Binary metal oxides supported on $\gamma$-Al$_2$O$_3$ for application in transesterification of low-grade cooking oil

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Graphical abstract

1. Triglycerides
2. Methanol
3. Fatty acid methyl ester (FAME)
4. Glycerol

Abstract

Recently, the production of biodiesel has increased greatly due to the less harmful effects of this fuel towards the environment which is sourced from renewable materials compared to a conventional diesel. The aim of this study is to produce biodiesel using low-grade cooking oil by heterogeneous base catalyzed transesterification reaction. The series of solid base catalysts, binary metal oxide (Cu/Zn) were synthesized by the modified wet impregnation method supported on $\gamma$-Al$_2$O$_3$. The investigation of Cu/Zn/$\gamma$-Al$_2$O$_3$ catalyst on the calcination temperature, copper loading and number of alumina coatings had significantly affected the catalytic performance. The optimum conditions from experimental data were achieved with 10 wt% of Cu loading of Cu/Zn/$\gamma$-Al$_2$O$_3$ catalyst calcined at 800°C with 3 times number of alumina coatings exhibited the highest fatty acid methyl ester (FAME) yields, 87.07% at mild reaction conditions (65°C, atmospheric pressure, 1:20 methanol-to-oil molar ratio, 10 wt% of catalyst loading and 2 hours of reaction time). The physicochemical properties studied by BET surface area of Cu/Zn(10:90)/$\gamma$-Al$_2$O$_3$ catalyst calcined at 800°C which gave high surface area, 149.32 m$^2$/g. FESEM-EDX analysis of Cu/Zn(10:90)/$\gamma$-Al$_2$O$_3$ catalyst indicated the amorphous in structure with undefined shapes and mixture of larger and smaller particles sizes. The production of biodiesel and the percentage conversion of FAME was analyzed by using GC-FID in the presence of methyl palmitate, cis-9-oleic acid methyl ester and methyl linoleate.

Keywords: Binary metal oxides, biodiesel, transesterification, catalytic performance

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INTRODUCTION

Recently, the depleting of the earth’s finite resource such as fossil fuel and the emissions of greenhouse gases in the environment is unsustainable that lead to the much interest in converting biomass resources into biodiesel as an alternative substituted energy (Hameed et al., 2009; Atadashi et al., 2011; Nakatani et al., 2009). As the world is experiencing rapid social, economic and environmental transformation, many researchers are study on topic of biodiesel production and development.

Biodiesel which recognised as a fatty acid methyl ester (FAME) is known as a clean-burning fuel, since it is biodegradable, nontoxic, sulfur and aromatic-free that produce less air pollutants in comparison with petroleum-based fuels (Nas and Berktay, 2007). This new source of energy can be derived from renewable resources such as vegetable oils including palm, sunflower, rapeseed, canola and soybean oil (Granados et al., 2007; MacLeod et al., 2008).

Several modification techniques have been developed to biodiesel production and application such as direct use of vegetable oil, microemulsions, pyrolysis and transesterification (Farobie and Matsumura, 2015; Shuit et al., 2012; Avhad et al., 2015). Recently efforts have been focused on the use of heterogeneous catalysts due the simplifying of biodiesel production and purification steps resulted in declining amount of waste water (Gao et al., 2009). The heterogeneous catalysts that most commonly used in transesterification of biodiesel are single metal oxides such as calcium oxide, zinc oxide, magnesium oxide and inorganic compound due to its cheap price, relatively high basic strength and less environmental impacts.

Much interest has been taken in the application of structure promoters or catalyst supports which can provide more specific surface area and pores for active species (Zabeti et al., 2009). Furthermore, to increase the basic strength of a single metal oxide, mixed metal oxides are synthesized. Therefore, in this study, the modification with more active substance in order to prepare a base heterogeneous catalyst was introduced in biodiesel production due to the environmental constraints and simplifications in the existing process. This modified base heterogeneous catalyst, Cu/Zn/$\gamma$-Al$_2$O$_3$ which are non-leaching and recyclability for the transesterification of biodiesel has not been revealed.

