Heterogeneous and efficient transesterification of *Jatropha curcas* L. seed oil to produce biodiesel catalysed by nano-sized SO$_4$$^2$$^-$/TiO$_2$

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Developing high-efficiency hetero-catalysts for transesterification reaction is of great importance in the production of biodiesel from *Jatropha curcas* L. seed oil (JO). Here, we synthesized a series of sulfated TiO$_2$ by treating with varying H$_2$SO$_4$ concentration ($\times$SO$_4$$^2$$^-$/TiO$_2$) and TiO$_2$ catalysts and applied to the transesterification of JO. Furthermore, these heterostructures were characterized by many characterization methods including XRD, FT-IR, N$_2$-adsorption, SEM, TEM, TG, py-IR and NH$_3$-TPD, and their catalytic performance was investigated under various operating conditions. The results reveal that both the Bronsted and Lewis acid sites are presented in the $\times$SO$_4$$^2$$^-$/TiO$_2$ catalysts, while only Lewis-type sites are observed in the TiO$_2$ catalyst. And the acid intensity, surface area and mesoporous volume of catalysts are improved obviously after treating TiO$_2$ with sulfuric acid. Then the $\times$SO$_4$$^2$$^-$/TiO$_2$ catalysts exhibit much higher catalytic activity than TiO$_2$ catalyst, which is attributed to the larger surface area and mesoporous volume and stronger acidity. Furthermore, the reusability behaviour of 1.5SO$_4$$^2$$^-$/TiO$_2$ catalyst in the transesterification of JO was also studied.

1. Introduction

The consumption of finite fossil fuels (e.g. petroleum, coal and natural gas) constantly and rapidly increases due to the course of industrialization and population growth. However, there are still
many deficiencies of these non-renewable sources, such as high costs, lowly efficiency and environment unfriendly [1–6]. Therefore, the research effort focused on alternative sources of highly efficient, green and renewable energy has become very popular in recent years. Biodiesel, the monoalkyl esters of long chain fatty acids (C_{12}–C_{22}) derived from a renewable lipid feedstocks such as vegetable oil (VO) or animal fat, is providing a substitute or additive to diesel as a kind of alternative energy in developing as well as developed countries [7–10]. Usually, vegetable oils are preferred to be used as the feedstock due to its low cost and simple method in the production process of biodiesel [3,5,11]. As shown in Scheme 1, the biodiesel can be prepared by transesterification process combining VO with alcohol in the presence of the catalyst to form fatty acid alkyl esters (i.e. biodiesel) and glycerol [4,12].

*Jatropha curcas* L. seed oil (JO), as a typical non-edible oil, which is one of the best-suited feedstocks for biodiesel production in terms of economical, sociological and environmental implications [3,13]. Therefore, many researchers have paid great attention to the studies on the production of low-cost biodiesel from JO. Generally, catalytic transesterification of JO can be carried out over homogeneous [14–16] or heterogeneous catalysts [17–22]. Unfortunately, the homogeneous catalysts exhibit the fast reaction rate and high conversion, but the removal and reusability of catalysts are difficult and producing a large amount of hazardous wastewater. To overcome the above drawbacks, heterogeneous catalysts are the preferred catalysts which allow the catalysts to be easily separated and re-used. Furthermore, heterogeneous catalytic transesterification is divided into base catalysed [17,23,24], acid catalysed [18,25,26] and enzymatic catalysed [21,27–29]. Clearly, the solid base is not a suitable catalyst for biodiesel production because of the high free fatty acid (FFA) content of JO, which will result in soap formation [30,31]. Additionally, enzymatic transesterification has severe disadvantages of high costs, long residence times and poor stabilities, although it is more efficient, highly selective and involves less energy consumption [2,3,25,31]. However, heterogeneous acid catalysis can be a good way to produce the biodiesel using the solid acid catalysts, such as H-form zeolites [32,33], carbon-derived materials [26,34], heteropolyacids [30,35], acidic ion-exchange resins and mesostructure silica [36,37], etc.

As well known, the sulfated metal oxides (e.g. SO_4^{2–}/ZrO_2, SO_4^{2–}/Nb_2O_5 and SO_4^{2–}/TiO_2) are typical solid super acid, and they possess potential economic and green benefits for a wide variety of hydrocarbon reactions [4,13]. Hence, we think that the sulfated metal oxide catalyst can also exhibit good catalytic activity in the transesterification of JO. Actually, sulfated metal oxides have been applied in esterification and transesterification reaction and shown good catalytic performance in catalytic reaction systems [16,38,39].

