

Catalytic activity of Cu-CeO₂-ZrO₂ for biodiesel production

W. Wongvitvichot, S. Jampa, A. Luengnaruemitchai, T. Chaisuwan, and S. Wongkasemjit*

*The Petroleum and Petrochemical College, Chulalongkorn University,
BKK, Thailand, dsujitra@chula.ac.th

ABSTRACT

CeO₂-ZrO₂ has been synthesized by co-precipitation (CZ copre) and nanocasting (CZ nanocast) to use as support material for Cu catalyst, applied for esterification reaction in biodiesel production. The structure and specific surface area of synthesized supports were characterized by XRD and BET techniques. The specific area of CZ copre less than CZ nanocast supports. 9%wt Cu catalyst were loaded onto CZ copre (CuCZ copre) and CZ nanocast (CuCZ nanocast) by deposition-precipitation method (DP). XRD result of CuCZ copre exhibits the diffraction peak of CuO, indicating the agglomeration of Cu species on support. While, CuCZ nanocast does not presents peaks from CuO crystallites. It means Cu is high dispersing. These catalysts were treated with sulfuric acid. The catalytic activity was using oleic acid, methanol, and operating by the energy-efficient microwave. The optimal condition of these catalyst is 2.0 M Sulfuric acid on 5 wt% catalyst and 12:1 molar ratio at 60 °C on 1h.

Keywords: Cu-CeO₂-ZrO₂, biodiesel production

1 INTRODUCTION

Biodiesel (fatty acid methyl ester; FAME) is renewable energy and eco-friendly. It can substitute fossil fuel which is non-renewable energy and nearly extinct. Biodiesel is derived from triglyceride or free fatty acid with methanol. The conventional biodiesel is performed via alcoholysis that is composed of transesterification and esterification reaction. Both transesterification and esterification need a catalyst, either homogeneous or heterogeneous catalyst, to accelerate reaction [1, 2].

Porous materials have been widely studied for being used as catalysts or catalyst supports because of their high surface area and high absorption [2, 3]. Ceria (CeO₂) is a good candidate as catalyst support for biodiesel production because of its well-known ability to exchange lattice oxygen, oxygen storage capacity, and stability [2]. Zirconium dioxide (ZrO₂) or zirconia is also used as acid catalyst for biodiesel production, such as sulfate zirconia, that is well-known as heterogeneous acid catalyst for various organic reactions [4, 5].

Copper catalyst has good electrical and thermal conductivity and shows acid property with high selectivity. Thus, copper was loaded onto ceria and zirconia support via deposition-precipitation technique, resulting in highly strong interaction and well dispersion [6, 7].

Transesterification, esterification, or hydrolysis reaction can be conducted using conventional or microwave heating technique. The latter technique provides more advantages, e.g., reactants are rapidly heated, leading to an increase in the reaction rate. This method, thus, can reduce time and save energy [8].

In the research, ceria-zirconia supports were synthesized by nanocasting, using MCM-48 as a hard template, and co-precipitation methods. Copper was loaded onto ceria-zirconia supports by deposition-precipitation method. The synthesized catalysts were treated by sulfuric acid for esterification reaction via microwave technique.

2 EXPERIMENTAL

2.1 Synthesis of mesoporous CeO₂-ZrO₂ via nanocasting method (CZ nanocast)

CZ nanocast was synthesized using MCM-48 as a template by dissolving Ce(NO₃)₃·6H₂O and ZrOCl₂·8H₂O in 5 ml of ethanol under stirring at room temperature. The studied Ce:Zr composition was equal to 0.75:0.25. Then, MCM-48 was added and continuously stirred for 4 h. The mixture was taken into an oven at 100 °C. The obtained solid was calcined at 550 °C for 6 h. The product was then removed the template using 2 M NaOH, followed by washing with deionized water until neutral and drying at 80 °C overnight [9].

2.2 Synthesis of CeO₂-ZrO₂ by co-precipitate method (CZ copre)

Pojanavaraphan's synthetic method was followed by separately dissolving Ce(NO₃)₃·6H₂O and ZrOCl₂·8H₂O in 75 and 25 ml of deionized water, respectively. The studied Ce:Zr composition was equal to 0.75:0.25. These solutions were mixed together and adjusted pH to 8 by Na₂CO₃ as precipitating agent. The mixture was heated at 80 °C, followed by 1 h aging. Then the product was filtered, washed by distilled water, and dried at 80 °C overnight before calcination in air at 400 °C for 6 h [10].

