SO$_4^{2-}$/ZrO$_2$ as a Solid Acid for the Esterification of Palmitic Acid with Methanol: Effects of the Calcination Time and Recycle Method

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1. INTRODUCTION

With the rapid socioeconomic development, limited fossil fuels are facing the danger of exhaustion, and, on the other hand, the excessive emission of CO$_2$ derived from the usage of fossil fuels has been causing global warming, and thus it is necessary and urgent to find a renewable green fuel to alleviate the dependence on fossil fuels. Comprising fatty acid methyl esters (FAME), biodiesel has received great attraction recently, owing to its good combustibility, reproducibility, and eco-friendliness, and it is considered to be one of the best alternative fuels for petroleum-based diesel in the future. The biodiesel production is via the transesterification of the oil sourcing from algae, jatropha seeds, and waste cooking oil (WCO) over alkaline catalysts; nevertheless, a large amount of free fatty acids (FFAs) and water contained in the untreated WCO brings a series of problems such as catalyst neutralization, saponification of triglycerides, hydrolysis of the FAME product, and attendant separation issues. The feedstock needs water removal and pre-esterification over acid catalysts to eliminate FFAs prior to the transesterification step. Therefore, the study of esterification of FFAs with methanol over acid catalysts is essential. Methyl palmitate is one of the most important components in biodiesel, and thus the catalyst for the esterification of palmitic acid with methanol is widely studied.

Although homogeneous acid catalysts can well catalyze the esterification reactions, they are nonrenewable and generate a large amount of wastewater during biodiesel separation. On the contrary, solid acids can offer plentiful acidic sites for esterification and enable catalyst separation and recycling, and thus they can be used for continuous biodiesel production. The number and types (Brensted/Lewis) of acid sites as well as the structure and properties of the catalyst greatly affect the catalytic activity. Numerous solid acids such as sulfated...
metal oxides, cation exchange resins, and zeolites have been employed to catalyze the esterification reaction. Sulfated metal oxides have received much attention due to the superacidity features of SO$_4^{2-}$ groups on the surface of the metal oxides such as ZrO$_2$, TiO$_2$, and WO$_3$. Typically, the sulfated acids are synthesized via three steps: the preparation of metal oxides by a sol–gel or coprecipitation method, the introduction of SO$_4^{2-}$ groups using H$_2$SO$_4$, HSO$_3$Cl, or (NH$_4$)$_2$SO$_4$ as acid sources, and calcination at a high temperature. The acidity of the solid acids is greatly dependent on the sulfonation method, preparation method, SO$_4^{2-}$ concentration, and calcination temperature. However, despite the extensive studies in recent years, the exact nature of SO$_4^{2-}$ and the mechanism of its superacidic property over the sulfated ZrO$_2$ remains questionable. The SO$_4^{2-}$ groups could interact with neighboring strong Lewis acid sites on the metal oxides, forming bidentate adsorption geometries with low sulfate loadings, whereas forming more Brønsted acid sites without a significant activity loss. These results are expected to be valuable for the future biodiesel production using the sulfated solid acid.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. The X-ray diffraction (XRD) patterns of the ZrO$_2$ support and the calcined catalysts are presented in Figure 1. The synthesized ZrO$_2$ support only dried at 110 °C for 12 h does not show any obvious diffraction peaks on the XRD patterns, indicating the amorphous property of the support without calcination. This is in accordance with the reference result that the dehydration of Zr(OH)$_4$ occurs at around 82 °C, forming the amorphous ZrO$_2$. In contrast, strong diffraction peaks corresponding to ZrO$_2$ (PDF 50-1089) are shown in the catalysts calcined at 600 °C, suggesting that the calcination at a high temperature is required for the crystallization of ZrO$_2$. Two types of ZrO$_2$ phase are found in the catalyst calcined for 3 h, one is tetragonal zirconia oxide (PDF 50-1089) and the other is baddeleyite (monoclinic ZrO$_2$) (PDF 37-1484). It is reported that calcination of the amorphous ZrO$_2$ at a low temperature (300 °C) is favorable to the formation of tetragonal zirconia, whereas, at 600 °C, the main decomposed product is monoclinic zirconia with a little tetragonal species. The catalyst calcined for 3 h shows much stronger diffraction peaks than the catalyst calcined for 9 h, and on the other hand, the diffraction peaks corresponding to monoclinic ZrO$_2$ (PDF 37-1484) disappear for the catalyst calcined for 9 h. This suggests that long-time calcination not only impedes the crystal formation but also changes the crystal structure, which may have effects on the catalyst performance in palmitic acid esterification. It is believed that the monoclinic ZrO$_2$ phase on the sulfated catalyst is more active in some reactions. It is noteworthy that the diffraction peaks corresponding to Zr(SO$_4$)$_2$ (PDF 20-1474) appear in the catalyst calcined for 9 h, indicating that long-time calcination could induce the transformation of SO$_4^{2-}$ on the support into Zr(SO$_4$)$_2$. This explains the weaker diffraction peaks of tetragonal zirconium oxide (PDF 50-1089) and the disappearance of baddeleyite (PDF 37-1484). Similar conclusions were drawn by other researchers that the gradual weakening of XRD reflections associated with tetragonal zirconia was observed, which was attributed to the formation of the amorphous bulk Zr(SO$_4$)$_2$. The formation of Zr(SO$_4$)$_2$ could decrease the density of SO$_4^{2-}$ on the catalyst, which is unfavorable to the esterification reaction.

