Synthesis of SrO.SiO$_2$ Catalyst and Its Application in the Transesterification Reactions of Soybean Oil

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Abstract

The synthesis and characterization of SrO.SiO$_2$ were carried out. The rice hull ash was utilized as a source for SiO$_2$. The SrO.SiO$_2$ was prepared by sol-gel technique, and the ratios of SrO:SiO$_2$ were varied as 0:1, 1:0, 3:2, 2:4, and 2:7. The sol-gel was calcined at 800 °C for 4 hours. The result was characterized using XRD and FTIR. The diffraction pattern shows that the diffraction angle was shifted, and the intensity of the main peaks was increased. This research indicated that the crystallinity of SrO was improved at the higher SiO content. Further, a new peak was observed in the IR spectra at a wavenumber of 900 cm$^{-1}$ indicating the appearance of new functional groups of the SrO.SiO$_2$. The catalytic activity of SrO.SiO$_2$ on transesterification reaction was optimized. The optimum condition was obtained at SrO.SiO$_2$ of 2:7, reaction time of 30 minutes, reaction temperature of 65 °C, the amount of catalyst of 1 % w/v of reactants, and the biodiesel yield of 96.66 %. Copyright © 2017 BCREC Group. All rights reserved

Keywords: Biodiesel; Catalyst; Soybean Oil; SrO.SiO$_2$; Transesterification


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1. Introduction

The development of biofuels (BBN) that is used to replace fossil fuel which is becoming scarce is continuously developed in Indonesia. One of the efforts that was made by the government is through Presidential Decree No. 5 of 2006 on national energy policy that is principled on the pricing policy, diversification, and energy conversion.

Various vegetable oils can be utilized as a new energy source that can be renewable and reliable. According to ISO (2012), biodiesel is defined as a biofuel in the form of methyl esters of fatty acids of vegetable oils. The vegetable oil will be in the transesterification should have acid numbers smaller than 1 [1] and soybean oil acid number is 0.84 [2]. Synthesis of biodiesel can be made through the transesterification reaction of triglycerides from vegetable oil with methanol using homogeneous catalysts, heterogeneous, and an enzyme catalyst. Homogeneous alkaline catalysts are typically used, such as NaOH solution, NaOCH$_3$, and KOH. The use of
homogeneous catalysts bases produces some water that forms as a reaction between hydroxide and alcohol. The presence of water leads to an ester hydrolysis that produces soap through a saponification reaction and can reduce yields, thus require the separation process. Enzyme catalyst is expensive, and it can only react with short-chain alcohols and easily denatured. Therefore, heterogeneous catalysts are now much more developed than the homogeneous catalyst [2]. The SrO can accelerate many chemical reactions [3]. Biodiesel yield is 90 % in 20 minutes, and the SrO weakness is still homogeneous, so it is necessary to add a support such as SiO$_2$ [4]. The modification of SrO catalyst is made by formulating SrO with Musa Balbisiana Colla Underground Stem (MBCUS) to form agglomeration [5]. The result is used to synthesize biodiesel oils with a high free fatty acid level through esterification and transesterification reaction.

In this study, the catalyst was prepared by modifying SrO with SiO$_2$ from rice husk ash for biodiesel synthesis reaction of soybean oil. The result of synthesized catalyst was used for transesterification reaction of soybean oil. In the previous study, impregnation method was used for modification of catalyst, while in this study using the sol-gel method of the SrO:SiO$_2$ catalyst is purposed for improving catalytic activity and decrease the homogenous phase of SrO.

2. Material and Instrumentations

2.1. Material and Method

The materials used in this research were waste cooking oil, potassium hydroxide (85.0 %, Merck), sodium hydroxide (99 %, Merck), ammonium hydroxide (25 %, Merck), hydrochloric acid (37 %, Merck), nitric acid (65 %, Merck), strontium nitrate (99 %, Merck), alcohol (95 %, Merck), methanol (99.8 %, Merck), and soybean oil.

The instruments used in this research were analytical balance (GR-200), hotplate magnetic stirrer (Yellow MAG HS 7), muffle furnace (Barnstead Thermolyne 1400), hydrothermal reactor, oven (Memmert), centrifuge, X-Ray diffraction (PW3 710, Shimadzu XRD 6000), SEM (Scanning Electron Microscope JEOL JSM-65101-A), Gas Chromatography Mass Spectrometry (QP2010S Shimadzu), and Infra-red spectrometer (FTIR Shimadzu-8201 PC).