EXPERIMENTAL

Materials

Zinc nitrate hexahydrate, Zn(NO$_3$)$_2$.6H$_2$O, copper(II) nitrate trihydrate, Cu(NO$_3$)$_2$.3H$_2$O, gamma-alumina oxide (beads), $\gamma$-Al$_2$O$_3$, methanol, CH$_3$OH and n-hexane, C$_6$H$_{14}$ were purchased from Merck. All chemicals and solvents were used without further purification. The low-grade cooking oil was obtained from local market.

Catalyst preparation

The bimetallic oxides catalysts were prepared by using wet impregnation method supported on $\gamma$-Al$_2$O$_3$ (specific area 253 m$^2$/g and 3-5 mm diameter). Cu(NO$_3$)$_2$.3H$_2$O as a dopant was dissolved into 5 mL of distilled water according to the dopant ratio to based. About 5.0 g of Zn(NO$_3$)$_2$.6H$_2$O as a based metal oxides were dissolved into 5 mL of distilled water. Both based and dopant solutions were mixed and
dissolved together. Then, 5.0 g of γ-Al₂O₃ that is most widely used as support material was dipped into precursor solution within 1 hours varied with 1 to 5 times of coating respectively. After coating, γ-Al₂O₃ beads were aging at ambient room temperature and followed by at temperature of 80 to 90°C in the oven for 24 hours to remove water and to allow good coating of the metal on the surface of the supported catalysts. Then, the samples were calcined at temperature of 700, 800 and 900°C for 5 hours using a ramp rate of 5°C/min to eliminate all the metal precursor impurities.

**Catalyst characterization**

The prepared catalysts were characterized using Brunauer Emmett Teller (BET), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX). The nitrogen adsorption analysis of the catalyst was studied using Micromeritics ASAP 2010. Prior to analysis, the 0.2-0.3 g of powder sample was degassed at 120°C to remove the previously adsorbed gasses and evacuating the dead space by vacuum pump to cool at room temperature. The specific surface area was calculated from the adsorption curve according to the Brunauer–Emmett–Teller (BET) method.

FESEM-EDX analysis was accomplished by using Philips XL 40 microscope with energy of 15.9 kV coupled with EDX analyser and bombarded using electron gun with tungsten filament under 25 kV resolutions to get the required magnification image. EDX was used in this study to determine the elemental composition on the submicron scale. The supported catalyst sample was attached by carbon tape on this study to determine the elemental composition on the submicron scale. The supported catalyst sample was attached by carbon tape on the carbon coated stub, coated with platinum using a platinum sputter at 10⁻¹ Mbar using a Bio Rad Polaron Division SEM coating system machine. The sample was bombarded using an electron gun with a tungsten filament under 25 kV resolutions in order to get the required magnification image.

**Catalytic reaction and product analysis**

About 1.2 g of the prepared catalyst, 18.5 g of methanol and 20.0 g of low-grade cooking oil were added into a two-necked round bottom flask and refluxed at 65 ± 5°C for 3 hours to complete the transesterification reaction. The mixture was centrifuged at 3000 rpm for 10 min to separate the solid catalyst from the solution. Three layers were obtained after the centrifugation. An excess of methanol at the top layer, a biodiesel at middle layer and the bottom layer was catalyst samples and glycerol. The biodiesel was collected for further analysis, the 0.2-0.3 g of powder sample was degassed at 120°C to remove the previously adsorbed gasses and evacuating the dead space by vacuum pump to cool at room temperature. The specific surface area was calculated from the adsorption curve according to the Brunauer Emmett Teller (BET), Rosid et al. (2014) proposed that the well-defined morphology of the catalyst calcined at higher temperature (Abdullah et al., 2014) showed more agglomeration and their catalyst surfaces were densely packed. It is due to the sintering effect that occurred during the calcination process hence form larger particle size. It was expected that the dense packed surface of catalyst leads to the reduction of surface area as well as the catalytic activity performance. Oh et al. (2007) and Rosid et al. (2014) proposed that the well-defined morphology of the catalyst surface was highly correlated with the calcination temperatures of catalysts.