The objective of this work is to develop and test sulfated metal oxide catalysts in the transesterification of JO. Firstly, a series of sulfated TiO_2 treated with different H_2SO_4 (xSO_4^{2–}/TiO_2) and TiO_2 catalysts have been prepared and characterized carefully by multiple techniques. Furthermore, particular focus has been given to the effect of H_2SO_4 concentration of the xSO_4^{2–}/TiO_2 catalysts on the transesterification reaction, and the operation conditions, such as reaction time, CH_3OH : JO (molar ratio), catalyst content and reaction temperature, were also systematically investigated. Additionally, the reusability behaviour of sulfated TiO_2 catalyst in this reaction was also studied.

2. Material and methods

2.1. Materials

*Jatropha curcas* seeds were supplied by Lv You Seed of Shuyang Co. Ltd, China. Titanium tetrachloride (TiCl_4) and methyl heptadecanoate were purchased from Aladdin Chemistry Co. Ltd, China.
Acid methyl ester standards were purchased from Nu-Chek-Prep, Inc., USA. Ammonia solution (28 wt\% in H\textsubscript{2}O) was purchased from Chinasun Specialty Products Co. Ltd, China. Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and hexane were purchased from Tianjin Yongda Chemical Reagent Co. Ltd, China. Methanol and petroleum ether were purchased from Tianjin Damao Chemical Reagent Factory, China.

2.2. Synthesis of catalyst samples

The TiO\textsubscript{2} was prepared according to the literature with modification and carried out in a 500 ml three-neck round-bottom flask with mechanical stirring and the following procedure [40]. An amount of TiCl\textsubscript{4} (10 ml) was slowly added to deionized water (200 ml) and cooled by ice water. Ammonia solution was then added dropwise to the above mixture to a final pH around 8.0 \textasciitilde 9.0. The precipitate was filtered, washed with deionized water until no Cl\textsuperscript{2} (tested by 1.0 mol l\textsuperscript{-1} AgNO\textsubscript{3} solution) and dried at 393 K for 12 h. The obtained solids (Ti(OH)\textsubscript{4}) were powdered below 100 mesh, then calcined at 823 K for 3 h in air to obtain the TiO\textsubscript{2} sample.

The SO\textsubscript{2}/C\textsubscript{0}/TiO\textsubscript{2} was prepared by the impregnation of the above Ti(OH)\textsubscript{4} with 0.5 mol l\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} under stirring for 12 h. Afterwards, the mixture was filtered, washed with deionized water until no SO\textsubscript{2} (tested by 1 mol l\textsuperscript{-1} BaCl\textsubscript{2} solution), dried at 393 K for 12 h and finally calcined at 823 K for 3 h, as synthesis sample denoted as 0.5SO\textsubscript{2}/C\textsubscript{0}/TiO\textsubscript{2}. Similarly, the other SO\textsubscript{2}/C\textsubscript{0}/TiO\textsubscript{2} samples are denoted as xSO\textsubscript{2}/C\textsubscript{0}/TiO\textsubscript{2}, with x varied at 1.0, 1.5 and 2.0, respectively.

2.3. Catalyst characterization

X-ray powder patterns (XRD) were obtained with a RIGAKU Ultima IV diffractometer using Cu K\textalpha radiation. Nitrogen physisorption (N\textsubscript{2}-adsorption) measurements were carried out on a Micromeritics ASAP 2020 M apparatus at the temperature of liquid nitrogen (77 K). The specific surface area and pore volume were calculated according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Fourier-transform infrared (FT-IR) spectra of the catalyst samples were recorded on a Thermo Nicolet iS5 FT-IR spectrometer (KBr pressed flake). The acidity of the catalysts was measured using temperature-programmed desorption of ammonia (NH\textsubscript{3}-TPD) on a Micromeritics ASAP 2920 instrument. The acid properties of the catalysts were also investigated by pyridine FT-IR (Py-IR), performed on a Bruker TENSOR 27 instrument equipped with an in situ reactor cell. The samples were pre-treated firstly, the system was then degassed and evacuated at designated temperature, and the IR spectra were recorded. Scanning electron microscopy (SEM) images were recorded on a SUPRA55 apparatus. Transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscope. Thermo-gravimetric analyses (TG) of the samples were carried out on an SDT Q600 apparatus from 298 to 1073 K with a heating rate of 10 K min\textsuperscript{-1} in air (25 ml min\textsuperscript{-1}).

2.4. Preparation of JO

*Jatropha curcas* seeds were put in a desiccation oven and dried at 393 K for 24 h. They were then chopped using a grinder to a size of 80 meshes. Extracting the *Jatropha curcas* L. seed oil (JO) with solvents was carried out in a 500 ml three-necked round-bottom flask fitted with a reflux condenser under vigorous stirring. In a case, 40 g *Jatropha curcas* seeds powder and 250 ml of hexane (solvent) were used. The extraction process was heated at 343 K for 5 h. A rotavapor was used at 348 K for 25 min in order to remove the solvent. Finally, the JO was dried at 333 K until its weight was consistent. And the acid value and FFA content of the JO are 15.30 mgKOH g\textsuperscript{-1} oil and 7.65\% w/w, respectively.

