

## CATALYTIC ACTIVITY of Cu-CeO<sub>2</sub>-ZrO<sub>2</sub> for BIODIESEL PRODUCTION

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### ABSTRACT

Cu loaded on mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> support as acid catalyst was successfully prepared by deposition-precipitation method. The synthesized catalysts treated with sulfuric acid by wet-impregnation showed a good efficient activity for esterification reaction in biodiesel production. Mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> support was first synthesized via nanocasting process using MCM-48 as a hard template. All catalysts characterized by N<sub>2</sub> adsorption-desorption and XRD to confirm structure and dispersion of Cu on the support exhibited high surface area around 176 m<sup>2</sup>/g with 3.6 nm pore size. Moreover, the XRD result indicated that Cu species were well dispersed on mesoporous CeO<sub>2</sub>-ZrO<sub>2</sub> support. The catalyst activity was evaluated in esterification reaction using oleic acid and methanol via microwave technique to produce fatty acid methyl ester (FAME). The suitable conditions giving high %FAME of 94.28% are following: 2 M sulfuric acid for treating 5 wt% of catalyst, 12:1 molar ratio of methanol to oleic acid, 1.5 h reaction time at 60 °C reaction temperature.

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### INTRODUCTION

Biodiesel is a renewable and non-toxic biodegradable fuel. Biodiesel can be considered as an environmental friendly fuel produced from biomass and able to substitute fossil fuel. Moreover, the net CO<sub>2</sub> emission is rather low when taking into account its renewable origin and the toxic emission, such as CO, SO<sub>x</sub>, un-burned hydrocarbon, and char particles considerably reduced when burnt in Diesel engine. The cetane number, flash point, cold filter plug point and lubricant properties are acceptable to extend the engine life, which makes it is very interesting alternative fuel (Granados *et al.*, 2007).

In the past, the catalyst for biodiesel normally is homogeneous catalyst; which is fast reactive and easier to use. However, these catalysts are corrosive that not only can destroy the reactor in manufacture, but also cannot be reused. Alternatively, the heterogeneous catalyst could be reutilized without any complication for removing the catalyst. The activity of heterogeneous catalyst depends on their nature, active site, structure, morphology, porosity, and thermal stability (Ma *et al.*, 1999, Granados *et al.*, 2007, Avhad *et al.*, 2015). MCM-48 is one of the most interesting mesoporous materials because it has cubic structure and interconnected channel that provides resistant blocking and good mass transfer. The material has been evaluated to be used in various applications, such as, catalysts, catalyst supports, template for nanostructure preparation via nanocasting process, etc. (Motasemi *et al.*, 2012, Avhad *et al.*, 2015).

Cerium oxide ( $\text{CeO}_2$ ) or ceria is widely used in several reactions and has been reported as active material for esterification reaction. It is also a good candidate for using as catalyst support for biodiesel production because of its well-known ability to exchange lattice oxygen, oxygen storage capacity and stability (Ghesti *et al.*, 2009, Avhad *et al.*, 2015).

Zirconium dioxide ( $\text{ZrO}_2$ ) or zirconia is well-known to be used as heterogeneous acid catalyst, especially, sulfate zirconia for various organic reactions (Shay 1993, Verma *et al.*, 2016).

Both ceria and zirconia were used as support for copper catalyst in this study. Copper catalysts show acid property and high selectivity. Deposition-precipitation is a good pathway to load copper onto the support because it provides high dispersion of catalyst (Li *et al.*, 2013, Okoye *et al.*, 2016).

In many reactions, microwave irradiation is used to generate heat. Thus, the microwave irradiation is very attractive technology for transesterification, esterification, or hydrolysis reaction since the mixture is rapidly and homogeneously heated, leading to an increase reaction rate. As a result, this method is better than conventional method due to reducing time and saving energy (Mazubert *et al.*, 2013).

This research used ceria-zirconia as a support synthesized by nanocasting using MCM-48 as a hard template. The copper catalyst was loaded onto ceria-zirconia supports by deposition-precipitation method and treated with sulfuric acid for esterification reaction. The reaction was studied via microwave heating.

## EXPERIMENTAL

### A. Synthesis of mesoporous $\text{CeO}_2\text{-ZrO}_2$ (MSP CZ)

MSP-CZ was prepared by MCM-48 as a templated. Ethanol dissolves the  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ; the composition of Ce to Zr was equal to 0.75:0.25; under stirring at room temperature. After that, MCM-48 was added with continuously stirring for 4 h. The mixture was then taken into an oven at 100 °C. Then, the support was calcined at 550 °C for 6 h before removing the template using 2 M NaOH, followed by washing with deionized water (DI water) until neutral and drying at 80 °C overnight.

### B. Synthesis of Cu loaded mesoporous $\text{CeO}_2\text{-ZrO}_2$ catalyst (Cu-MSP CZ)

Copper loaded onto MSP CZ was prepared via deposition-precipitation (DP) technique by dissolving 9% wt of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in DI water before adding the synthesized supports and continuous stirring for 1 h. The mixture pH was adjusted to 7 by adding dropwise the precipitating agent,  $\text{Na}_2\text{CO}_3$ . After that, the mixture was heated at 80 °C for 1 h to age. Then, the resulting was filtered, washed, dried at 80 °C overnight, and calcined in air at 500 °C for 6 h. Finally, the catalyst was obtained.

### C. Treated catalyst by sulfuric acid (SCu-MSP CZ)

Cu-MSP CZ (0.3 g) was treated with various sulfuric acid concentrations. The catalysts were kneaded for 30 min and heated at 100 °C overnight.

