Biodiesel Production via Transesterification of Low Grade Cooking Oil over Heterostructure Nano Particles of Ni/Mg/Al₂O₃ Catalyst

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1. INTRODUCTION

Depleting of fossil fuel due to its global usage has become a worldwide crisis. The demands of fossil fuels for transportations, industrial processes and power generations may lead to the total distinction of these most valuable energy resources [1]. To overcome the problem, new sustainable energy resources has been introduced, particularly by production of biodiesel from biomass, non-edible oil and animal fat are the best solutions and become one of the promising alternative energy [2].

Biodiesel as one of alternatives fuel had been attracted researchers’ and scientists’ attention around the world due to the several advantages. Firstly, it was regard as a non-toxic and relatively produce a lower emission in contrast to petroleum based fossil fuel. Secondly, it was also eco-friendly in which it has no sulphur content that can cause acid rain formation [3]. Moreover, biodiesel has several good fuel properties such as good lubricity, carbon neutral and less emission of carbon dioxide in the atmosphere, a cetane number and cloud point which makes it volatile and easy to handle [4,5].

Biodiesel was synthesized from vegetable oils or animal fats and an alcohol, through a transesterification reaction [6]. This chemical reaction converts an ester into a mixture of esters of the fatty acids that makes up the oil. It was obtained from the purification of the mixture of fatty acid methyl esters (FAME) and the

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catalyst was used to accelerate the reaction as given in Equation (1).

Previous studies suggested that the catalysts used in transesterification can be basic, acidic or enzymatic [7]. In industrial development, most common method to produce biodiesel is through transesterification of vegetable oil with methanol using liquid base catalysts such as NaOH, KOH and CH₃ONa [8, 9]. However, they are highly corrosive, and technically difficult to remove from the final product. Therefore, conventional homogeneous base catalysts need to be replaced by solid strong heterogeneous base catalysts, which are more environmentally friendly, low cost of production, less time consuming and can be recycle [10].

According to Kesic et al. [11] by introducing active species on porous support material like alumina gave high catalytic activity compared to the unsupported catalyst. A study reported that, the nature of alumina support played an important role on the catalytic activity. Among the support materials, Al₂O₃ shows higher activity, due to sufficient stability and dispersion properties and also enhanced surface reactants interaction [12].

It has been reported that the support materials can greatly affect the performance of catalysts. For example, immobilizing Ni nanoparticles inside the pore channels of order mesoporous alumina matrix by the confinement effect of the mesopores can prevent the sintering of Ni particles. However, among them, the addition of modifiers, including alkali, alkaline earth, and rare-earth metal oxides was widely reported to be an effective strategy which can provide more basic sites on the surface of the catalysts [13].

Therefore, the present study focus on introducing bimetallic catalyst Ni/Mg/Al₂O₃ used in transesterification of low grade cooking oil to biodiesel. The catalyst then was characterized to investigate the properties that lead to the highest performance in biodiesel production.

2. EXPERIMENTAL

2.1 Materials Low grade of palm cooking oil was purchased from the commercial market. Chemicals such as Ni(NO₃)₂.6H₂O (dopant), Mg(NO₃)₂.6H₂O(base), γ-Al₂O₃ 3-5 mm (beads) and methanol (CH₃OH) were purchased from Sigma-Aldrich. All chemicals used were analytical reagent grade.

2.2 Catalyst Preparation In this study, aqueous incipient wetness impregnation method was applied to prepare series of catalysts. Nitrate salts were used as metal precursors since the solubility was high in water. 5 g of base (M⁺ = Mg) was weighed in a small beaker and dissolved it in distilled water to obtained 5 mol/L of Mg(NO₃). The solution was stirred continuously for 15 minutes by a magnetic stirrer to homogenize the mixture at ambient temperature. The mixed catalyst solution was prepared for addition of second (M⁺⁺ = Ni) metal salt solution with base catalyst solution according to the molecular weight with different ratio (10:90, 20:80 and 30:70). After the solution was homogenized, 5g of Al₂O₃ with diameter of 4 mm to 5 mm was immersed in the solution mixture until the solution was evenly absorbed on the surface of the support. The support then was filtered and transferred onto glass wool. Next, the catalyst was aged in the oven for 24 hours at 80-90°C. After that, it was calcined in the furnace at 600°C for 5 hours using a ramping rate of 5°C/min to eliminate all metal counter ions and water molecule. The similar procedure was repeated for all catalyst preparation at different calcinations temperature.

