO-γ-Al_2O_3@Ru core shell can increase carbon conversion of bio-oil much more than Ni/CaO-γ-Al_2O_3 catalyst.

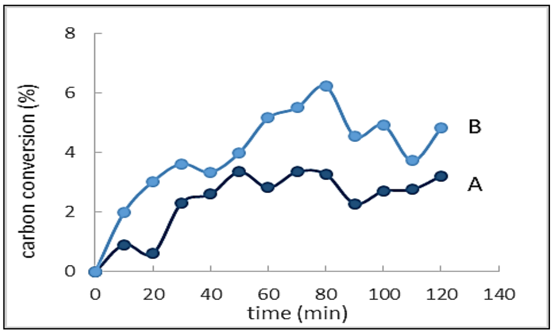

Fig. 3: Carbon conversion of steam reforming by using: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γ-Al_2O_3@Ru core shell

The B profile in **Figure 3** shows that carbon conversion increases during in minute 0 to 30 due to the yield of CO, CO_2 and CH_4 increase. The A and B profile data decreased in minute 80 to 90 because of CO_2 adsorption of catalysts. The B profile in minute 70 to 120 due to side reactions of CO, CO_2 and CH_4. It is happened because of catalyst coke deposition from nickel.

Carbon deposit was analyzed for the in bio-oil steam reforming reaction. The carbon deposit formation can occurs due to the Bouduard reaction in Eq. (6) as a side reaction of steam reforming. Catalyst can have better resistance to coke formation by adding Ru (See **Figure 4**). Coke deposit analysis results shows that Ni/CaO-γ-Al_2O_3 and Ni/CaO-γ-Al_2O_3@Ru core shell has 0.21g and 0.07g, respectively.

$$2\,CO \leftrightarrows CO_2 + C \qquad (6)$$

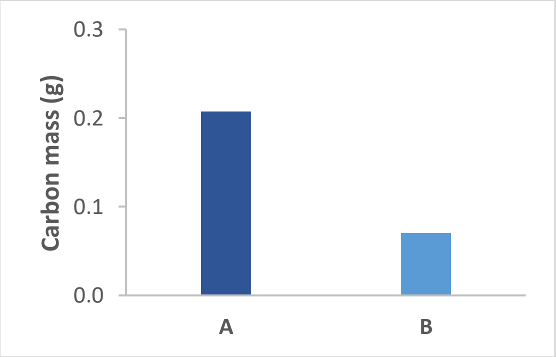

Fig. 4: Carbon deposit in: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γ-Al_2O_3@Ru core shell

Figure 5 shows the hydrogen yield as time function for Ni/CaO-γ-Al_2O_3 catalysts and Ni/CaO-γ-Al_2O_3@Ru core shell. As the reaction time increases in minute 10 to 40, the hydrogen yield decreases. It indicates that the catalysts are deactivated due to coke depositions and sintering of nickel. Besides, the other effects of side products such as CO, CO_2, CH_4 and other hydrocarbons (Valle et al, 2013). Ni/CaO-γ-Al_2O_3@Ru core shell can increase hydrogen yield because core shell has higher surface area, pore volume and can decrease catalytic performance. The highest hydrogen yield by using Ni/CaO-γ-Al_2O_3@Ru core shell is 5.6 % in minute 10.

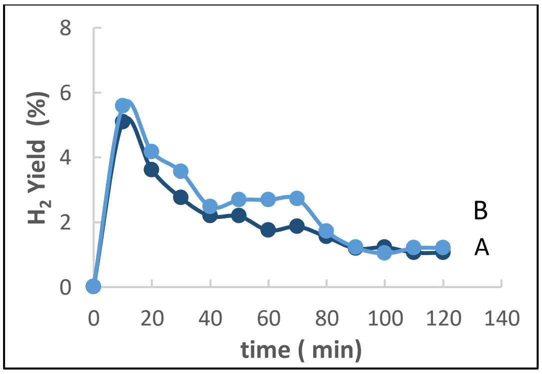

Fig. 5: H_2 yield of: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γ-Al_2O_3@Ru core shell

The high hydrogen yield can be affected by promoted Ru and formed core shell. The data shows that the addition of Ru can increase hydrogen yield. Ishihara et al (2005) reported that, in the effect of addition of Ru onto support of nickel steam reforming catalyst can enhance the catalytic performance. The presence of side products such as CO, CO_2 and CH_4 are needed to analyze for understanding about side reaction.