2.3 Synthesis of Cu loaded mesoporous CeO₂-ZrO₂ catalyst (CuCZ nanocast and CuCZ copre)

CuCZ nanocast and CuCZ copre catalysts were synthesized via deposition-precipitation (DP) technique.

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (9 wt%) was dissolved in deionized water, followed by adding the synthesized supports and continuous stirring for 1 h. After that, Na_2CO_3 as precipitating agent was added dropwise to the mixture to adjust pH to 7. The mixture was then heated at 80 °C, followed by 1 h aging. The resulting solid was filtered, washed, and dried at 80 °C overnight before calcination in air at 500 °C for 6 h to obtain catalysts.

2.4 Treated catalyst by sulfuric acid (SCuCZ nanocast and SCuCZ copre)

Both CuCZ nanocast and CuCZ copre catalysts (0.3 g each) were treated with various concentrations of sulfuric acid. The samples were kneaded for 30 min and heated at 100 °C overnight.

2.5 Catalytic activity for biodiesel production

Oleic acid, methanol, and catalysts were mixed with stirring for 5 min and the mixture was transferred to a microwave reactor vessel. The microwave temperature and time were varied to obtain an optimal condition. The obtained mixture was centrifuged to separate catalyst from the biodiesel product mixture before heating at 80 °C for 1.5 h.

2.6 Characterization

The catalysts were characterized on a Rigaku DMAX 2200HV X-ray diffractometer (XRD) with a scanning speed of 1 °C/min and $\text{CuK}\alpha$ source ($\lambda = 0.154 \text{ \AA}$) in a range of $2\theta = 20^\circ - 80^\circ$, the Quantasorb Jr. (Autosorb-1), and Nicolet Nexus 670 Fourier transform infrared spectrometer (FT-IR). Fatty acid methyl esters was determined by Gas chromatography (GC) on Hewlett-Packard 5800 GC equipped with $100 \text{ m} \times 0.25 \text{ mm}$ HP-88 fused-silica capillary column. Helium was used as carrier gas with a flow rate of 70 mL/min. The injector temperature was set at 200 °C with a split ratio of 75:1; whereas the detector and the oven temperatures were set at 230° and 130 °C, respectively.

3 RESULTS AND DISCUSSION

3.1 Characterization of catalysts

XRD results of both CZ nanocast and CZ copre supports synthesized by nanocasting process and coprecipitation show the fluorite cubic structure of CeO_2 . Figures 1a and 1b show main peaks at $2\theta = 28.5^\circ, 32.9^\circ, 47.5^\circ, 56.2^\circ, 59.1^\circ, 69.0^\circ, 76.7^\circ,$ and 78.9° . CZ nanocast show no peak at $2\theta = 22^\circ$, indicating that the template was completely removed [11].

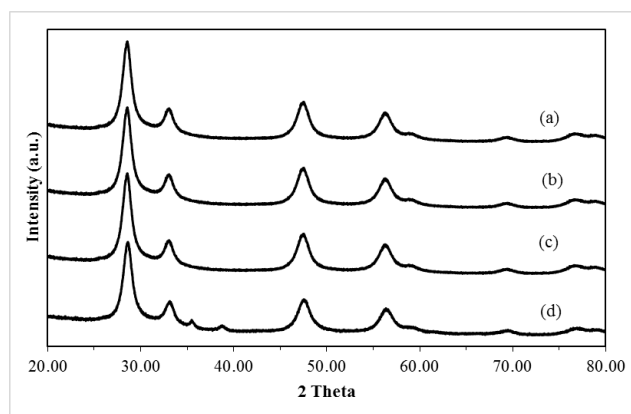


Figure 1: WAXD patterns of a) CZ nanocast, b) CZ copre, c) CuCZ nanocast, and d) CuCZ copre.

The CZ nanocast and CZ copre characterized by N_2 adsorption-desorption showed isotherm type IV and H3 hysteresis loop belonging to mesoporous materials. The pore size of both CZ nanocast and CZ copre shown in Table.1 was equal to 3.62 nm. The surface area of CZ nanocast was much larger than that of CZ copre due to the fact that the structure of CZ copre is not ordered structure and interconnected channel [10, 12].

Table 1: Properties of catalysts; CuCZ nanocast and CuCZ copre and supports; CZ nanocast and CZ copre.

