Facile and Low-cost Synthesis of Mesoporous Ti–Mo Bi-metal Oxide Catalysts for Biodiesel Production from Esterification of Free Fatty Acids in \textit{Jatropha curcas} Crude Oil

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Abstract: Mesoporous Ti–Mo bi-metal oxides with various titanium–molybdenum ratios were successfully fabricated via a facile approach by using stearic acid as a low-cost template agent. thermal gravity (TG) / differential scanning calorimetry (DSC) analysis, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, nitrogen adsorption-desorption isotherm, NH$_3$ temperature-programmed desorption (NH$_3$-TPD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements indicated these materials possessing mesoporous structure, sufficient pore size and high acid intensity. The catalytic performance of prepared catalysts was evaluated by esterification of free fatty acids in \textit{Jatropha curcas} crude oil (JCCO) with methanol. The effects of various parameters on FFA conversion were investigated. The esterification conversion of 87.8\% was achieved under the condition of 180$^\circ$C, 2 h, methanol to JCCO molar ratio of 20:1 and 3.0 wt.\% catalyst (relative to the weight of JCCO). The mesoporous catalysts were found to exhibit high activities toward the simultaneous esterification and transesterification of JCCO. Furthermore, the catalyst could be recovered with a good reusability.

Key words: \textit{Jatropha curcas} crude oil, heterogeneous acid catalyst, esterification, biodiesel

1 Introduction

Rapid depletion of fossil fuels and global environmental concerns resulting from over consumption of fossil fuels has prompted an urgent demand for alternative fuels. biodiesel, which is a renewable, less polluting, carbon neutral, biodegradable and can be mixed with petroleum diesel in any proportion or used directly in diesel engines with minor modifications liquid fuel, has attracted increasing attention in recent years$^{1,2}$. At present, the biodiesel is produced by esterification or transesterification of free fatty acids (FFAs), vegetable oil, animal oil, or waste oil with short-chain alcohols using homogeneous or heterogeneous catalyst.

However, the major hurdle in the use of biodiesel for replacing conventional petroleum fuels is its higher cost. The two main factors that affect the cost of biodiesel are the cost of feedstock and the processing cost (such as catalysts, equipments and postprocessing, etc.). Therefore, cheap non-edible oil has been found to be effective feedstock replacements to reduce the cost of biodiesel but not compete with food crop$^{3,4}$. As such, \textit{Jatropha curcas} as a multipurpose species has considerable potential$^{5-6}$. However, \textit{Jatropha curcas} crude oils, like most of non-edible oils, contains a significant amount of FFAs$^{7,8}$, which cannot be directly used in the base-catalyzed transesterification reaction. It was reported that a significant drop in the conversion of ester took place when the FFAs content was above 2\%, owing to the reaction of FFAs with the alkali catalyst to form soap and result in difficulties in process separation and reutilization of catalyst$^{9}$. Therefore, some pretreatment processing (esterification process) was carried out to reduce the amount of FFAs in the feedstock beforehand$^{10}$. Among the available biodiesel production methods, homogeneous acid (or base) is the most commonly used pro-
cessing technique for catalytic esterification or transesterification. However, they suffer from problems of product separation, poor catalyst recyclability and the need for treatment of waste effluent. The use of heterogeneous catalyst can solve some of these problems through the ease of product separation and good catalyst recyclability. To date, various heterogeneous acid catalysts have been reported for biodiesel production, such as metal complexes, various heterogeneous acid catalysts have been reported for biodiesel production, such as metal complexes, zeolites, heteropolyacids, ion exchange resins and mesoporous solid acid. Nevertheless, metal complex catalysts with complex preparation process and low activity limit their applications. Zeolites catalysts have small (micron-sized) pores are not suitable for biodiesel production because of the diffusion limitations induced by the large fatty acid molecules. Ion exchange resins have good catalytic activity, but have a low thermal stability at high reaction temperature. For mesoporous materials, it possessed uniform pore size and high surface areas, which are always relatively responsible for the high catalytic activity in esterification, transesterification, etherification, etc. But the modification template agents (such as P123) of synthesizing mesoporous materials are rather expensive with tedious catalyst preparation processing, which will largely limit the industrial applications. Herein, a facile and low-cost approach for preparing mesoporous mixed metal oxides catalyst is proposed. In our preliminary work, we have reported the synthesis of biodiesel by esterification over monofunctional carboxylic acids modified Zr–Mo and Al–Mo mixed metal oxides. Compared with other carboxylic acids, stearic acid modified metal oxide having higher acid intensity and surface area showed the best catalytic performance. It was well indicated that stearic acid might replace P123 as a low-cost template agent for preparation of porous catalysts.

