Effect of Application of Mesoporous Silica on Titanium Dioxide Sulfate catalyst for Synthesis of Palmitate Ethyl Ester as Biodiesel

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Abstract. This research studied the effect of the addition of mesoporous silica on the active site SO₄²⁻/TiO₂. Mesoporous silica was designed to be a matrix that affects the surface area of the catalyst activity. This study aimed to obtain a solid acid catalyst capable of treating palmitic acid with ethanol through an esterification reaction. The research began with the synthesis of SO₄²⁻/TiO₂ catalyst, followed by the addition of synthetic mesoporous silica support. Both of these catalysts were applied to the palmitic acid esterification reaction. The activity of the SO₄²⁻/TiO₂ catalyst was observed at variations of 5%, 10%, 15%, 20%, and 25% in the application. Observations through the analysis of gas chromatography-mass spectra for the indicated application of 20% obtained the highest % area of ethyl ester palmitate was reached at 96.15. For the modified SO₄²⁻/TiO₂ catalyst with mesoporous silica support synthesized with different purification steps. They are ethanol-acid and calcined, which are indicated to have a % area of 83.14 and 94.22. In order to be able to define the ethyl ester palmitate and this catalyst, the microstructure characterization was carried out using the FTIR and XRD methods. Several indications resulting from the characterization of SO₄²⁻/TiO₂ supported by mesoporous silica for 2θ were 23.43° and 25.19°, which indicate the presence of silica in the position of mesoporous silica and TiO₂ in the anatase phase.

1. Introduction
Heterogeneous catalysts can be used to overcome problems in producing biodiesel. This catalyst is non-corrosive, non-toxic, and easily separated from the product mixture. In addition, the possibility of being used repeatedly can support the biodiesel synthesis process to become more economical. Especially for homogeneous catalysts, they are generally acid or base-specific in their application. According to previous research, metal oxides can be used as special heterogeneous catalysts in the transesterification reaction of triglycerides into fatty acid alkyl esters [1]. The types of metal oxides are alkali metal oxides, alkaline earth metal oxides, transition metal oxides and mixed metal oxides. Apart from being the active site, metal oxides can be modified into a support or catalyst matrix. Synthesis of biodiesel with the help of heterogeneous catalysts has been widely carried out. Generally, solid base catalysts can be prepared from alkali metal oxides (Li, Na, K) and alkaline earth metals (Mg, Ca, Ba) and have been applied to biodiesel synthesis [2], [3]. Its catalytic activity is very selective and maximal in the transesterification of triglycerides up to 98.64% on the performance of...
CaO/Al₂O₃ solid base catalyst [4]. Although the catalytic performance is maximal in biodiesel synthesis, the catalyst activity can only transesterify triglycerides. Oil or fat raw materials with a high content of free fatty acids cannot use the help of this catalyst. This obstacle can be overcome by adding a neutralization process to minimize the free fatty acid content or converting it into biodiesel through the esterification process. The addition of this process, of course, will increase the production cost of biodiesel. Therefore, particular research is needed to focus on the development of solid heterogeneous catalyst performance. Several researchers have carried out the preparation of a modified heterogeneous catalyst by synthesizing a heterogeneous catalyst of titanium sulfate oxide (SO₄²⁻/TiO₂) and has used it in the esterification reaction or the transesterification reaction. SO₄²⁻/TiO₂ catalyst is a solid acid heterogeneous catalyst and has the performance for both reactions. The transition metal oxide (titanium oxide) serves as the catalyst's active site and is acidic. In addition, modification using sulfuric acid causes an increase in its acidity, so this catalyst is also called a superacid catalyst. However, the particle size of this catalyst was tiny and was a cluster of nanomaterials (< 7.0 nm). It will cause obstacles in the process of filtering the catalyst from the product [5]. So efforts need to be made to increase the particle size by adding support from silica [6]. Mesoporous silica can be used as catalyst support because it has three-dimensional channels that MCM-41 and SBA-15 did not have. With this channel model, blocking of the pores can be avoided, thereby increasing the ability of the material to diffuse into the pores [7]. SBA-15 had a two-dimensional hexagonal structure with channel length in microns [8]. It can inhibit the rapid exchange of molecules, which significantly affects the reaction rate. The catalyst preparation process uses the impregnation method, considering that the active sites will diffuse well and the treatment steps will not cause damage to the support structure. SO₄²⁻/TiO₂–Mesoporous silica catalyst will be synthesized by the impregnation preparation method. This research begins with the synthesis and modification, and application test of catalyst. The catalyst performance test was carried out on palmitic acid. The esterification reaction of free fatty acids (R-COOH) with alcohol (R'OH) was an alternating reaction.