2.5. Transesterification of JO

Transesterification of JO was carried out in a 25 ml PTFE-lined stainless steel autoclave under vigorous stirring, and the reaction temperature was achieved on a hot-plate stirrer (MR Hei-Tec, Heidolph, Germany) connected to an electronic temperature controller (EKT 3001, Reax 2, Heidolph, Germany) oil bath. In a typical experiment, the reaction mixture containing 3.0 g of JO, 1.0 g of methanol, 1.0 g of petroleum ether and 0.12 g of catalyst was added in the reactor. Then the reaction system was heated to 393 K and kept constant for 24 h under the stirring rate of 600 r.p.m. After the end of the reaction, the final solution was separated from the catalyst by centrifugation. The liquid phase obtained was kept in a separating funnel to separate the upper organic layer, containing the target
product (biodiesel), and finally rotary-evaporated to yield the biodiesel. The catalytic performance of the catalyst material in transesterification was tested with JO. The concentrations of fatty acid methyl esters (FAMEs) were analysed on a gas-chromatographic instrument (Agilent 7890B, GC) equipped with an FID detector and FFAP capillary column (30 m x 0.32 mm x 0.50 μm) with high purity nitrogen (99.99%) as the carrier gas. Analytical conditions were as follows: injector port at 493 K, FID detector at 513 K and the oven temperature was programmed from 423 K at 15 K min⁻¹ to 483 K (16 min). Methyl heptadecanoate was applied as an internal standard [41]. After transesterification of Jatropha curcas L. seed oil, the composition of FAMEs was determined by GC analysis, which was as follows (wt%): methyl palmitate = 14.6%, methyl stearate = 7.6%, methyl oleate = 44.5%, methyl linoleate = 32.5%, other products = 0.8%, which is very close to that result reported in the reference [42]. And the detail GC graph of biodiesel from JO is shown in figure 1.

Biodiesel (FAMEs) was the main target product. XJO, S_MP, S_MS, S_MO, S_ML and S_Biodiesel denote the conversion of JO (JO conv.) and the selectivity of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and biodiesel (biodiesel sel.), respectively. These key parameters were calculated as follows:

\[
X_{JO} = \frac{n^0_{JO} - n_{JO}}{n^0_{JO}} \times 100\%,
\]

(2.1)

\[
S_{MP} = \frac{n_{MP}}{n_{MP} + n_{MS} + n_{MO} + n_{ML} + n_{Other}} \times 100\%,
\]

(2.2)

\[
S_{MS} = \frac{n_{MS}}{n_{MP} + n_{MS} + n_{MO} + n_{ML} + n_{Other}} \times 100\%,
\]

(2.3)

\[
S_{MO} = \frac{n_{MO}}{n_{MP} + n_{MS} + n_{MO} + n_{ML} + n_{Other}} \times 100\%,
\]

(2.4)

\[
S_{ML} = \frac{n_{ML}}{n_{MP} + n_{MS} + n_{MO} + n_{ML} + n_{Other}} \times 100\%.
\]

(2.5)

and

\[
S_{Biodiesel} = S_{MP} + S_{MS} + S_{MO} + S_{ML}
\]

(2.6)

where \(n^0_{JO}\) and \(n_{JO}\) denote the initial and final molar content of JO, respectively. \(n_{MP}, n_{MS}, n_{MO}, n_{ML}\) and \(n_{Other}\) represent the molar content of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and other products, respectively. In all the experiments, the amounts of other products are too low to be measured, so they were not shown in tables and figures.

Figure 1. Representative gas chromatograms obtained from biodiesel samples produced from JO.
3. Results and discussion

3.1. Characterization results of the catalyst samples

Figure 2 shows the XRD patterns of TiO₂ and xSO₄²⁻/TiO₂ (x is 0.5, 1.0, 1.5 and 2.0) calcined at 823 K for 3 h. The typical diffraction pattern of TiO₂ clearly indicates that the sample is pure anatase phase (JCPDS Card No. 21–1272) [43]. Additionally, the similar characteristic peaks at 2θ of 25.3°, 37.9°, 48.0°, 54.0°, 55.1° and 62.7° are observed in the xSO₄²⁻/TiO₂ samples, indicating that the structures of these samples have no differences [40,44]. The N₂ adsorption–desorption isotherms of TiO₂ and xSO₄²⁻/TiO₂ samples show type IV behaviour with the typical hysteresis loop, suggesting narrow slit-shaped pores that are generally associated with plate-like particles. And these existing pores are ascribed to the aggregation of single crystals [43]. In addition, the results of the specific surface area and pore volume calculated with the BET and BJH method,
respectively, indicated that the TiO₂ and xSO₄²⁻/TiO₂ samples are mesoporous structures without any micropore. However, the xSO₂⁺/C₀₄/TiO₂ samples exhibit much larger surface area and mesopore volume than TiO₂ sample, and the surface area increases with the impregnation sulfuric acid content, which is in agreement with the results obtained in the previous reference [45]. This may be because the TiO₂ particles are partially dissolved by H₂SO₄, which would reduce the particle size and lead to the increase in BET area [46]. Similarly, the mesopore volume, which is the hole between the crystal particles, will increase when the catalyst particle size decreases in these xSO₂⁺/TiO₂ samples, in good agreement with the results obtained by nitrogen sorption (figure 3).