Catalyst	Surface area (m^2/g)	Pore diameter (nm)
CZ nanocast	244.3	3.62
CZ copre	95.3	3.62
CuCZ nanocast	176.2	3.62
CuCZ copre	77.3	3.62

The WAXD patterns of CuCZ nanocast, as shown in Fig 1c, exhibited diffraction peaks at $2\theta = 28.5^\circ, 32.9^\circ, 47.5^\circ, 56.2^\circ, 59.1^\circ, 69.0^\circ, 76.7^\circ$ and 78.9° , corresponding to the fluorite-type cubic crystal of ceria phase whereas the CuCZ copre in Fig. 1d showed two more extra peaks at $2\theta = 35.53^\circ$ and 38.70° , which are characteristics of CuO presenting as agglomerates of Cu species; and this is why a lower surface area was observed [13, 14].

3.2 Catalytic activity

The catalytic activity of the synthesized catalysts was investigated on esterification reaction. The reactants for the esterification reaction were oleic acid and methanol. The concentration of sulfuric acid, molar ratio of methanol to oleic acid, reaction temperature, reaction time, and %loading of the catalyst were examined for the optimum condition.

H_2SO_4 concentration affected the reaction by increasing concentration from 1.0 to 2.0 M which causes the increase of %FAME from 61.3 to 85.6% for SCuCZ nanocast and from 71.2 to 81.2% for SCuCZ copre, and the

yield became steady when using H_2SO_4 concentration beyond 2.5 M since the water, as by-product can deactivate the active site of the catalyst [15, 16]. As a result, 2.0 M H_2SO_4 was considered as the optimum condition.

The molar ratio of methanol to oleic acid was varied from 9:1 to 15:1. It was found that the excess methanol affects the increase of %FAME from 76.2 to 86.4% for SCuCZ nanocast and from 82.3 to 87.4% for SCuCZ copre when the molar ratio of methanol to oleic acid was varied from 9:1 to 12:1. The %FAME decreased with increasing the ratios more than 12:1 since the excess methanol can adsorb on the catalyst surface, inhibiting oleic acid to contact with the active site of catalyst [3].

The temperature is one of the most important parameter for esterification. However, in this study, the temperature did not have much effect on the %FAME for both types of catalysts even though the temperature was increased from 60° to 90 °C.

When the reaction time increases from 30 min to 1.5 h, the %FAME dramatically increased from 74.6 to 89.1% for SCuCZ nanocast before became steady. For SCuCZ copre, %FAME increased from 78.8 to 88.3% when the reaction time increased from 30 min to 2 h. As a result, the 1.5 h was chosen as the optimum time for esterification [17].

Effect of the catalyst amount on esterification was studied at 3, 5, 7, and 9wt%. For SCuCZ nanocast, %FAME increased from 74.6 to 94.3% and decreased to 90.6% when the amount of catalyst increases from 1 to 5 wt% and 5 to 9wt%, respectively. Likewise, %FAME of the SCuCZ copre increased to 99.0% when amount of catalyst increased to 5wt% and decreased when more catalyst was added. This phenomenon indicates that excess amount of catalyst can accelerate the reversible reaction of the esterification. The suitable amount of the catalyst for both SCuCZ copre and SCuCZ nanocast was 5wt% [8].

As a summary, SCuCZ copre showed better activity, than SCuCZ nanocast since the Cu species were well disperses on the SCuCZ nanocast surface and pores while the Cu species on the SCuCZ copre stayed on the surface only. Moreover, since a diameter of oleic acid as reactant (around 2.5 nm) is close to the pore diameter of SCuCZ nanocast, it was hard for a molecule to penetrate inside the pore. Therefore, SCuCZ copre had more catalyst active sites to react with the reactants than SCuCZ nanocast [18].

4 CONCLUSIONS

Copper was well disperse in CuCZ nanocast while the WAXD pattern of CuCZ copre showed diffraction peaks of Cu species. The CZ and CuCZ nanocast provided the higher specific surface areas than the CZ and CuCZ copre. The treated CuCZ nanocast and CuCZ copre catalysts with sulfuric acid by wet impregnation method showed the higher catalytic activity evaluated via esterification reaction using oleic acid and methanol as reactants. The optimal conditions providing the highest %FAME were to use 5wt% catalyst treated with 2.0 M sulfuric acid, 12:1

molar ratio of methanol:oleic acid at 60 °C for 1h, giving 99.0 and 94.3% FAME for SCuCZ copre and SCuCZ nanocast, respectively.

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