2.3 Catalytic Activity The catalytic activity of the potential catalyst was evaluated using the transesterification of low grade palm oil with methanol. Transesterification reaction was carried out in a three necked round bottom flask under refluxed with constant stirring. 6% w/w of catalyst loading with 1:24 ratio oil to methanol was added to the reaction mixture and heated at 65°C for 3 hours. After the reaction was completed the mixture was distilled for 15 minutes to remove excess methanol. The reaction mixture was then centrifuged for 30 minutes at 3000 rpm. The top layer was the biodiesel and the lower phase was by-product (glycerol). Catalytic performance of the potential catalyst from the transesterification reaction was analyzed using GC-FID SP2560 (100 m x 0.25 mm x 0.20 um) with split ratio 100:1 and helium gas as carrier.

2.4 Catalyst Characterization For NA analysis, Micromeritics ASAP 2010 was used to determine the surface area, pore volume and pore size of the potential catalyst. Prior to analysis, about 0.3g of the sample in powder form was degassed at 120°C in order to remove the previously adsorbed gases and evacuating the dead space by vacuum pump.

BIO-TEM specimen was prepared by dissolving small amount of the catalyst in powder form in appropriate amount of acetone in the 10 ml of glass.
vial. The solution mixture was dispersed using ultrasonic bath for 2 hours to provide better dispersion before it has been dropped onto the surface of the carbon filmed copper grid. The specimen was then dried for 30 minutes at 80-90°C to let the evaporation of the solvent before analysis was started.

The CO$_2$-TPD was done using Micromeritics Autochem 2920 to study the amount of basic sites present on the surface of the catalyst. 40-50 mg of the catalyst was placed in a quartz U-tube and cleaned under helium flow for 20 mL/min at 150°C for one hour. The temperature was ramped down to 40°C and the CO$_2$ gas was then flow continuously through the sample at 40°C for one hour. The gas flow was changed to He gas for another one hour at 80°C before subsequently ramped down to 40°C. The TPD was then carried out by ramp-up the temperature to 1000°C at 10°C/min and the response was recorded.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity

The catalytic screening performance of Ni/Mg/Al$_2$O$_3$ is indicated in Table 1. The catalyst was prepared based on three different parameters which is numbers of alumina coating, dopant ratio to base and calcinations temperature. These three parameters were used in order to study the effect towards biodiesel conversion.

From the data displayed in Table 1, catalyst calcined at temperature of 700°C with 20:80 dopant ratios to base and two times alumina coating gave 78.53% biodiesel conversion which recorded the highest value compared to others. Overall, it can be seen that calcination temperature was the main parameter that has major effects in the biodiesel conversion. Calcination temperature affect largely on the structural and catalytic properties of the catalyst [14]. Therefore, the effect of the calcination temperature for Ni/Mg/Al$_2$O$_3$ catalyst on biodiesel conversion was investigated.

As illustrated in Figure 1, the data shows that as the calcination temperature increased, the biodiesel production was significantly increased. Mostly, at calcination temperature 600°C the biodiesel conversion was low compared to 700°C. This phenomenon occurred might due to the calcination temperature was not sufficient enough to activate the catalyst [15].

The study also reveals that 700°C was the optimum temperature where the biodiesel conversion recorded was the highest with 78.53%. Previous study reported that when catalyst showed the highest activity at certain calcination temperature might due to the improvement and the dispersion of metal oxide.