Fourier transform infrared (FTIR) spectra of the support and the catalysts are shown in Figure 2. The strong broad characteristic peaks at 3500 cm$^{-1}$ are attributed to the O–H stretching vibration, indicating the presence of the physically absorbed water on the samples. The strong characteristic peaks
at 1632 cm$^{-1}$ are due to the bending vibration of the chemisorbed water. The broad peaks centered at 1006 and 1142 cm$^{-1}$ correspond to the vibrations of O=S=O and O=S-O, which are regarded as the characteristic peaks of SO$_4^{2-}$-promoted superacid. The pure zirconia also shows similar peaks, which are unrelated to SO$_4^{2-}$. The peaks at 1029, 1076, and 1222 cm$^{-1}$ are ascribed to a chelating SO$_4^{2-}$ coordinated to the one zirconium ion through two of its oxygens. A bridged bidentate complex also exhibits bands at 1195−1160, 1110−1105, 1035−1030, and 990−960 cm$^{-1}$. This suggests that both chelating and bridged SO$_4^{2-}$ coordinate with the ZrO$_2$ support, as shown in Scheme 1.

Scheme 1. Possible Surface Structures for SO$_4^{2-}$ Chemisorption on Zirconia: Chelating Complex (Type I) and Bridged Bidentate Complex (Type II)

Comparison to the catalyst calcined for 3 h, the much weaker peaks at 1006 and 1142 cm$^{-1}$ on the catalyst calcined for 9 h reflect the smaller loading amount of SO$_4^{2-}$ on the catalyst calcined for 9 h to some extent. This indicates that SO$_4^{2-}$ is partially lost after long-time calcination, leading to a decrease in the Bronsted acid sites on the catalyst, which play an important role in catalyzing the esterification reaction. The bands centered at 625 and 748 cm$^{-1}$ are attributed to the Zr=O bond. According to the XRD results, the much weaker absorption peak at 625 cm$^{-1}$ on the catalyst calcined for 9 h is probably ascribed to the partial transformation of ZrO$_2$ with SO$_4^{2-}$ into Zr(SO$_4$)$_2$.

2.2. Catalytic Performance in the Esterification of Palmitic Acid with Methanol. The resulted oil was analyzed by gas chromatography-mass spectrometry (GC-MASS) and the results are presented in Figure 3. The main product is methyl palmitate (96.28%), which is the target product in this reaction. A trace of methyl myristate (1.10%) was also detected in the products, indicating that the cleavage of the carbon chain occurs on the active sites. However, in comparison with methyl palmitate, the amount of byproducts is less. Therefore, the conversion of palmitic acid could well reflect the catalytic activity of the catalyst.