Catalyst and palmitate ethyl ester were characterized and expected to have a correlation with esterification performance. The model on palmitic acid raw material is used to test the performance of catalytic activity against the esterification reaction. This was done with this catalyst, which is expected to be a reused material and can be applied on an industrial scale.

2. Materials and Methods

2.1 Materials
The materials used in this study were setethyl trimethyl ammonium bromide (CTAB) (Sigma-Aldrich), Ludox HS40 (Sigma-Aldrich), Triton x100 (Sigma-Aldrich), NaOH (E.Merck), aquadest, acid acetate (E. Merck), HCl (E.Merck), ethanol (E.merck), H₂SO₄ (E.Merck), titanium dioxide (E.Merck), chloroform (E.Merck), palmitic acid (E.Merck) and Palmitate acid (E. Merck).
2.2 Procedures

2.2.1 Mesoporous Silica Synthesis

Mesoporous Silica Synthesis. This method was adopted from the modification of the Ryoo method by Taba [9]. Initially, the silica solution was prepared by reacting 14.3 grams of Ludox HS40 solution with 45.25 grams of 1 M NaOH solution at a temperature of 80 °C under lightly stirred conditions for 2 hours. The resulting silica solution is then cooled.

Next, the surfactant solution was prepared by mixing 6.12 grams of CTAB with 1.34 grams of Triton x-100, and 83.47 grams of aquadest. The mixture is then heated to form a homogeneous surfactant solution. The surfactant solution is then cooled.

Next, the silica solution and surfactant solution were mixed rapidly into a polypropylene bottle while shaking vigorously for 15 minutes. The mixture, which then turns into a gel, is heated under static conditions at 100 °C for 24 hours while occasionally being shaken. After that, it was cooled to room temperature, then 30% acetic acid was added until the pH reached 10. After that, it was heated again under static conditions at 100 °C for 24 hours. The material still consists of silica and surfactants, so a separation process is needed. 2 methods carried out purification for surfactant removal. The first method is through ethanol and acid washing, and the second method is by calcination.

Ethanol-Acid (EA). The white solid formed was separated from the liquid, then the result was washed with distilled water and finally crystallized in the oven at 120 °C. The resulting white powder was then washed using a mixed solution of HCl and ethanol (1 gram of silica was washed with 25 ml of 0.1 M HCl in a 50% ethanol solution). When washing, stir for 30 minutes, then filtered using a Buchner filter. The solid obtained was then rewashed using aquabidest and finally dried in an oven at 105 °C. [9], [10] The silica powder has been free of surfactants.

Calcination. The white solid formed is separated from the liquid portion and then dried in the open air. The powder is then calcined in a furnace at a temperature of 540 °C for 5 hours. [11], [12] The silica powder has been free of surfactants.

2.2.2 Catalyst Synthesis.

Initially, 10 grams of TiO₂ were immersed in 2M H₂SO₄. Then the synthesized silica was added while stirring continuously for 6 hours at a speed of 300 rpm. The gel was dried in an oven for 24 hours at a temperature of 105 °C. Then proceed with calcination in the furnace at a temperature of 400 °C for 4 hours. The X-ray diffraction pattern for catalyst (Calcination) was obtained using Cu Kα radiation (λ = 1.5406) in the BrukerD2 Phaser 2nd Gen diffractometer. Samples were evaluated at a scale of 2θ from 10 to 60 with an increment of 0.02 degrees and a scanning rate of 3°/min.

2.2.3 Esterification Reaction.

At first, 10 grams of raw material is melted using a hot plate; then, after melting, it is put into a flask reactor conditioned at a temperature of 80 °C with a stirrer speed of 300 rpm. Successively added an amount of ethanol with a molar ratio to the standard of 13 and some solid catalysts with various weight-to-standard ratios after being heated on a hot plate until it reaches the desired operating conditions. It was then that the start time of the reaction was set to 4 hours. Analysis of determining the amount of palmitate ethyl ester in the product was carried out using GC-MS (GCMS-QP2010 ULTRA SHIMADZU). Characterization of Infrared spectroscopy to determine the functional groups of compounds in materials using Shimadzu instruments, Fourier Transform Infra-Red (FTIR 8400S).