<table>
<thead>
<tr>
<th>No of Coatings</th>
<th>Ratio Co-catalyst loading (wt%)</th>
<th>Calc. Temperature (ºC)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One time</td>
<td>20:80</td>
<td>600</td>
<td>63.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>69.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>58.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>61.25</td>
</tr>
<tr>
<td>Two times</td>
<td>20:80</td>
<td>600</td>
<td>71.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>71.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>62.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>60.87</td>
</tr>
<tr>
<td>Three times</td>
<td>20:80</td>
<td>600</td>
<td>68.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>80.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>56.36</td>
</tr>
</tbody>
</table>

Table 1. Percentage conversion of low grade oil to biodiesel using Ni/Mg/Al$_2$O$_3$

![Figure 1. Effect of calcination Temperature of Ni/Mg(20:80)/Al$_2$O$_3$ with two times alumina coating](image)
It also might be due to the changes that occurred on the surface structure (amorphous to polycrystalline structure) during the calcination process which lead to the generation of active species [16]. Furthermore, it strengthens the metal–support interaction and increase the number of medium strength basic sites on the catalyst surfaces [17].

After the calcination temperature of the catalyst was increased further to 800ºC, the biodiesel conversion was significantly reduced. At calcination temperature 800ºC, the biodiesel conversion was slightly lower which was 69.87% recorded. Some other studies reported a similar pattern. It has been reported that the performance of the catalyst was reduced due to the sintering effect and recrystallization metal oxide which gives in consequence decreasing of dispersion and catalyst activity, respectively [18].

Meanwhile, when dopant ratio to base was increased (as illustrated in Figure 2), the percentage conversion of biodiesel significantly decreased. Consistent with previous study which reported that, this phenomenon was due to the poor interactions between the active basic metal oxide and its support material [19]. The metals are easily migrated and sintered to form large metal particles which lead to the agglomeration on the surface of the catalyst. The agglomeration will cause a reduction in the active site and decreased the performance in catalytic activity [20].

The incorporation of nickel species as promoters could favour the Lewis basicity of the alumina supported catalyst, and mainly increase the strength basic sites, which could enhance the production of biodiesel [21]. Additionally, the increasing of the Ni species impregnated on the catalyst surface could also effectively hinder the formation biodiesel. It can be seen from the reducing of biodiesel conversion at 30:70 wt% of nickel to calcium.

For the effect of alumina coating, the present study discovered two times of alumina coating has been found as the optimum parameter for this effect. The conversion recorded slightly highest compared to others.
In order to study the relationship between catalytic activity and the characteristic of potential catalyst, Ni/Mg (20:80)/Al₂O₃ with 2 times alumina coating catalyst was selected. The catalyst was characterized to study on the surface area, surface morphology and the basic strength analysis at different calcinations temperature.

3.2. N₂ Adsorption Analysis  
Surface area of catalyst was recognized as an important factor in transesterification reaction. Thus, the activities of the catalyst calcined at different temperatures against their specific surface area were examined. A detail about the N₂ adsorption/desorption isotherms is illustrated in Figures 5. Meanwhile, the details on surface area, pore volume and pore sized at different calcinations temperature were recorded in Table 3.

From the results, Ni/Mg(20:80)/Al₂O₃ catalyst calcined at 700°C recorded the highest surface area of 139 m²/g followed by 125 m²/g for Ni/Mg(20:80)/Al₂O₃ calcined at 600 °C. As the temperature reached 800 °C the surface area reduced to 94 m²/g.

It shows that, as the calcination temperature increased, the surface area decreased. The decreasing in surface area of the catalyst at high calcination temperature was probably because of the modification of the catalyst structure in which the particle started to agglomerate and form a crystalline structure [24]. It can be conclude that, when the catalyst calcined at high temperature, the particles also tend to agglomerate intensively. Meanwhile, when the calcination temperature increased the surface area of Ni/Mg(20:80)/Al₂O₃ decreased, but the pore diameter and pore size increased. This was attributed to the agglomeration of magnesium oxide species, as well as of nickel oxide.