The FT-IR spectra of all samples are given in figure 4. The broad peak at about 500 cm⁻¹ belongs to Ti–O stretching vibration. As for the xSO₂⁺/TiO₂ samples, the absorbance bands at 1177 cm⁻¹ demonstrate that the SO₂⁺-dopant might coordinate with TiO₂ in the network [47,48]. And these samples exhibit obvious absorption at 1640 cm⁻¹, corresponding to the stretching vibration of the hydroxyl group on the surface [49]. As we know, although TiO₂ itself possesses the acidity, the acidity of TiO₂ can be further enhanced by modifying its surface with sulfate groups [50]. The NH₃-TPD spectra of TiO₂ and SO₂⁺/C₀₄/TiO₂ with different impregnation sulfuric acid concentration samples are shown in figure 5 and table 1. The peaks shown in these profiles are assigned to the desorption of NH₃ from the acid sites of the sample surface. Desorption temperature is related to the acid strength of xSO₂⁺/TiO₂, and the higher desorption temperature, the stronger acid strength [51]. There are three principal desorption peaks in the range of 390–450, 530–590 and 720–790 K. And these peaks correspond to the weak acid sites, middle acid sites and strong acid sites, respectively [52]. It can be obviously seen that TiO₂ contains some weak acids and middle acids. The acidity of xSO₂⁺/TiO₂ is stronger than that of TiO₂ after treatment of sulfuric acid. And the laws remain static that more middle acids and strong acids between SO₂⁺ and TiO₂ form with the increase in sulfuric acid concentration. And these stronger acids can promote the transesterification reactions [3,4].

**Table 1.** The specific surface areas, pore volumes and NH₃-TPD measurements of all catalysts.

| sample          | S BET (m² g⁻¹) | V Mesopore (cm³ g⁻¹) | V Micropore (cm³ g⁻¹) | total NH₃ desorbed (mmol g⁻¹) |
|-----------------|---------------|----------------------|-----------------------|-------------------------------|
| TiO₂            | 33.8          | 0.08                 | 0                     | 0.16                          |
| 0.5SO₂⁺/TiO₂    | 70.4          | 0.19                 | 0                     | 0.33                          |
| 1.0SO₂⁺/TiO₂    | 74.7          | 0.23                 | 0                     | 0.38                          |
| 1.5SO₂⁺/TiO₂    | 80.9          | 0.26                 | 0                     | 0.39                          |
| 2.0SO₂⁺/TiO₂    | 81.2          | 0.23                 | 0                     | 0.37                          |

![Figure 4. FT-IR spectra of the TiO₂ and xSO₄²⁻/TiO₂ samples.](image)