2.2. Experimental

2.2.1. Synthesis of SrO:SiO$_2$

The SrO:SiO$_2$ catalyst was conducted by the sol-gel method [6]. Silica sol-gel was made by adding 30 g silica powder to 1000 mL of 5 % NaOH; then it was stirred with a magnetic stirrer for 3 hours in a closed container without heating to form a silica sol. The silica sol was added by SrO dopants which were made by dissolving some Sr(NO$_3$)$_2$·2H$_2$O in distilled water according to the composition of desideratum. The synthesis was done by various mole composition ratio of 3:2; 2:4; and 2:7. The mixture was stirred for 3 hours at a speed of 450 rpm to form a solution of strontium silicate. Then, a solution of HNO$_3$ 65 % was added slowly to the solution of strontium silicate to form a gel and then let it stand. After that, the solution was filtered and washed with distilled hot water. The gel was dried in an oven at 105 °C for 3 hours and then crushed to obtain powder strontium silicate. The powder was calcined at 800 °C for 4 hours and characterized.

2.2.2. Characterization of catalyst

The SrO:SiO$_2$ catalyst was characterized by X-Ray Diffraction, FTIR, and SEM. The identification of SrO:SiO$_2$ crystal phase was conducted by Cu-Ka ($\lambda$ = 1.5405 Å) radiation at 40 kV and 30 mA, 20 = 0-90° with a scan speed of 0.04 °/second. The analysis of SrO:SiO$_2$ catalytic functional groups were done by FTIR using KBr film, and the spectrum was measured at the wavenumber of 4000-400 cm$^{-1}$. The observation of the catalyst surface was conducted using SEM (Scanning Electron Microscope JEOL JSM-65101-A).

The characterization of biodiesel was carried out by using Gas Chromatography to find out the optimization of catalyst compositions, whereas the GC-MS was used to determine the types of methyl ester groups. The identification of functional groups of methyl ester was carried out by FTIR.

2.2.3. Synthesis of biodiesel from soybean oil

The synthesis of biodiesel was carried out through a transesterification reaction. The transesterification reaction was conducted by mixing the reactants of oil and methanol in the ratio of 1:4 and the catalyst of 1 % w/v. The reaction was conducted with various ratios of SiO:SrO (0:1, 1:0, 3:2; 2:4, and 2:7), and variations of reaction time of 30, 60, 90, and 120 minutes. These experiments were carried out
by refluxing the mixture at a temperature of 65 °C with stirring a speed of 300 rpm for 30 minutes and let it stand for 24 hours. Then, it was filtered to separate the catalyst from the reaction product. The biodiesel reaction products were tested for density, viscosity and the refractive index to determine the quality of biodiesel product and analyzed by using GC-MS to determine the type of methyl ester formed. The biodiesel level was calculated based on the amount of chromatogram area of methyl ester which was the result of GC-MS compared to the entire area of the chromatogram. Total biodiesel is calculated by comparing the total number of moles of methyl ester which is formed by the number of moles of first oil.

3. Results and Discussion

Heterogeneous catalysts are usually used in the transesterification reaction of soybean oil with alcohol [2]. The result of the synthesis of silica is shown in Figure 1. Figure 1 shows (a) the formation of silica sol-gel, (b) gel of SrO.SiO$_2$, and (c) SrO.SiO$_2$ powder that was calcination product. The gel (b) still has a large water content so that it is necessary to eliminate the moisture content of the material by calcination 800 °C to obtain the optimum catalyst. The result of catalyst diffractogram from the synthesis is shown in Figure 2. The SrO is indicated by the emergence of peak 2θ of 29.77°; 34.69°; 49.88°, and 59.33°. This pattern is almost similar to previous literature [7]. The SrO catalyst is indicated by the emergence of peak 2θ of 29.64°; 34.65°, and 49.95° [7]. The crystallinity level is similar to JCPDS library. The SiO$_2$ diffractogram pattern in this study is shown by the emergence of peak 2θ of 21.18°; 26.96°; and 31.31° which is similar to previous literature [8]. The SiO$_2$ component appears at the 2θ peak of 21.18° which is a polymorph of silica tridymite. The 2θ of 26.96° shows quartz, while the 2θ peak of 31.31° shows a cristobalite [8]. The SiO$_2$ diffractogram in this study indicates the widening peak at 2θ of 20-23 °. The SiO$_2$ component is amorphous as it widens peak at 2θ of 21-22 ° [9]. A raising crystallinity is very important about the catalytic properties [10].

The SrO.SiO$_2$ (3:2) catalyst has SrO peak at 2θ of 29.83°, 34.63°, 50.47°, 59.97°, and SiO$_2$ peak at 2θ of 21.66°, 26.79°, 35.42°, and 38.67°, the SrO.SiO$_2$ (2:4) catalyst has peak of SrO at 2θ of 29.70°, 34.67°, 50.52°, 59.94°, SiO$_2$ peak at 2θ of 21.74°, 26.60°, 34.67°, 38.72°, and SrO.SiO$_2$ (2:7) catalyst has SrO peak at 2θ of 30.00°, 34.76°, 49.98°, and SiO$_2$ peak at 2θ of 21.84°, 26.95°, and 40.17° [7,8].