2.2.1. Effect of the Reaction Time. Palmitic acid conversions with various reaction times in the esterification with methanol over these two types of catalysts are shown in Figure 4. In general, the palmitic acid conversion increases with the reaction time because a longer contact time of the catalyst and the reactant is favorable to the esterification reaction. For the SO$_4^{2-}$/ZrO$_2$ catalyst calcined at 600 °C for 3 h, after 8 h reaction time, the palmitic acid conversion could reach up to 90.27% at 65 °C under atmospheric pressure, indicating that the catalyst has excellent catalytic performance for the esterification of palmitic acid. In the initial stage of the reaction, the reaction rate is high and the palmitic acid conversion could reach over 80% after 4 h. In the later reaction stage, the palmitic acid conversion increases with the reaction time slowly and only less than 10% increment is observed in the later 4 h. With economic consideration, 4 h reaction time may be suitable for the esterification of palmitic acid. In the
case of the catalyst calcined for 9 h, a similar palmitic acid conversion variation trend with the reaction time is observed, while the conversion is much lower than that over the catalyst calcined for 3 h with around a 10% gap in the palmitic acid conversion. This indicates that long-time calcination of the catalyst is unfavorable to its catalytic performance. This could be explained by the partial loss of SO$_4^{2-}$ and the phase transformation of ZrO$_2$ during long-time calcination according to XRD and FTIR analyses. It is believed that Brønsted acid sites on the catalyst contribute more to the catalytic activity in esterification.\textsuperscript{14,21,23,24} The calcination at 600 °C could enhance the interaction between SO$_4^{2-}$ and zirconia, forming superacidic sites, while it is also accompanied by the loss of SO$_4^{2-}$, and long-time calcination results in a decrease in the Brønsted acid sites on the catalyst leading to lower activity in the esterification reaction.

2.2.2. Effect of the Reaction Temperature. The conversion of palmitic acid in the esterification under different temperatures is shown in Figure 5. The catalyst calcined for 3 h was tested at 50–65 °C, while the catalyst calcined for 9 h was tested at 65–80 °C to investigate the effect of reaction temperature and calcination temperature on the catalytic performance. When the reaction conditions are kept identical (65 °C), as expected, the conversion of palmitic acid over the catalyst calcined for 3 h is much higher than that over the catalyst calcined for 9 h due to the loss of SO$_4^{2-}$ on the catalyst during long-time calcination. In the range of 50–65 °C, the conversion of palmitic acid increases drastically, indicating that reaction temperature is an important factor to affect the reaction and is kinetically favorable to the esterification. However, above 65 °C, the reaction is not affected by the temperature significantly, only with a slight decrease in the palmitic acid conversion. This could be explained by the poor contact between the reactant and the catalyst. Because the boiling point of methanol is very low (64.7 °C) and the reaction system is kept under atmospheric pressure, when the water bath is heated above 65 °C, the partially boiled methanol hinders the adsorption of the reactants on the catalyst. The higher the reaction temperature, the more the vaporized methanol bubbles around the catalyst. As a result, when the reaction temperature is too high, it is unfavorable to the esterification reaction and the most suitable temperature is 65 °C for an atmospheric reaction system.

2.2.3. Effect of the Molar Ratio of Methanol to Palmitic Acid. The effect of the molar ratio of methanol to palmitic acid was investigated under the optimized temperature (65 °C) and the run time of each experimental point is 4 h. The conversion of palmitic acid with molar ratios from 14:1 to 30:1 is shown in Figure 6. Overall, a high molar ratio facilitates the conversion of palmitic acid in the reaction because besides the palmitic acid, methanol also participates in the esterification reaction as a reactant, and a high content of methanol could favor the adsorption of methanol on the catalyst, which accelerates the conversion of palmitic acid. The conversion increases with the ascent of the molar ratio rapidly from 14:1 to 22:1 and then rises slowly and reaches the highest value under the molar ratio of 25:1. A further increase in the molar ratio could not favor the conversion of palmitic acid instead the conversion undergoes a little drop. It should be noted that methanol in the reaction system is not only a reactant but also a solvent, and palmitic acid is a solid powder at room temperature. A very small amount of methanol in the system could not dissolve the palmitic acid well, which is not beneficial to the esterification, while excessive methanol content would decrease the concentration of palmitic acid in the solvent and further reduce its adsorption on the acid sites of the catalyst. Therefore, the molar ratio of methanol to palmitic acid should have an optimal value and 25:1 is the best suited under current reaction conditions.