3. Result and Discussion

The focus of this research is the synthesis of mesoporous silica for heterogeneous catalysts, and was applied to fatty acid esterification reactions. It is expected that the ester produced belongs to the category of high-quality biodiesel liquid fuel, so it is tried to process palmitic acid as raw material. The ester product of palmitic acid has been known as a biodiesel component with a cetane number greater than 80 [8]. The experiment was designed on the variation of % w/w catalyst against the raw
materials. The results obtained were analyzed using GC-MS to identify the type of alkyl ester and its quantity.

At first, the performance of the \(\text{SO}_4^{2-}/\text{TiO}_2\) catalyst was tested with variations of 5%, 10%, 15%, 20%, and 25% by weight against palmitate acid. The results of this experiment inform that the best 20% (w/w) application with the conversion of palmitic acid to an ester (hexadecanoic ethyl ester) is 96.15%. It was suspected that the phenomenon of mass transfer in the catalytic process in this experiment succeeded in achieving the best conditions. It can be proven that when the catalyst quantity is increased to 25%, the ester product obtained is even lower until it reaches only 20.07%. This condition occurs due to the high quantity of catalyst used to increase the viscosity of the reactants. The viscous state of the reactants will inhibit the mass transfer process in the catalytic reaction so that the product conversion was reduced.

![Figure 1.](image)

**Figure 1.** a. Performance of \(\text{SO}_4^{2-}/\text{TiO}_2\) catalyst; b. Performance of \(\text{SO}_4^{2-}/\text{TiO}_2\)-Mesoporous Silica (AE); c. Performance of \(\text{SO}_4^{2-}/\text{TiO}_2\)-Mesoporous Silica (Calcination)

The very high catalyst activity of about 96.15% can help the separation or purification process after the reaction. The low levels of residual fatty acids will not form an emulsion when it meets water. However, other problems arise due to the very small size of the catalyst particles so that they are easily suspended with a slight shock. Seeing this, the research continued by synthesizing mesoporous silica for catalyst modification. The synthesized silica was then added to \(\text{SO}_4^{2-}/\text{TiO}_2\) in the hope that it could become support and increase catalytic activity. Specifically, in this research, the catalyst was modified by the addition of mesoporous silica (EA and Calcination) as a synthesis product. At the start of the process, the catalyst synthesized consisting of mesoporous silica (EA) was 1 part and 3 parts TiO\(_2\). This catalyst was applied to 10%, 15% and 20%. It turned out that there was support for the type of mesoporous silica (EA), the catalyst activity decreased, and it was suspected that its presence could not support \(\text{SO}_4^{2-}/\text{TiO}_2\). The result is only 54.7% which is very different from the catalyst activity \(\text{SO}_4^{2-}/\text{TiO}_2\) can reach 96.15% in the same treatment. Subsequent studies with the quantity of TiO\(_2\) increased to 1: 4 and 1: 5, as shown in Figure 1c. Increased conversion of ethyl ester to 74.48% with increasing the quantity of TiO\(_2\) (sample 1: 5). Purification (release of surfactant) on mesoporous silica as its function as support for this catalyst was carried out by calcining at 540\(^\circ\)C for 5 hours [11],[12].

The mesoporous silica was tried to be used for the next catalyst synthesis, and its activity was tested again. In fact, this catalyst is very competent and has been tested for a palmitic acid esterification conversion percentage of 94.22% in Figure 2c. Based on several experiments carried out in Figure 1a, 1b, and 1c, it is concluded that the conversion rate (\% ester) depends on the quantity of TiO\(_2\) in the site active catalyst.
To prove the presence and composition of the ethyl ester formed, a Gas Chromatography-Mass Spectrometry (GC-MS) characterization was carried out. The results of the analysis can be seen in Figure 2, which shows the sample before and after palmitic acid esterification.