The infrared spectra of the catalyst are shown in Figure 3. The crystallinity of SrO increased as the addition of SiO$_2$ shifting the diffraction angles. High calcination temperature increases purity catalyst from various dirt [12]. The shift angle was occurred due to the effect of treatment into the SrO catalyst modified by SiO$_2$.

The SrO catalyst is shown at the peak of 966 cm$^{-1}$ that is a Sr–O bond. This pattern is similar to a research by Pavlyuchenko, in which the Sr–O functional groups appears at the wavenumber of 700-1000 cm$^{-1}$ [12]. The SrO appears at 900 and 950 cm$^{-1}$ [12]. The peak at 1460 cm$^{-1}$ indicates –OH bending vibration that still allows the formation of Sr(OH). Meanwhile, the SiO$_2$ has a width and a sharp absorption in 1095 cm$^{-1}$ that indicates Si–O symmetric stretching vibration of the Si–O–Si. The peak of 1633 cm$^{-1}$ indicates –OH bending vibration.
vibration from Si–OH. The peak at 798 cm\(^{-1}\) indicates Si–O symmetric stretching vibration of Si–O–Si, while the absorption pattern in 479 cm\(^{-1}\) shows Si–O–Si bending vibration. The SiO\(_2\) pattern in this research has similarity to previous literature [13]. At wavenumber of 1635 cm\(^{-1}\) indicates –OH bending vibration of Si–OH [14]. The pattern of 794 cm\(^{-1}\) indicates Si–O symmetric stretching vibration from Si–O–Si, and the absorption pattern of 470 cm\(^{-1}\) shows Si–O–Si bending vibration.

Based on Figure 3, it can be understood that the functional groups in the catalyst modification of SrO:SiO\(_2\) (3:2) of 1477 cm\(^{-1}\) indicates –OH bending vibration of Si–OH. The pattern of 1074 cm\(^{-1}\) indicates Si–O symmetric stretching vibration from Si–O–Si. The peaks at 972 cm\(^{-1}\) and 928 cm\(^{-1}\) indicate Sr–O. The peak at 706 cm\(^{-1}\) indicates Si–O symmetric stretching vibration of Si–O–Si. The SrO:SiO\(_2\) catalysts (2:4) is showed by the peak of 1632 cm\(^{-1}\) indicating –OH bending vibration within Si–OH. The peak at 1075 cm\(^{-1}\) indicates Si–O symmetric stretching vibration of Si–O–Si. The peak at 970 cm\(^{-1}\) and 925 cm\(^{-1}\) indicate Sr–O, while the peak at 703 cm\(^{-1}\) indicates Si–O symmetric stretching vibration of Si–O–Si. Based on the analysis of functional groups on SrO, SiO\(_2\), and SrO:SiO\(_2\) from infrared spectral data, a new peak of 900 cm\(^{-1}\) indicating that SrO catalysts have been successfully modified with SiO\(_2\).

The optimum catalyst characteristic was carried out by Scanning Electron Microscope. The SrO:SiO\(_2\) catalyst ratio of 2:7 is shown in Figure 4 (a) 3000x magnification and Figure 4 (b) 5000x magnification. The surface morphology of SrO:SiO\(_2\) shows agglomeration.

The lumps or agglomeration structure shows their metal oxides that formed on the treatment of the catalyst [14].

Figure 5 shows percentage of product concentration from the catalyst. The addition of more SiO\(_2\) increases the percentage of product concentration. This is due to the influence of SiO\(_2\) which functions as a buffer. The buffer causes the active component of the catalyst that was dispersed evenly, improving mechanical strength, spreading reaction heat and improving the stability of the catalyst [14]. The optimum results were obtained at SrO:SiO\(_2\) 2:7.

Figure 6 shows the percentages of products concentration of methyl ester. The products are methyl linoleic, methyl elaidic, and methyl linolenic. The optimum ratio of oil and methanol is 1:12, in which the higher methanol ratio converts fatty acid into methyl ester whereas the ratio of oil and methanol of 1:4 tends to a little methyl ester [3]. The optimum condition is obtained with a reaction time of 30 minutes.