**Energy Dispersive X-ray (EDX)**

Table 2 shows the chemical compositions expressed as weight percentage over Cu/Zn(10:90)/γ-Al₂O₃ catalyst obtained from EDX analysis. The composition of the Al was determined to be around 46.00 – 49.00 wt% over all the catalysts prepared. Meanwhile, the composition of Cu/Zn(10:90)/γ-Al₂O₃ catalyst calcined at various calcination temperatures showed slight differences with its original composition. The detected Cu content decreased from 3.90 wt% at temperature of 700°C to 2.00 wt% at temperature of 800°C and increased to 3.60 wt% at calcination temperature of 900°C. This was probably due to the increase of particles size and the agglomeration of Cu particles that occurred on the surface of the catalyst after being calcined at higher temperature (Abdullah et al., 2014). As can be seen, Cu and Zn elements in Cu/Zn(10:90)/γ-Al₂O₃ calcined at 800°C was more active during the reaction as it was able to convert a maximum 87.07% of biodiesel. The BET surface area decreased drastically to 53.09 m²/g when the catalyst was calcined at 900°C due to the partially collapsed of the pore structure after its contact with the catalyst at the higher calcination temperature. It will lead to the increasing of particle size of the catalyst and thus, surface area will be reduced (Rao et al., 2011).

Field Emission Scanning Electron Microscopy (FESEM)

Figure 1 shows that an increase in calcination temperature from 700 to 900°C leads to the formation of aggregates with undefined shapes and mixture of larger and smaller particles size. Such morphology of Cu/Zn(10:90)/γ-Al₂O₃ catalyst calcined at 800°C should provide the space for the access of active metal components to attract hydrogen molecules on the catalyst surface. However, when the calcination temperature reached at 900°C, it showed more agglomeration and their catalyst surfaces were densely packed. It is due to the sintering effect that occurred during the calcination process hence form larger particle size. It was expected that the dense packed surface of catalyst leads to the reduction of surface area as well as the catalytic activity performance. Oh et al. (2007) and Rosid et al. (2014) proposed that the well-defined morphology of the catalyst surface was highly correlated with the calcination temperatures of catalysts.

**RESULTS AND DISCUSSION**

**Catalytic activity tests**

The synthesized binary metal oxides catalysts, Cu/Zn/γ-Al₂O₃ were tested in the transesterification reaction of low-grade cooking oil at identified reaction conditions which were reaction temperature of 65°C, oil to methanol ratio of 1:24, reaction time of 3 hours and catalyst loading of 6 wt%. The series of Cu/Zn/γ-Al₂O₃ catalysts were varied with the different calcination temperatures (700 to 900°C), percentage of Cu loading (5 to 30 wt%) and number of alumina coatings (1 to 5 dip). The optimum conditions from experimental data were achieved with 10 wt% of Cu loading of Cu/Zn/γ-Al₂O₃ catalyst calcined at 800°C with 3 times number of alumina coatings exhibited the highest fatty acid methyl ester (FAME) yields, 87.07% due to the most optimum active sites strength for biodiesel reaction. Based upon the experimental results, Cu/Zn (10:90)/γ-Al₂O₃ catalyst calcined at 800°C was selected for further studies to optimize the biodiesel production from low-grade cooking oil.

**Table 1** The specific BET surface area, \(S_{BET}\) or Cu/Zn(10:90)/γ-Al₂O₃ catalyst calcined at different temperatures for 700, 800 and 900°C for 5 hours.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination Temperature (°C)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Zn(10:90)/γ-Al₂O₃</td>
<td>700</td>
<td>146.77</td>
</tr>
<tr>
<td>Cu/Zn(10:90)/γ-Al₂O₃</td>
<td>800</td>
<td>149.32</td>
</tr>
<tr>
<td>Cu/Zn(10:90)/γ-Al₂O₃</td>
<td>900</td>
<td>53.09</td>
</tr>
</tbody>
</table>