The FT-IR spectra of all samples are given in figure 4. The broad peak at about 500 cm⁻¹ belongs to Ti–O stretching vibration. As for the xSO₄²⁻/TiO₂ samples, the absorbance bands at 1177 cm⁻¹ demonstrate that the SO₄²⁻-dopant might coordinate with TiO₂ in the network [47,48]. And these samples exhibit obvious absorption at 1640 cm⁻¹, corresponding to the stretching vibration of the hydroxyl group on the surface [49]. As we know, although TiO₂ itself possesses the acidity, the acidity of TiO₂ can be further enhanced by modifying its surface with sulfate groups [50]. The NH₃-TPD spectra of TiO₂ and SO₄²⁻/TiO₂ with different impregnation sulfuric acid concentration samples are shown in figure 5 and table 1. The peaks shown in these profiles are assigned to the desorption of NH₃ from the acid sites of the sample surface. Desorption temperature is related to the acid strength of xSO₄²⁻/TiO₂, and the higher desorption temperature, the stronger acid strength [51]. There are three principal desorption peaks in the range of 390–450, 530–590 and 720–790 K. And these peaks correspond to the weak acid sites, middle acid sites and strong acid sites, respectively [52]. It can be obviously seen that TiO₂ contains some weak acids and middle acids. The acidity of xSO₄²⁻/TiO₂ is stronger than that of TiO₂ after treatment of sulfuric acid. And the laws remain static that more middle acids and strong acids between SO₄²⁻ and TiO₂ form with the increase in sulfuric acid concentration. And these stronger acids can promote the transesterification reactions [3,4]. The acid
type of the solid samples is further determined by using pyridine-IR technology (figure 6). The peaks around 1542 and 1445 cm\(^{-1}\) can be assigned to the adsorption of coordinated pyridine in Brønsted (B) acid sites and Lewis (L) acid sites, respectively, and the peak at 1490 cm\(^{-1}\) is ascribed to a combination of B and L acid sites \[53\]. The results show all the samples contain an amount of L acid sites, which may result from the coordination between SO\(_2^-/\text{C}_0\text{O}_4^-\) and TiO\(_2\) in the network \[48\]. However, the Brønsted acidic sites are formed in the xSO\(_2^-/\text{C}_0\text{O}_4^-\)/TiO\(_2\) but are not presented in TiO\(_2\) sample, attributing to the surface adsorption between SO\(_2^-/\text{C}_0\text{O}_4^-\) species and TiO\(_2\). As shown in figure 7, in one SO\(_2^-/\text{C}_0\text{O}_4^-\)/TiO\(_2\) unit, two oxygen atoms from S–O bonds are bonded to Ti atoms in addition to the coordination of an S=O group with a Ti atom, and the acidic proton is derived from the surface hydroxyl group of TiO\(_2\) induced by the sulfate group. This acidic proton can be released easily owing to three S–O–Ti bonds linking one SO\(_2^-\) group with the TiO\(_2\) matrix, which results in the Brønsted acidic strength of the SO\(_2^-/\text{C}_0\text{O}_4^-\)/TiO\(_2\) \[4\]. That is to say, the sulfated TiO\(_2\) samples exhibit stronger acidity than pure TiO\(_2\) which is in good agreement to the experimental results of NH\(_3\)-TPD. And the stronger acidity of the solid acid catalysts could promote the transesterification reactions \[4\].

**Figure 5.** NH\(_3\)-TPD spectra of the TiO\(_2\) and xSO\(_2^-/\text{C}_0\text{O}_4^-\)/TiO\(_2\) samples.

**Figure 6.** Py-IR spectra of the TiO\(_2\) and xSO\(_2^-/\text{C}_0\text{O}_4^-\)/TiO\(_2\) samples after degassing at 473 K.
The texture and morphology of catalysts are very important parameters and may influence the catalytic activity. The SEM images of pure TiO2 and $xSO_2^2-/TiO_2$ are shown in figure 8. As shown in figure 8a, the SEM image of the TiO2 depicts that the particles are in the form of aggregates and the surface is irregular. The $xSO_2^2-/TiO_2$ samples show the particles are not only massively agglomerated, but also the particle size of samples is smaller than that of TiO2, which corresponds with the report of reference [54]. These results are further confirmed by TEM images (figure 9). Figure 9 shows that all samples have similar particle morphology. And the nanoparticle size of the TiO2 and $xSO_2^2-/TiO_2$ is around 20 nm (figure 9a) and 15 nm (figure 9b–e), respectively, which is consistent with previous report [54].
3.2. Catalytic activity of the catalysts for transesterification of JO

A series of solid acid catalysts including TiO₂ and $x\text{SO}_4^2-/\text{TiO}_2$ as well as traditional liquid acid catalyst (H₂SO₄) for the transesterification of JO are compared, and the catalytic results of these catalysts are presented in table 2. The H₂SO₄ shows the highest catalytic activity and the JO conversion is 81.4%, which is attributed to a strong acidity of the homogeneous catalyst that has a full contact with the reactants and promotes the conversion of JO. However, this process shows some drawbacks of environment unfriendly, limitations of separating and difficult recycling use of catalysts. Compared with the liquid catalyst, TiO₂ catalyst exhibits the lowest catalytic activity and the JO conversion is only 24.8%. However, the catalytic activity of the $x\text{SO}_4^2-/\text{TiO}_2$ catalysts is enhanced remarkably and the conversion of JO reaches up to above 70.9%, which is three times higher than pure TiO₂. The reason is that the acidity and surface area of $x\text{SO}_4^2-/\text{TiO}_2$ catalysts are much higher than that of TiO₂ (figure 5 and table 1), which can promote the transesterification of JO. Furthermore, the 1.5SO₂⁻/TiO₂ catalyst reveals the highest JO conversion (73.1%) and others perform a little lower than it, because these catalysts have similar structure, surface, texture and acidic properties. Additionally, the high biodiesel selectivity (above 98%) is obtained and FAMEs composition is almost unchanged in the reaction over all catalysts. According to Scheme 1, it will see the amount and composition proportion of the various FAME products produced are as the same as the ones of JO, although the transesterification reaction is catalysed over different catalysts.