Figure 7 indicates the soybean oil contents where a peak at wavenumber of 723 cm\(^{-1}\) shows the band of =CH, while peaks at 1100, 1163, and 1239 cm\(^{-1}\) indicate the CO group of
esters that usually appears at the wavenumber of 1050-1300 cm\(^{-1}\). The wavenumber of 1378 cm\(^{-1}\) indicates the presence of functional groups of C–H\(_3\), while the wavenumber of 1463 cm\(^{-1}\) indicates the presence of methylene functional group of –CH\(_2–\). The peaks at the wavenumbers of 2855 and 2927 cm\(^{-1}\) show the CH functional groups that usually appears a peak at the wavenumber of 2850-2970 cm\(^{-1}\). The peak at wavenumber of 1747 cm\(^{-1}\) indicates the C=O functional groups of the ester that usually appears at the wavenumber of 1690-1760 cm\(^{-1}\) [2].

Biodiesel production from soybean oil over catalysts of SrO, SiO\(_2\), and SrO.SiO\(_2\) appears at peaks of 1053, 1112, 1172, 1197, and 1245 cm\(^{-1}\) indicating the CO group of ester that usually appears at the wavenumber of 1050-1300 cm\(^{-1}\). The peaks at 1363 and 1459 cm\(^{-1}\) indicates a C–H\(_3\) functional groups that usually appear a peak at the wavenumber of 1340-1470 cm\(^{-1}\). The CH functional groups appear at peaks of 2855 and 2928 cm\(^{-1}\) that usually appear at the peak of 2850-2970 cm\(^{-1}\). The peak at wavenumber of 1744 cm\(^{-1}\) indicates the functional groups of C=O of the ester that usually appears at the wavenumber of 1690-1760 cm\(^{-1}\) [2].

The biodiesel chromatogram is shown in Figure 8 indicates presence of a methyl ester, and interpretation of chromatograms is shown in Table 1. Figure 8 and Table 1 show the products from the transesterification reaction which are methyl palmitate, methyl elaidic, methyl linoleic and methyl linolenic and the biodiesel yield 96.66 %.

Table 2 shows the physical characteristics of biodiesel that have a density, kinematic viscosity and the refractive index by SNI 04-7128-2006.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (minutes)</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl palmitate</td>
<td>33.75</td>
<td>15.08</td>
</tr>
<tr>
<td>Methyl elaidic</td>
<td>40.01</td>
<td>19.90</td>
</tr>
<tr>
<td>Methyl linoleic</td>
<td>41.83</td>
<td>57.37</td>
</tr>
<tr>
<td>Methyl linolenic</td>
<td>44.34</td>
<td>7.65</td>
</tr>
<tr>
<td>Total methyl ester</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 5. Relations of the percentage of the catalyst concentration: (a) SiO\(_2\) (b) SrO (c) SrO:SiO\(_2\) 3:2 (d) SrO:SiO\(_2\) 2:4 (e) SrO:SiO\(_2\) 2:7, at a temperature of 65 °C during the 30 minutes, the catalyst weight of 1 % w/v of oil, the ratio of oil:methanol of 1:4

Figure 6. Relations of reaction time with the percentage of the product concentration, at a temperature of 65 °C with a SrO.SiO\(_2\) 2:7 catalyst 1 % w/v of reactants, the ratio of oil: methanol of 1:4

Figure 7. Results of biodiesel infrared spectra (A) soybean oil, (B) biodiesel SiO\(_2\), (C) biodiesel SrO, (D) biodiesel SrO.SiO\(_2\) 2:7
4. Conclusions

The characteristics of SrO$_2$SiO$_2$ catalyst showed the increase of crystallinity level of SrO in line with the increase of SiO$_2$ and shift in the diffraction angle that showed the modification on SrO$_2$SiO$_2$ catalyst. The functional groups of SrO$_2$SiO$_2$ catalyst was marked by the appearance of a new peak in the catchment concentration of about 900 cm$^{-1}$. The surface morphology of SrO$_2$SiO$_2$ catalyst had lumps or agglomeration structure indicating metal oxides SrO and SiO$_2$. The optimum condition of transesterification reaction is when using the SrO$_2$SiO$_2$ 2:7 catalyst, a reaction time of 30 minutes, the temperature of 65 ºC, the amount of catalyst used 1 % of total weight, and biodiesel yield of 96.66 %.

References


**Figure 8.** The chromatogram of biodiesel synthesis results with SrO:SiO$_2$ ratio of 2:7, at 30 minutes and temperature of 65 ºC, oil to methanol ratio of 1:4, (1) methyl palmitate, (2) methyl elaidic, (3) methyl linoleic,(4) methyl linolenic

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Soybean Oil</th>
<th>Biodiesel</th>
<th>Source of Biodiesel Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td>0.88</td>
<td>0.85</td>
<td>0.85-0.89 (SNI 04-7128-2006)</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>19.25</td>
<td>2.41</td>
<td>2.3-6.0 (SNI 04-7128-2006)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.4</td>
<td>1.3</td>
<td>1.3-1.4 (SNI 04-7128-2006)</td>
</tr>
</tbody>
</table>