Table 3. BET surface area for Ni/Mg(20:80)/Al₂O₃ at different calcination temperatures and 3 times alumina coatings

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>125</td>
<td>0.33</td>
<td>118</td>
</tr>
<tr>
<td>700</td>
<td>139</td>
<td>0.34</td>
<td>111</td>
</tr>
<tr>
<td>800</td>
<td>94</td>
<td>0.37</td>
<td>162</td>
</tr>
</tbody>
</table>

3.3. Transmission Electron Microscopy (TEM)  
TEM analysis was used to verify the morphology of potential catalyst calcined at different temperature. Figures 5a, 5b and 5c show the TEM images with magnification of x60.0k with 20 nm scale for Ni/Mg(20:80)/Al₂O₃ catalyst calcined at 600,700 and 800 for 5 hours with 2 times alumina coating.

As shown in Figures 5a-5c, the particle with in homogeneous shape which is a mixture of square sheet and one dimensional heterostucture nano-rod particles were observed. The images showed that the majority of the sample catalyst composed with smaller particles (rod shape) size in the range of 3-15 nm and some of the larger particles (square sheet like shape) with size of ~100 nm.

However, the size of the rod particles becomes larger when the catalyst was calcined at 800°C (Figure 5c). In addition, the irregular size (6-13 nm) of platelet shape was observed. The dark-field of TEM image of this catalyst shows the presence of agglomerated particles on the surface of the catalyst [26].

Figure 4. Nitrogen adsorption-desorption isotherms for Ni/Mg(20:80)/Al₂O₃ catalyst calcined at different temperatures of 600°C,700°C and 800°C for 5 hours

Figure 5. BIO-TEM image for Ni/Mg(20:80)/Al₂O₃ catalyst calcined at different temperatures of a)600°C, b)700°C and c) 800°C for 5 hours

Figure 5. BIO-TEM image for Ni/Mg(20:80)/Al₂O₃ catalyst calcined at different temperatures of a)600°C, b)700°C and c) 800°C for 5 hours
From this observation, it can be concluded that when the calcinations temperature increased the surface of the catalyst was tending to agglomerate and reduce the surface area as reported in the BET results. This also contributes to the reducing of biodiesel conversion as reported in Table 1.

3.3. CO$_2$-Temperature Programmed Desorption (CO$_2$-TPD) Previous study found that an excellent transesterification process can be attributed to the presence of high basic sites on the surface of the prepared catalyst which can be measured using CO$_2$-TPD. The number of CO$_2$ molecules adsorbed per unit surface area can be considered as a measurement of the amount of basic sites on the surface of the catalyst [27].

The basic strength on the surface of the Ni/Mg (20:80)/Al$_2$O$_3$ catalysts shown in the Figure 6. It is illustrating that the CO$_2$-TPD plot for Ni/Mg (20:80)/Al$_2$O$_3$ catalyst at different calcination temperature range from 600 to 800°C. The temperature range for CO$_2$ adsorption was related to the strength of the basic sites presence.

Furthermore, the temperature range whereby CO$_2$ was desorbed correlated to the strength of the basic sites. The adsorption of CO$_2$ from 50-200 °C referred to the weak basic sites; while 200-400°C referred to the moderate basic sites and temperature range of 400-800°C correspond for strong basic sites [24].

The data summarized in Table 4 shows that the total amount of CO$_2$ desorbed (total basic sites) from the surface of the catalyst at calcination temperature 700°C (2.80 mmol/g) showed the highest followed by 600°C (2.79 mmol/g) and 800°C. It can be concluded that, as the temperature of calcinations process increased, the total basic sites also increased. However, as the temperature reached to 800°C, the total basic sites were dropped to 1.79 mmol/g compared to others.

The main factor that influenced transesterification activity is the alkalinity and the type of basic strength of the catalysts [28].