Figure 6 shows that Ni/CaO-γ-Al_2O_3@Ru core shell increases CH_4 yield production for bio-oil steam reforming until in minute 30. The strong interaction of Ni/CaO-γ-Al_2O_3@Ru core shell resulted more 68.4 % carbon conversion and 18.6% hydrogen yield than using Ni/CaO-γ-Al_2O_3

catalyst. The presence of more CO and H_2 gas production, will involve methanation reaction that can describe from reaction (7).

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \qquad (7)$$

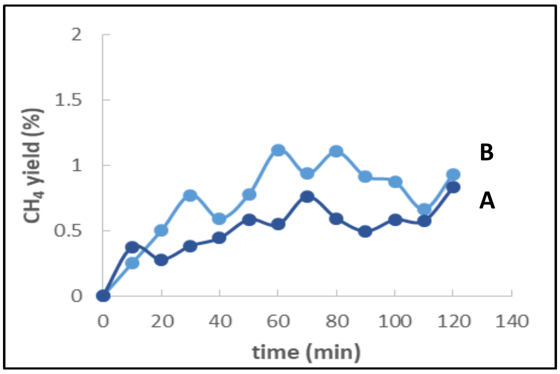

Fig. 6: CH_4 yield of: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γ-Al_2O_3@Ru core shell

For **Figure 7**, A in minute 10 to minute 60, CO yield increases due to reverse water gas shift (WGS) in Eq. (8) and steam reforming reaction. The reverse WGS reaction happened due to the presence of calcium that can increase base condition for CO_2 selectivity.

$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad (8)$$

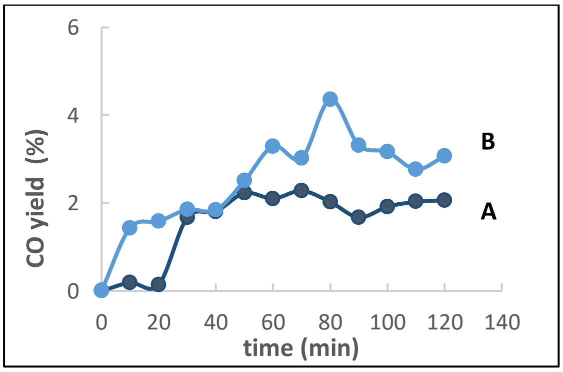

Fig. 7: CO yield of: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γ-Al_2O_3@Ru core shell

The influence by adding Ru can give CO_2 production (**Figure 8**). The Ni/CaO-γ-Al_2O_3@Ru core shell catalyst can increase CO_2 yield in minute 0 to 30 because of reverse reaction of Eq. 7.

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O \qquad (9)$$

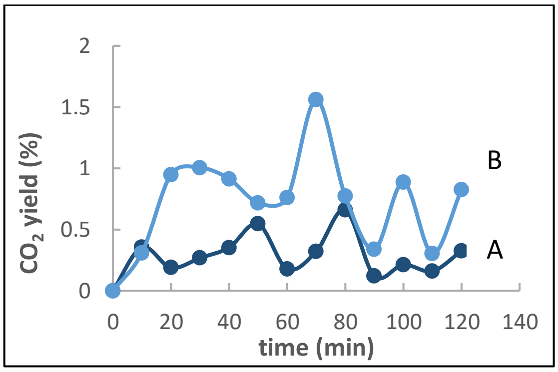

Fig. 8: CO_2 yield of: (A) Ni/CaO-γ-Al_2O_3 (B) Ni/CaO-γAl_2O_3@Ru core shell

CONCLUSION

The Ni/CaO γ-Al_2O_3@Ru core shell was prepared by using micro-emulsion. The highest hydrogen yield by using Ni/CaO-γ-Al_2O_3@Ru core shell is 5.6 % in minute 10 with 0.07 g of coke deposit. The strong interaction of Ni/CaO-γ-Al_2O_3@Ru core shell resulted more 68.4% carbon conversion and 18.6% hydrogen yield than using Ni/CaO-γ-Al_2O_3 catalyst. The core shell exhibited better activity in carbon conversion, hydrogen yield and coke deposit for bio-oil steam reforming than using Ni/CaO-γ-Al_2O_3 catalyst.

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