### D. Catalytic activity for biodiesel production

The reactants, oleic acid, methanol, and catalysts were mixed and stirred for 5 min. After that, the mixture was placed into a microwave reactor vessel. The reaction temperature and

time for esterification reaction were varied to obtain the optimal condition. Then, the obtained product was centrifuged to separate catalyst from biodiesel mixture before heating at 80 °C for 1.5 h.

### E. Characterization

The catalysts were characterized using Quantasorb Jr. (Autosorb-1) and a Rigaku DMAX 2200HV X-ray diffractometer (XRD). The obtained biodiesel (Fatty acid methyl ester) was determined by Gas chromatography (GC) on Hewlett-Packard 5800 GC equipped with 100 m × 0.25 mm HP-88 fused-silica capillary column. The detector and the oven temperatures were set at 230° and 130 °C, respectively.

## RESULTS AND DISCUSSION

### A. Characterization of catalyst

The MSP CZ support prepared by nanocasting process showed the fluorite cubic structure of ceria (CeO<sub>2</sub>) at 2 $\theta$  = 28.5°, 32.9°, 47.5°, 56.2°, 59.1°, 69.0°, 76.7°, and 78.9°. The XRD result showed no peak at 2 $\theta$  = 22°, indicating the absence of amorphous silica, thus implying that the template was completely removed (Zhang *et al.*, 2006).

The surface area measurement of MSP CZ using N<sub>2</sub> adsorption-desorption showed isotherm type IV with H3 hysteresis loop, indicating the mesoporous structure. The pore size of MSP CZ was equal to 3.62 nm and the surface area was around 240 m<sup>2</sup>/g. This obtained high surface area is due to the structure copied from MCM-48, which is interconnected channel and ordered structure (Ji *et al.*, 2008).

The WAXD result of Cu-MSP CZ exhibited diffraction peaks at 2 $\theta$  = 28.5°, 32.9°, 47.5°, 56.2°, 59.1°, 69.0°, 76.7° and 78.9°, corresponding to the fluorite-type cubic crystal of ceria phase. The peak of Cu species was not observed, meaning that Cu was well dispersed on the support. Therefore, it can be stated that deposition-precipitation technique is a suitable and effective method to load Cu onto MSP CZ supports. The surface area of the catalyst was lower than that of MSP CZ, probably due to the deposition of Cu on the support without agglomeration since the pore size did not change (Jia *et al.*, 2010).

### B. Catalytic activity

The activity of SCu-MSP CZ catalyst was evaluated on esterification reaction using oleic acid and methanol as reactants. The optimum condition was examined by varying concentration of sulfuric acid, molar ratio of methanol to oleic acid, reaction temperature, reaction time, and % loading of the catalyst.

It was found that the concentration of H<sub>2</sub>SO<sub>4</sub> affected to the esterification product by increasing %FAME from 61.3 to 85.6% when increasing H<sub>2</sub>SO<sub>4</sub> concentration from 1.0 to 2.0 M. The reaction reached constant when the concentration was beyond 2.0 M since water, as by-product, deactivated the active site of the catalyst. As a result, 2.0 M H<sub>2</sub>SO<sub>4</sub> was the optimum concentration (Shu *et al.*, 2010, Grecea *et al.*, 2012).

When the molar ratio of methanol to oleic acid was varied from 9:1 to 12:1, %FAME increased from 76.2 to 86.4%, meaning that the excess methanol from stoichiometry of esterification affected the increase of %FAME. However, when the ratio of methanol to

oleic acid was increased more than 12:1, the %FAME decreased. This result is from the fact that excess methanol was adsorbed on the catalyst surface, resulting in reduction of the active sites (Motasemi *et al.*, 2012).

The reaction temperature and time are also important parameters for esterification reaction. Generally, if the temperature reaction increases, the reaction time will decrease. In this study, the temperature was increased from 60° to 90 °C, but the %FAME was hardly affected since the %FAME of SCu-MSP CZ was slightly increased from 86.4 to 88.8%. Thus, it is indicated that the reaction does not depend on temperature (Zu *et al.*, 2009). In contrast, the reaction time seemed to be more affected to %FAME. Increasing the reaction time from 30 min to 1.5 h, the %FAME rapidly increased from 74.6 to 89.1%, and became steady after 1.5 h reaction time (Doyle *et al.*, 2016). Consequently, the reaction time of 1.5 h was the optimum time.

The amount of catalyst in esterification was studied at 3, 5, 7, and 9 wt%. From the study, this parameter was the most important for biodiesel production. %FAME increased from 74.6 to 94.3% when increasing the amount of catalyst from 1 to 5 wt%, and then decreased to 90.6% when the amount of catalyst was beyond 5%. This phenomenon can be explained that excess amount of catalyst can accelerate the reversible reaction of esterification (Mazubert *et al.*, 2013). The suitable condition in this case for SCu-MSP CZ was 5wt%.

The reusability of catalyst was evaluated after obtaining the optimal conditions and investigated for 3 cycles. After each test, the activity of the catalysts significantly decreased from around 94 to 67 and 30% because H<sub>2</sub>SO<sub>4</sub> was leached out (Patel *et al.*, 2013).

## CONCLUSIONS

MSP CZ was successfully synthesized via nanocasting process using MCM-48 as template. Copper loaded MSP CZ was prepared via deposition-precipitation technique. The WAXD pattern of Cu-MSP CZ showed no diffraction peaks of Cu species due to good dispersion. Both MSP-CZ and Cu-MSP CZ provided high specific surface area although Cu-MSP CZ had lower surface area. Cu-MSP CZ treated with sulfuric acid via wet impregnation method to increase acidity of the catalysts gave a higher catalytic activity on esterification reaction using oleic acid and methanol as reactants. The optimal conditions providing high %FAME of 94.28% were to use 5wt% catalyst treated with 2.0 M sulfuric acid, 12:1 methanol:oleic acid, and 60°C reaction temperature for 1 h.

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