2.2.4. Effect of the Catalyst Amount. The esterification of palmitic acid (methanol/palmitic acid = 25) with various amounts of catalysts was conducted at 65 °C and each experimental point was tested for 4 h. As shown in Figure 7, the palmitic acid in the blank experiment is hardly converted, while the conversion in the reaction with 3 wt % catalyst could achieve 67.4%, indicating that the synthesized catalyst could well catalyze the esterification of palmitic acid with methanol. The conversion increases with the ascent of the catalyst amount and could reach up to 85.9% when the catalyst amount...
methanol/palmitic acid = 25 and 65

Figure 8. Recycle test of the catalyst in the esterification of palmitic acid with methanol. Reaction conditions: atmospheric pressure, methanol/palmitic acid = 25 and 65 °C, 4 h reaction time.

Figure 7. Effect of the catalyst amount on the esterification of palmitic acid with methanol. Reaction conditions: atmospheric pressure, methanol/palmitic acid = 25 and 65 °C, 4 h reaction time.

is 9 wt %. This is because the more the catalyst loaded, the more the active sites. However, a further increase in the catalyst amount does not improve the yield notably but increases the economic cost.

2.2.5. Recycle Test of the Catalyst. The recycle test of the catalyst was conducted under optimal conditions (65 °C, methanol/palmitic acid: 25, catalyst amount: 6 wt %) with a run time of 4 h for each test. To determine the best suitable recycle method, the spent catalysts were regenerated by methanol washing, ultrasonic methanol washing, and calcination, respectively, followed by centrifugal separation of the catalyst from the reaction system. The (ultrasonic) methanol washing was conducted 3 times and maintained for 10 min for every washing. The calcination regeneration was conducted at 600 °C in a muffle furnace for 1 h, followed by the separation of the catalyst. The conversion of palmitic acid for each test with various regeneration methods is shown in Figure 8. Similar conversions are exhibited over all of the fresh catalysts, while the activity of the recycled catalyst is quite different. For the catalyst regenerated by methanol washing, the conversion drops by a large margin to 61.1% in the second test cycle and further decreases to less than 50% in the third cycle. This suggests that the catalyst is deactivated after each test cycle and could not be regenerated by the common methanol washing. The catalyst deactivation may be attributed to the adsorption of some organic compounds on the catalyst, which could not be eliminated by the common methanol washing. For the catalyst regenerated by ultrasonic methanol washing, the conversion of palmitic acid drops to 70.0% in the second cycle, which is better than that regenerated by the common washing, indicating that ultrasonic methanol washing could better remove the adsorbed contaminant on the catalyst. To confirm the removal by the ultrasonic methanol washing, the catalyst was regenerated by calcination in the third cycle. It can be found that the catalyst activity recovered to a higher value than that in the second cycle. This demonstrates that some contaminant residues are still left in deep pores of the catalyst after twice ultrasonic methanol washing. The catalyst still undergoes a little decrease in the activity in the fourth cycle regenerated by calcination, indicating that besides the organic contaminant, there are some other reasons for catalyst deactivation. For the catalyst regenerated by calcination, only traces of activity decrease are observed in the second cycle, which is much better than those of catalysts regenerated by methanol washing and ultrasonic methanol washing. After five cycles, the catalyst still maintains a relatively high activity with a palmitic acid conversion of 74.8%. It is noteworthy that the conversions over the catalyst regenerated by calcination (marked as green triangles) in the third and fourth cycle are a little higher than those over the catalyst regenerated by ultrasonic methanol washing (marked as red circles), although it was also regenerated by calcination in the third and fourth cycle. This suggests that long-time ultrasonic methanol washing also leads to the deactivation of the catalyst, which is probably attributed to the partial leaching of SO42− during calcination. Therefore, the most suitable regeneration method for the spent catalyst is calcination at 600 °C.

2.3. Elucidation of the Catalyst Deactivation. To further investigate the mechanism of the deactivation, the catalyst recycled 5 times was analyzed by FTIR and oxygen temperature-programmed oxidation (O2-TPO) with a MASS detector.