![Figure 2](image)

**Figure 2.** a. Palmitic Acid; b. ethyl ester palmitate with application $\text{SO}_4^{2-}/\text{TiO}_2$; c. ethyl ester palmitate with application $\text{SO}_4^{2-}/\text{TiO}_2$–Mesoporous silica (calcination)

Figure 2a. the results of GC-MS analysis of palmitic acid or n-Hexadecanoic acid with a retention time of 19,865 minutes. After being reacted with ethanol with the help of $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst and $\text{SO}_4^{2-}/\text{TiO}_2$–mesoporous silica catalyst can be seen in Figures 2b and 2c. The product of the performance of the $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst in the 20% application in Figure 2b produces several different ethyl ester components according to their carboxylate groups. It was suspected that the performance of the catalyst had not been perfect or that the reaction has not been completed. The details of the product components are; tetradecanoic ethyl ester 0.04%; pentadecanoic ethyl ester 0.25%; hexadecanoic ethyl ester 96.15%; heptadecanoic ethyl ester 0.34% and octadecanoic ethyl ester 2.81%. Meanwhile, in the performance of the $\text{SO}_4^{2-}/\text{TiO}_2$ supported catalyst, mesoporous silica (calcination) produces 94.22% hexadecanoic ethyl ester, and the remaining hexadecanoic acid component which had not reacted was around 5.78%. In this case, it can be concluded that the addition of support to the catalyst, such as $\text{SO}_4^{2-}/\text{TiO}_2$–Mesoporous silica (calcination), can improve the overall performance of the catalyst activity.

![Figure 3](image)

**Figure 3.** Spectrum FTIR a. ethyl ester from palmitate acid; b. ethyl ester from palm fatty acid destillate
Another characterization of the esterification product was carried out using the Fourier Transform Infra Red (FTIR) method to determine the functional groups that could support the presence of esters. The results are shown in Figure 3 with the appearance of peaks at wavelengths of 1095.60 cm\(^{-1}\) and 1199.76 cm\(^{-1}\) indicating the presence of C-O groups of esters which usually appear at wave numbers of 1050-1300 cm\(^{-1}\). The presence of a peak at a wavelength of 1737.92 cm\(^{-1}\) indicates the presence of C=O esters which generally appear in the range of wave numbers 1690-1760 cm\(^{-1}\).

The peaks that appear at the wavelengths of 1348.29 cm\(^{-1}\), 1371.43 cm\(^{-1}\), and 1456.30 cm\(^{-1}\) indicate the C-H\(_3\) (alkane) function which usually peaks in the wavelength range of 1340-1470 cm\(^{-1}\). Another peak at the wavelength of 2854.74 cm\(^{-1}\) and 2926.11 cm\(^{-1}\) by indicating the presence of the C-H functional group (alkane) which usually appears at the wave number 2850-2970.

From the results of the FT-IR spectra analysis, it can be concluded that the sample from the research is suspected to be biodiesel or ethyl ester based on the functional groups that have been indicated.

![Figure 4. Diffractogram](attachment:image.png)

**Figure 4.** Diffractogram (a). SO\(_4^{2-}/\)TiO\(_2\) - Mesoporous silica (Calcination); (b) SO\(_4^{2-}/\)TiO\(_2\) – Mesoporous silica(EA); (c) SO\(_4^{2-}/\)TiO\(_2\); (d) TiO\(_2\)

In this research, the XRD measurement results in figure 4a show a very high intensity peak at 2\(\theta\) = 25° as a characteristic pattern of TiO\(_2\). This peak then shifted to 2\(\theta\) = 26° after TiO\(_2\) was modified into SO\(_4^{2-}/\)TiO\(_2\) catalyst through impregnation and calcination processes. In addition, this pattern informs that the characteristics of TiO\(_2\) have been in the anatase phase [13], [14]. In addition, in the XRD pattern of SO\(_4^{2-}/\)TiO\(_2\)–mesoporous silica (calcination) catalyst there is another peak at a low intensity of approximately 2\(\theta\) = 23.43° indicating that TiO\(_2\) has been supported by mesoporous silica. The peak that appears at 2\(\theta\) = 12.25° indicates that the material was amorphous.

**4. Conclusion**

The synthesized material can be used as a supported catalyst. All its advantages can be used to help the rate of esterification reaction, in the case of converting palmitic acid to palmitic ethyl ester or high-quality biodiesel. The synthesis and modification of the catalyst with the addition of synthetic support
was a novelty in this research study. Where the support is nanoporous silica in mesoporous clusters which were treated to become composites by means of impregnation. The characterization results indicate that the active site of SO₄²⁻/TiO₂ is in the filler position, and the mesoporous silica functions as a matrix or support. The performance of the catalyst activity will greatly increase if the silica support after being synthesized, purification treatment was carried out by calcination.

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