### Table 2. Effect of different catalysts on the transesterification of JO. Reaction conditions: JO 3.0 g, methanol 1.00 g, petroleum ether 1.00 g, catalyst 0.12 g, 393 K, stirring rate 600 r.p.m., reaction time 24 h.

| Catalyst         | JO conversion (%) | Biodiesel selectivity (%) | FAMEs composition (%) | Methyl palmitate | Methyl stearate | Methyl oleate | Methyl linoleate |
|------------------|-------------------|---------------------------|-----------------------|------------------|----------------|---------------|------------------|
| TiO₂             | 24.8              | 98.3                      | 14.43                 | 7.24             | 42.84          | 29.72         |
| 0.5SO₂⁻/TiO₂     | 72.6              | 99.0                      | 14.05                 | 7.06             | 44.5           | 31.86         |
| 1.0SO₂⁻/TiO₂     | 71.7              | 98.7                      | 14.21                 | 6.99             | 44.34          | 31.92         |
| 1.5SO₂⁻/TiO₂     | 73.1              | 98.7                      | 14.00                 | 6.98             | 44.38          | 32.09         |
| 2.0SO₂⁻/TiO₂     | 70.9              | 98.7                      | 14.02                 | 6.97             | 44.46          | 31.98         |
| H₂SO₄            | 81.4              | 98.2                      | 13.79                 | 6.85             | 44.56          | 32.39         |

3.3. Effect of various parameters over 1.5SO₂⁻/TiO₂ catalyst

In order to further study systematically, the catalytic performance of the 1.5SO₂⁻/TiO₂ catalyst on the transesterification of JO, the various reaction parameters (reaction time, $n_{\text{CH}_3\text{OH}}:n_{\text{JO}}$, catalyst content and reaction temperature) were investigated carefully. And these researches are also very useful in the production of biodiesel in industry.

3.3.1. Effects of reaction time

The transesterification of JO is carried out for 8, 12, 16 and 24 h, and the results are given in figure 10. The conversion of JO increases remarkably with the increase in reaction time within 16 h. And the JO conversion increases slowly from 70.3% to 73.1% with further increasing the reaction time to 24 h. This result may be ascribed to the JO molecules being adsorbed and reacted gradually on the active sites of the solid acid catalyst along with the transesterification reaction progressed. In addition, as the reaction time increases, the selectivity to biodiesel is relatively stable and remains above 99.0%, and the composition of FAMEs is also almost unchanged (methyl palmitate = 15%, methyl stearate = 8%, methyl oleate = 44%, methyl linoleate = 31%). Thus, the time of 24 h is selected as the reaction time in the following transesterification process.

3.3.2. Effects of $n_{\text{CH}_3\text{OH}}:n_{\text{JO}}$

The appropriate methanol content is a crucial parameter in JO transesterification that could affect the reaction rate and conversion significantly. The effect of the different molar ratio of methanol and JO
from 4.5 to 27 on biodiesel production was investigated and the results are shown in figure 11. The JO conversion increases with the increase in the $n_{\text{CH}_3\text{OH}} : n_{\text{JO}}$ and reaches the maximum (84.6%) at the $n_{\text{CH}_3\text{OH}} : n_{\text{JO}}$ of 18 then begins to decrease. It is well known that the addition of methanol into the reaction mixture during the stage of transesterification could enhance the JO conversion and biodiesel selectivity [21]. However, excessive methanol results in the JO conversion decrease, which may be due to the decline of the contact probability between catalyst and reactants. This is also in good agreement with the literature reported earlier [46]. Clearly, the selectivity to biodiesel (greater than 98.8%) and FAMEs composition is almost unchanged with the rising of $n_{\text{CH}_3\text{OH}} : n_{\text{JO}}$. 

**Figure 10.** Effect of reaction time on transesterification of JO. Reaction conditions: JO 3.0 g, methanol 1.0 g, petroleum ether 1.0 g, 1.5SO$_4^{2-}$/TiO$_2$ catalyst 0.12 g, 393 K, stirring rate 600 r.p.m.

**Figure 11.** Effect of the $n_{\text{CH}_3\text{OH}} : n_{\text{JO}}$ on transesterification of JO. Reaction conditions: JO 3.0 g, methanol, petroleum ether 1.0 g, 1.5SO$_4^{2-}$/TiO$_2$ catalyst 0.12 g, 393 K, 24 h, stirring rate 600 r.p.m.
3.3.3. Effects of catalyst content

The results that the transesterification of JO is carried out in several different catalyst amounts (0.06, 0.09, 0.12 and 0.15 g) are shown in figure 12. As catalyst amount is increased from 0.06 to 0.12 g, the conversion of JO increases remarkably from 45.5% to 73.1%, while the XJO almost remains constant even though increasing the loading amount of 1.5SO$_4^{2-}$/TiO$_2$. This can be because the higher amounts of available catalyst allow more JO molecules to be absorbed to the catalytic active centre. Additionally, both the S$_{biodiesel}$ and fatty acids composition have no obvious change with the increasing catalyst content. Thus, 0.12 g is the best 1.5SO$_4^{2-}$/TiO$_2$ catalyst content for biodiesel synthesis from JO considering the low production cost.