**Table 2** shows the chemical compositions expressed as weight percentage over Cu/Zn(10:90)/γ-Al₂O₃ catalyst obtained from EDX analysis. The composition of the Al was determined to be around 46.00 – 49.00 wt% over all the catalysts prepared. Meanwhile, the composition of Cu/Zn(10:90)/γ-Al₂O₃ catalyst calcined at various calcination temperatures showed slight differences with its original composition. The detected Cu content decreased from 3.90 wt% at temperature of 700°C to 2.00 wt% at temperature of 800°C and increased to 3.60 wt% at calcination temperature of 900°C. This was probably due to the increase of particles size and the agglomeration of Cu particles that occurred on the surface of the catalyst after being calcined at higher temperature (Abdullah et al., 2014). As can be seen, Cu and Zn elements in Cu/Zn(10:90)/γ-Al₂O₃ calcined at 800°C was more active during the reaction as it was able to convert a maximum 87.07% fatty acid methyl esters yield.
Effect of percentage of catalyst loading

Figure 3 illustrates the effect of catalyst loading towards percentage conversion of biodiesel using Cu/Zn(10:90)/γ-Al₂O₃ as catalyst. Catalyst amount is one of the most important factors that affect the biodiesel production in the transesterification reaction. From previous study, it showed that different amounts of catalyst loading affect the percentage conversion of biodiesel (Wang and Yang, 2007). Based on the results, it was found that the surface area should give higher activity. The effect of the catalyst amount with biodiesel production was studied by varying wt. % loading of Cu/Zn(10:90)/γ-Al₂O₃ catalyst which were 2 to 13 wt% respectively with 3 hours reaction time.

Based on these results, it showed that 10 wt% catalyst loading performed the optimum percentage conversion of biodiesel, 84.27%. The percentage yield was increased with the increasing of catalyst loading because the catalyst provides more active sites for reaction. This suggested that at 10 wt% catalyst loading contact between the reactants and solid catalyst was maximum which directly influenced the forward transesterification reaction speed, thus provided maximum biodiesel yield. For the 2 wt% catalyst loading, the percentage conversion of biodiesel was low with only 59.82% due to the less active surface area of catalyst present. It gave lower defect sites that could decrease the conversion of biodiesel. When 13 wt% catalyst loading was applied in the reaction, the percentage conversion of biodiesel was decreased at similar reaction conditions. This was due to the mixing problems of the reaction mixture involving reactants, products and solid catalyst.

Effect of reaction times

Figure 4 shows the effect of reaction time towards the percentage conversion of biodiesel with 10% of catalyst loading. It showed that the percentage conversion was increased with increasing the reaction time from 1 to 2 hour. The rate of transesterification reaction is strongly influenced by the reaction time. The conversion increased progressively with increasing reaction time and then reached optimum value representative of a nearly equilibrium conversion. Cu/Zn(10:90)/γ-Al₂O₃ catalyst gave a maximum conversion at 2 hour reaction time was 87.07%. After 2 hour reaction time, the biodiesel yield was decreased due to reverse reaction which was the formation of triglycerides.
The transesterification process consists of a sequence of three consecutive and reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride, and finally into glycerin and the fatty acid methyl esters. The molar ratio of oil to methanol is one of the important factors that affect the conversion to methyl esters. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products.

Figure 4 illustrates the effect of oil to methanol ratio towards conversion of biodiesel. As shown in this figure, with an increase in the methanol-loading amount, the conversion was increased considerably. The maximum conversion was obtained when the molar ratio was 1:20. However, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of oil to methanol to produce methyl esters was 1:20 with 86.90% yield of biodiesel, 87.07% using Cu/Zn(10:90)/γ-Al2O3 catalyst calcined at 800°C with 86.90%.

CONCLUSION

As a conclusion, the optimum conditions for transesterification reaction was achieved 10 wt% catalyst loading at 2 hours reaction times with 1:20 wt% methanol to oil ratio which gave the highest percentage yield of biodiesel, 87.07% using Cu/Zn(10:90)/γ-Al2O3 as catalyst. The best conditions for catalyst obtained with 3 times number of alumina coatings, 10:90 dopant ratio to based and calcined at temperature of 800°C. The physicochemical properties studied by BET surface area supported the results of Cu/Zn(10:90)/γ-Al2O3 catalyst calcined at 800°C which gave high surface area, 149.32 m²/g, that influenced the catalytic activity of transesterification process. FESEM-EDX analysis of Cu/Zn(10:90)/γ-Al2O3 catalyst indicated the amorphous in structure with undefined shapes and mixture of larger and smaller particles sizes.

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