The FTIR spectra of the resulting oil, spent catalyst calcined for 3 h are shown in Figure 9. After the reaction, the catalyst was separated from the liquid phase by centrifugation and the resulting oil was distilled under reduced pressure at 50 °C to remove methanol from the system. All of the samples exhibit broad absorption peaks centered at 3690 and 1638 cm−1 corresponding to the stretching vibration and bending vibration of water, respectively, indicating that some chemisorbed water is still left on the catalyst, although the samples are dried at 110 °C for 2 h. The characteristic peaks at 2300–2400 cm−1 are attributed to the trace of CO2 adsorption on the sample, although the background spectra have been eliminated. As expected, both the fresh and spent catalysts exhibit absorption peaks corresponding to S=O and Zr−O. The weaker absorption peaks of S=O and Zr−O over the recycled catalyst may be due to the partial loss of SO42− and the transformation of the ZrO2 crystal after five cycles of calcination, since long-time calcination is unfavorable to the catalytic activity as previously analyzed. The peaks centered at 1740 cm−1 are ascribed to the C=O stretching vibration and
the peaks centered at 1155 and 1071 cm\(^{-1}\) are due to the C=O–C stretching vibration. These peaks are detected on the obtained oil samples, suggesting that the ester group is formed in the product. Besides, the obtained oil also exhibits absorption peaks centered at 2927 cm\(^{-1}\) (corresponding to the stretching vibration of CH\(_2\) and CH\(_3\)), and 1460 cm\(^{-1}\) (corresponding to the bending vibration of CH\(_2\) and CH\(_3\)), indicating the formation of methyl palmitate. However, over the spent catalyst, no peaks derived from the vibration of C=O or C–O–C group are observed, but significant peaks corresponding to CH\(_2\) and CH\(_3\) groups are detected, indicating that the refractory residue contaminant left in the catalyst may be some alkane species, which are formed by the decarbonylation of palmitic acid over the acidic sites of the catalyst. In the previous study on the pre-esterification of waste cooking oil, a similar result was obtained: besides methyl esters, alkane species such as tetradecane, n-pentadecane, and n-hexadecane are detected by GC-MASS. These alkanes are probably the reason for catalyst deactivation because they are generally insoluble in methanol and rather difficult to be eliminated by (ultrasonic) methanol washing.

To study the variation of water and SO\(_4^{2-}\) during the TPO process, the mass signals with \(m/z = 17, 18, 64, \) and 80 of the fresh catalyst calcined at 600 °C for 3 h are shown in Figure 10. As shown in Figure 10a, the mass signals of \(m/z = 17\) and 18 appear in the TPO profiles, indicating the existence of water in the catalyst, although the sample is calcined at 600 °C. This is because the catalyst could easily absorb the water in air, forming physisorbed or chemisorbed water, which greatly affects the acidic sites on the catalyst. The broad peaks corresponding to the water reach the largest value at around 120 °C with an extension until 600 °C, suggesting that calcination at 600 °C could efficiently eliminate the water contained in the catalyst. Figure 10b shows the oxidation peaks associated with SO\(_2\) and SO\(_3\) during the TPO process. For \(m/z = 64\), two peaks centered at 725 and 850 °C appear, indicating that partial SO\(_4^{2-}\) on the catalyst could be removed through the formation of SO\(_2\) above 600 °C. The decomposition of SO\(_4^{2-}\) depends on the conformation of surface-bound sulfates on zirconia. It can be speculated that the peaks centered at 725 and 850 °C are attributed to the decomposition of SO\(_4^{2-}\) in two various types of chemisorption, i.e., chelating and bridged bidentate complexes. This is in accordance with the FTIR results that these two types of SO\(_4^{2-}\) coexist on the zirconia surface. Therefore, a too high calcination temperature is unfavorable to the activity of the catalyst due to the loss of SO\(_4^{2-}\). In spite of the visible loss from 650 °C, it could be inferred that long-time calcination at 600 °C also induces a slow loss of SO\(_4^{2-}\), which is verified by the previous analysis. However, no peak is observed for \(m/z = 80\), which is probably because SO\(_3\) is more thermodynamically stable than SO\(_3\) at such a high temperature. According to the thermodynamic calculation, the formation of SO\(_3\) from SO\(_2\) and O\(_2\) (2SO\(_2\) + O\(_2\) → 2SO\(_3\)) is an exothermic reaction and could be negligible above 600 °C. Therefore, it is appropriate to calcine the catalyst at 600 °C, where most of the water could be removed, and on the other hand, ZrO\(_2\) could be crystallized from an amorphous state. The calcination time should remain until the water removal and crystallization processes are finished.