3.3.4. Effects of reaction temperature

Reaction temperature is a key factor that influences biodiesel production. The effect of reaction temperature on JO conversion and selectivity to biodiesel is shown in figure 13. The conversion of JO increases remarkably from 23.3% to 85.8% with the increase in reaction temperature from 353 to 413 K. It is generally known that the catalytic activity is improved when the reaction temperature is risen, attributing to the formation of more active species in the catalyst at a higher temperature. Meanwhile, the selectivity of biodiesel remains unchanged (nearly 99.0%) as the temperature increases, and the composition and content of all fatty acids are also not found obviously different.

3.4. Possible transesterification reaction mechanism over SO$_4^{2-}$/TiO$_2$ catalyst

The results of NH$_3$-TPD and Py-IR spectra show that the SO$_4^{2-}$/TiO$_2$ catalyst possesses many acid sites (figures 5 and 6), and it is well known that both Brønsted and Lewis acid sites are presented. Furthermore, the Brønsted acidity of the catalyst can be further enhanced by modifying its surface with sulfate groups. Furthermore, based on previous research reports on the principle of transesterification reaction catalysed by sulfated metal oxides [55,56], the possible mechanism for the transesterification of triglyceride using SO$_4^{2-}$/TiO$_2$ catalyst is provided in figure 14.

3.5. Reusability behaviour of SO$_4^{2-}$/TiO$_2$ catalyst and comparison of the solid acidic catalyst with other catalysts in the literatures

To investigate the reusability of 1.5SO$_4^{2-}$/TiO$_2$ catalyst, a recycling experiment was conducted under the same reaction condition. After each cycle of the reaction was completed, the 1.5SO$_4^{2-}$/TiO$_2$ particles were recovered.
by centrifugation and washed several times with n-hexane to remove any polar impurities. The washed catalyst was dried at 393 K for 8 h and re-used again in the next run. The reuse catalytic performances of 1.5SO2-/C04/TiO2 are listed in table 3. Compared with the fresh 1.5SO2-/C04/TiO2 catalyst, the selectivity of biodiesel and FAMEs composition has no significant change, although the JO conversion drops significantly from 74.8% to 27.5%, 25.7% and 25.3% in the first, second and third cycle of the catalyst, respectively.

In order to further explore the causes of the descending activity of the used catalyst in JO transesterification reaction. The fresh and used 1.5SO2-/C04/TiO2 catalysts are characterized by the methods of N2-adsorption, NH3-TPD, XRD and TG. The XRD diffraction patterns have confirmed that the structure destruction of used 1.5SO2-/C04/TiO2 did not occur (figure 15a). However, as shown in table 1, compared with the fresh catalyst, the S_{BET} and V_{Mesopore} of used catalyst decrease obviously from 76.4 m² g⁻¹ and 0.26 cm³ g⁻¹ to 62.1 m² g⁻¹ and 0.18 cm³ g⁻¹, respectively. And the TG analyses also show that the weight loss of the used catalyst (3.0%) is much greater than that of the fresh catalyst. 

![Figure 13](rsos.royalsocietypublishing.org)  
**Figure 13.** Effect of the reaction temperature on transesterification of JO. Reaction conditions: JO 3.0 g, methanol 1.0 g, petroleum ether 1.0 g, 1.5SO2-/C04/TiO2 catalyst 0.12 g, 24 h, stirring rate 600 r.p.m.

![Figure 14](rsos.royalsocietypublishing.org)  
**Figure 14.** Possible mechanism of transesterification reaction over SO2-/C04/TiO2 catalyst.
(0.6%), indicating that some carbonaceous residues (cokes) are formed on the used catalyst (figure 15b). It is well known that deposits of cokes on the catalyst surface can cover the active center and block the mesopore channels [57,58]. So the catalytic activity of the used catalyst decreases significantly. Additionally, the regenerated 1.5SO$_2$/C0$_4$/TiO$_2$ is obtained by calcining at high temperature, which successfully removes these cokes on the surface of the used 1.5SO$_2$/C0$_4$/TiO$_2$, being verified sufficiently by the results of TG analysis. However, compared with the used catalyst (27.5%), the JO conversion merely rises slightly over a regenerated catalyst (31.8%). In other words, the deposition of coke is unlikely to be a major reason for the deactivation of SO$_2$/C0$_4$/TiO$_2$ catalyst in this reaction. On the other hand, the result of NH$_3$-TPD analysis (table 1) shows that the total NH$_3$ desorbed of the used 1.5SO$_2$/C0$_4$/TiO$_2$ (0.24 mmol g$^{-1}$) is much less than that of the fresh 1.5SO$_2$/C0$_4$/TiO$_2$ (0.39 mmol g$^{-1}$), which means the acidity and activity of the catalyst reduces significantly after being used in transesterification reaction. The reason is that conventional preparation of SO$_2$/C0$_4$/TiO$_2$ is via a post-synthesis grafting method, which leads to relatively weak interactions between SO$_2$ and TiO$_2$ framework and thereby poor catalytic stability, and the leaching of sulfate group also easily happens from SO$_2$/C0$_4$/TiO$_2$ catalyst in a solvent system for a long-running process [4,59,60]. Consequently, the 1.5SO$_2$/C0$_4$/TiO$_2$ catalyst shows poor catalytic stability and deactivates easily in the transesterification of JO, attributing to leaching of SO$_2$ and blocking of the active sites by carbonaceous residues deposition. Therefore, the approaches of improving the reusability of sulfated TiO$_2$ need to be developed by the researchers in the future.