![Figure 6. CO$_2$-TPD curves for Ni/Mg(20:80)/Al$_2$O$_3$ at calcination temperature of (a) 600°C, (b) 700°C and (c) 800°C, 5 hours and 3 times alumina coatings](image)

**TABLE 4.** Total amount of CO$_2$ desorbed (total basic sites) from the surface of the catalyst at different calcination temperature

<table>
<thead>
<tr>
<th>Calc. Temp. (°C)</th>
<th>Temp. at Maximum (°C)</th>
<th>Basic site Total basic site (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>123.1</td>
<td>0.2274</td>
</tr>
<tr>
<td></td>
<td>229.8</td>
<td>2.1077</td>
</tr>
<tr>
<td></td>
<td>830.2</td>
<td>0.0281</td>
</tr>
<tr>
<td></td>
<td>953.8</td>
<td>0.4257</td>
</tr>
<tr>
<td></td>
<td>124.0</td>
<td>0.1212</td>
</tr>
<tr>
<td>700</td>
<td>220.5</td>
<td>2.5049</td>
</tr>
<tr>
<td></td>
<td>812.7</td>
<td>0.0216</td>
</tr>
<tr>
<td></td>
<td>878.3</td>
<td>0.1562</td>
</tr>
<tr>
<td></td>
<td>140.4</td>
<td>0.2870</td>
</tr>
<tr>
<td>800</td>
<td>236.1</td>
<td>1.5009</td>
</tr>
<tr>
<td></td>
<td>960.2</td>
<td>2.984x10$^{-13}$</td>
</tr>
</tbody>
</table>

From the data obtained, Ni/Mg (20:80)/Al$_2$O$_3$ catalyst calcined at 700°C has the highest weak and moderates basic sites that contribute to the highest percentage conversion of low grade cooking oil to biodiesel compared to others.

It is also shows the similar trend with the BET surface area analysis where, the temperature increased the surface area decreased. The data obtained from BET surface area analysis and the CO$_2$-TPD analysis proved that high basicity and high surface area of Ni/Mg (20:80)/Al$_2$O$_3$ catalyst led to the highest percentage conversion of low grade palm oil to biodiesel.

4. CONCLUSION

In conclusion the result reveal that Ni/Mg/Al$_2$O$_3$ calcined at temperature 700°C, with ratio dopant to base 20:80 and 2 times alumina coating recorded the best performance in transesterification of low grade cooking oil to biodiesel. The calcination temperature was the highest influence parameter that contributed to the highest performance of the catalyst in transesterification reaction. In addition, this study confirmed that high surface area and high pore volume can improve the biodiesel performance in transesterification reaction. Based on surface morphology analysis in BIO-TEM indicated at calcination temperature 700 °C the catalyst shows one dimensional heterostucture nano-rod particles. According to the CO$_2$-TPD results, the basicity of the catalyst functions as an important role in base-catalyzed biodiesel production. In this case Ni/Mg (20:80)/Al$_2$O$_3$ catalyst calcined at 700 °C having the highest number of basic site which is determined as the prime contributor to the highest activity for the transesterification reaction.

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6. REFERENCES


Biodiesel Production via Transesterification of Low Grade Cooking Oil over Heterostructure Nano Particles of Ni/Mg/Al$_2$O$_3$ Catalyst

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Biodiesel is a clean and renewable fuel, which is produced from low grade cooking oil via transesterification over heterostructure nano particles of Ni/Mg/Al$_2$O$_3$ catalyst. The transesterification reaction is conducted at 65$^\circ$C for 3 hours using a molar ratio of 1:24 of oil to methanol. The catalysts were characterized by TEM, BET, and TPD. The catalyst Ni/Mg/Al$_2$O$_3$ (20:80)/Al with a surface area of 125 m$^2$/g and a specific surface area of 2.80 mmol/g was found to be the most active catalyst for Biodiesel production. The conversion of the low grade cooking oil was 78.53% after 3 hours of reaction. The biodiesel produced meets the international standards for biodiesel fuel.