To investigate the catalyst deactivation by the organic residual contamination, after five cycles of the activity test, the spent catalyst was ultrasonically washed 3 times with methanol, and the TPO profiles of the spent catalyst with \(m/z = 12, 28, \) and 24 are shown in Figure 11. Because of the identical shape

**Figure 9.** FTIR spectra of (a) the obtained oil, (b) SO\(_4^{2-}\)/ZrO\(_2\) catalysts recycled 5 times, and (c) fresh SO\(_4^{2-}\)/ZrO\(_2\) catalysts calcined at 600 °C for 3 h.

**Figure 10.** TPO profiles of the fresh SO\(_4^{2-}\)/ZrO\(_2\) catalysts calcined at 600 °C for 3 h: (a) water and (b) SO\(_2\) and SO\(_3\).
and the position of the peaks at $m/z = 12$ and 28, it is concluded that these peaks are attributed to the formation of CO rather than N$_2$. The resulting peaks at $m/z = 44$ correspond to the formation of CO$_2$. The appearance of these peaks indicates that the ultrasonic methanol washing method could not eliminate the organic residue in the catalyst, while the calcination method could regenerate the spent catalyst. The peaks centered at 372 and 460 °C represent the combustion of different organic species in the catalyst, suggesting that various residues result from the deactivation of the catalyst. The broad peaks end at about 600 °C, indicating that calcination at 600 °C could well regenerate the spent catalyst and the calcination time should remain until the contaminants are thoroughly combusted. However, the deactivation due to the loss of SO$_4^{2-}$ in the repetitive catalyst regeneration or reaction is irreversible, which explains the slow decrease in activity during the recycle test of the catalyst regenerated by the calcination method.

3. CONCLUSIONS

The influence of calcination time, reaction conditions, and catalyst regeneration method on the catalytic activity of SO$_4^{2-}$/ZrO$_2$ toward the esterification of palmitic acid with methanol was investigated and the catalyst deactivation mechanism was further elucidated. To activate the catalyst activity, a calcination procedure of the catalyst is required, while the calcination temperature and time have a great influence. Too high temperature is unfavorable to the catalyst activity because of the partial loss of SO$_4^{2-}$. The calcination at 600 °C could eliminate the water in the catalyst as well as bring the transformation of the amorphous form to the crystal form. Long-time calcination at 600 °C also results in the slow partial loss of SO$_4^{2-}$, which in turn decreases the catalyst activity. Generally, a higher catalyst loading amount is favorable to the conversion of palmitic acid. Under atmospheric conditions, the catalyst activity increases with the reaction temperature, while decreases over 65 °C because of the low boiling point of methanol. A high molar ratio of methanol to palmitic acid can facilitate the conversion of palmitic acid, but excessive methanol also impedes the adsorption of palmitic acid on the catalyst leading to an activity drop. The spent catalyst could not be well regenerated by the (ultrasonic) methanol washing method due to the refractory organic residue in the catalyst, while the calcination method is an efficient regeneration method without major activity loss. The catalyst deactivation is due to the contamination by the refractory residues in the catalyst as well as the partial loss of SO$_4^{2-}$ during the reaction or the regeneration process. Employing the SO$_4^{2-}$/ZrO$_2$ solid catalyst with a simple calcination regeneration method to catalyze the fatty acid esterification reaction thus appears workable to replace the conventional liquid acid.

4. EXPERIMENTAL SECTION

4.1. Materials. Zirconyl chloride octohydrate (ZrOCl$_2$·8H$_2$O, ≥98%, Adamas), phenolphthalein (Adamas), methanol (CH$_3$OH, ≥99.5%), ammonium solution (NH$_4$)$_2$SO$_4$, ammonium hydroxide solution (25–28%, Adamas), potassium hydroxide (KOH, ≥85%, Greagent), palmitic acid (C$_{16}$H$_{32}$O$_2$, ≥98.0%, Adamas), and ethanol (≥99.7%, Greagent) were used as received without further purification.