Table 3. Reusability and regenerative performance of 1.5SO$_2$/C0$_4$/TiO$_2$ for transesterification reaction runs. Reaction conditions: JO 3.0 g, methanol 1.00 g, petroleum ether 1.00 g, 1.5SO$_2$/C0$_4$/TiO$_2$ 0.12 g, 393 K, 24 h, stirring rate 600 r.p.m.

| catalyst     | JO conversion (%) | biodiesel selectivity (%) | FAMEs composition (%) |
|--------------|------------------|----------------------------|-----------------------|
|              |                  |                            | methyl palmitate      |
|              |                  |                            | methyl stearate       |
|              |                  |                            | methyl oleate         |
|              |                  |                            | methyl linoleate      |
| fresh        | 73.1             | 98.7                       | 14.00                 |
| first reuse  | 27.5             | 99.1                       | 14.69                 |
| second reuse | 25.7             | 99.1                       | 14.75                 |
| third reuse  | 25.3             | 99.1                       | 14.79                 |
| regenerated  | 31.8             | 99.5                       | 15.87                 |

*aThe regenerated 1.5SO$_2$/C0$_4$/TiO$_2$ is obtained from used 1.5SO$_2$/C0$_4$/TiO$_2$ by calcining at 823 K for 3 h.*
unsatisfactory economy. In addition, Raia et al. [19] reported that the production of biodiesel from JO can be realized at the similar reaction temperature and atmospheric pressure, but the low yield of biodiesel (59.4%) was obtained even though the amount of the catalyst reached 10 wt%. This result therefore shows the superiority of the findings in this work in producing biodiesel with high quality from JO.

### 4. Conclusion

An efficacious and heterogeneous approach to produce the biodiesel from JO catalysed by $\text{SO}_3^-/\text{TiO}_2$ catalysts has been developed. The $\text{TiO}_2$ and $\alpha\text{SO}_3^-/\text{TiO}_2$ catalysts were successfully synthesized and characterized and used in the transesterification of JO. The results demonstrate that the new Brønsted acid sites are formed and the crystalline structure is not destroyed after treating with sulfuric acid of $\text{TiO}_2$ catalyst. And the acid intensity, BET surface area and mesoporous volume of $\alpha\text{SO}_3^-/\text{TiO}_2$ catalysts are stronger than that of $\text{TiO}_2$ catalyst. Furthermore, the catalytic activity tests show that the $\alpha\text{SO}_3^-/\text{TiO}_2$ catalysts exhibit higher catalytic activity than $\text{TiO}_2$ catalyst, attributed to the larger surface area, smaller particle size and stronger acidity. Then the effects of operation conditions were obtained by testing of catalytic activity under the different reaction conditions (time, $\text{CH}_3\text{OH}:\text{JO}$, catalyst content and temperature). In addition, the reusability and deactivation behaviour of 1.5$\text{SO}_3^-/\text{TiO}_2$ was further studied. Combined with the experiment and characterization results of the fresh and used catalysts, the cause for a decrease in the catalyst activity is due to a combination of $\text{SO}_3^-$ leaching and the blocking of the active sites by carbonaceous residues deposition. These researches are very useful in the scaling-up of this sustainability transesterification process for the production of biodiesel from low-cost feedstocks.

Data accessibility. We include all the experimental data in the electronic supplementary material, which are available at https://dx.doi.org/10.5061/dryad.ds6p94f [63].

Authors’ contributions. G.W., C.C. and Y.H. designed the study. C.C., S.G., L.C. and L.L. synthesized the catalysts, performed the characterization of the XRD, BET, SEM, TEM, NH$_3$-TPD, IR and TGA, participated in data analysis and tested the catalytic activity. G.W., C.C. and Y.H. wrote the manuscript. And all the authors gave their final approval for publication.

Competing interests. We declare we have no competing interests.

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