4.2. Catalyst Preparation. ZrO$_2$ was prepared by the precipitation of ZrOCl$_2$·8H$_2$O in an alkaline environment. Typically, the ZrOCl$_2$ aqueous solution (0.5 mol/L) was added to a flask, followed by 5 min of ultrasonication. An ammonium hydroxide solution was slowly dropped into the ZrOCl$_2$ solution under vigorous magnetic stirring at room temperature until the pH was 9–10. The resulting slurry was aged at room temperature for 12 h. The aqueous phase was removed by filtration. The obtained ZrO$_2$ precursor was washed using deionized water until the pH was 7 and Cl$^-$ in the solution cannot be detected by AgNO$_3$, and subsequently dried at 110 °C for 12 h.

The catalyst was prepared by incipient wetness impregnation. Generally, 2 g of Zr(OH)$_4$ powder was added to 100 mL of (NH$_4$)$_2$SO$_4$ solution (1 mol/L), subsequently ultrasonicated for 5 min, and aged for 3 h. After the water was removed, the powder was dried at 110 °C and subsequently calcined at 600 °C for 3 or 9 h to obtain the SO$_4^{2-}$/ZrO$_2$ solid acid catalyst.

4.3. Catalyst Characterization. X-ray diffraction (XRD) analysis of the catalysts was performed with an X-ray powder diffractometer (XRD-7000, SHIMAZU Corp.) with Cu Kα radiation (40 kV, 30 mA) at room temperature. The XRD patterns were collected in a range of 2θ with a step interval of 0.02°.

Oxygen temperature-programmed oxidation (O$_2$-TPO) of the catalysts was performed in a chemisorption–physisorption analyzer (DAS-7200, HUASI Corp.). Typically, approximately 100 mg of a sample was loaded into a quartz tube. Helium (48 mL/min) with 6.25% of oxygen (volume fraction) was used as the carrier gas. The O$_2$-TPO analysis was carried out from 30 to 900 °C with a heating rate of 10 °C/min. The product in the outlet was detected via a residual gas analyzer (StanfordRGA-200).

Fourier transform infrared (FTIR) spectroscopy of a sample was performed in an FTIR spectrometer (Tracer 100, SHIMAZU Corp.) by adding 16 scans for the samples at a resolution of 4 cm$^{-1}$. The catalyst was diluted by potassium bromide with a mass ratio of 1:200. Before the samples were pressed into wafers, the samples were fully ground and blended.

GC-MASS of the resulted oil was performed in an Agilent 7890 series gas chromatograph and an Agilent 5975A series mass spectrometer. The samples were diluted with acetone. The temperature program of the column was as follows: 60 °C for 3 min and then raised to 230 °C at 10 °C/min and held for 15 min.
4.4. Catalytic Activity. The catalytic activity test for the palmitic acid esterification reaction was carried out in a threenecked flask under stirring batch conditions at atmospheric pressure, as shown in Figure 12. The catalyst, palmitic acid, and methanol were added to the flask with the designated catalyst amount (3, 6, and 9 wt %) and molar ratios of methanol to palmitic acid (14:1, 18:1, 22:1, 25:1, and 30:1). The flask was heated to the designated temperatures (50, 60, 65, 70, 75, and 80 °C) by a temperature-controlled water bath, which was monitored by a thermometer in the reaction system. The vaporized methanol was refluxed by a condenser. A magnet rotor in the water bath was used to ensure the magnet rotor in the water bath was used to ensure the reaction can be carried out under stirring conditions. The reaction system was monitored by a thermometer in the reaction system. The unreacted palmitic acid was determined by the titration of KOH (0.1 mol/L) using 0.1% phenolphthalein (alcoholic solution) as a pH indicator. Each experimental point was repeated 3 times parallelly to ensure the reliability of the results. The palmitic acid conversion was estimated by the following equation.

\[
\text{Con. (\%) = } \frac{\text{the added palmitic acid} - \text{the consumed KOH}}{\text{the added palmitic acid}} \times 100\%
\]

![Figure 12. Schematic diagram of the instrument for the palmitic acid esterification reaction.](image)

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### Notes
The authors declare no competing financial interest.

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