In the present study, a series of mesoporous Ti–Mo oxides with different titanium–molybdenum ratios were prepared in the presence of stearic acid. To the best of our knowledge, this is the first report on using stearic acid modified Ti–Mo oxides as mesoporous catalyst for the production of biodiesel. The mesoporous catalysts were characterized by various analytical and spectroscopic techniques such as TG-DSC, XRD, FT-IR, nitrogen adsorption–desorption isotherm, NH3-TPD, XRD, FT-IR and TEM, and their catalytic activity was determined in the esterification of JCCO free fatty acids with methanol. The influence of the methanol/oil molar ratio, amount of catalyst, reaction temperature and reaction time was studied, and the reusability of the catalyst was also checked. Moreover, simultaneous transesterification and esterification of JCCO with methanol was investigated.

2 Experimental

2.1 Materials

*Jatropha curcas* (JC) seeds were purchased from Luodian County, Guizhou Province. The low-grade *Jatropha curcas* crude oil (JCCO) was obtained through mechanical expression. Oleic acid (AR), methanol (AR, > 99%), titanium (IV) isopropoxide (C12H26O3Ti, AR, 98%), MoCl5 (AR, 99.6%) and stearic acid (AR, > 99%) were purchased from Sinopharm Chemical Regent Co., Ltd. All other chemicals were of analytical grade and used as received, unless otherwise noted.

2.2 Preparation of modified Ti–Mo oxides catalyst

A series of titanium–molybdenum mixed oxides with different Ti/Mo ratios were synthesized using a previously reported recipe. In a typical procedure, with a total Ti–Mo molar of 9 mmol, C12H28O4Ti and MoCl5 were first dissolved in a solution containing 10 g of n-propanol and a certain amount of stearic acid (the molar ratio of C12H28O4Ti and MoCl5 to stearic acid is 1/4 and 1/5, respectively), the mixture was stirred and maintained at room temperature for 1 h. Subsequently, the homogeneous mixture was heated at 100°C for 30 min and then heated at 170°C for 1 h to yield the melted precursor. Finally, the melted precursor was calcined at 600°C for 5 h at the heating rate of 4°C/min to give the product as a mesoporous catalyst. By varying the amounts of C12H28O4Ti and MoCl5, mesoporous Ti–Mo oxides with different compositions were fabricated and denoted as Ti10−nMon, where n refer to the mol% of Mo in Ti–Mo composites.

For comparison, stearic acid modified Al–W, Al–Mo and Ti–W oxides and P123 modified Ti–Mo oxides were prepared. These catalysts were denoted as Al1W0–SA, Al7Mo3–SA, Ti7W3–SA and Ti7Mo3–P123, respectively, where 3 refer to the mol% of W (or Mo) in mixed metal oxides composites.

2.3 Characterization of the catalyst

TG analysis was carried out with a Netzsch STA449C Jupiter instrument in dry air at a heating rate of 10°C/min.

X-ray diffraction patterns (XRD) of the samples were recorded on a RIGAKU D/MAX 2550/PC diffractometer using Cu Kα1 radiation (λ = 1.54056 Å) at 40 kV and 100 mA, over a 2θ range of 10–70° with a resolution of 0.02° at a scanning speed of 5°/min.

FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs).

SEM was performed using a field emission scanning electron microscope (FESEM, XL-30, Philips) at 25 kV.

Transmission electron micrographs (TEM) and high resolution TEM were taken on a JEM 2010 (200 kV) (JEOL) or Tecnai G2 F20 (200 kV) (FEI).

The acidity of the catalysts was measured by temperature-programmed desorption (TPD) of ammonia (Auto-
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The standard procedure for the TPD measurements involved the activation of the sample in flowing He at 573 K (60 min), cooling to 323 K, adsorbing NH₃ from a He–NH₃ (10%) mixture, desorbing in He at 323 K for 60 min, and finally carrying out the TPD experiment by raising the temperature of the catalyst in a programmed manner (10 K min⁻¹). The areas under the TPD curves were converted into mmol of NH₃ per gram of catalyst based on injection of known volumes of the He–NH₃ mixture under similar conditions.

The BET surface area, total pore volume and pore size distribution of the catalyst were determined with ASAP 2020M volumetric adsorption analyzer (Micromeritics, USA).

2.4 Catalytic reaction

2.4.1 Esterification reaction

The esterification of JCCO (or oleic acid) with methanol was conducted by adding Ti-Mo oxides catalyst into a stainless steel high-pressure autoclave reactor equipped with a temperature controller and mechanical stirrer, and the resulting mixture was heated at 180°C for 60 min under autogeneous pressure (1.0 – 1.2 MPa). After reaction completion, the catalyst was separated from the mixture containing products and reagents by simple decantation, and the excess methanol with water was removed under reduced pressure to purify the product. The acid value of the product was determined via a titration method, and the conversion could be calculated using our previously reported technique²⁴, ²⁵. All data presented are averages of at least duplicate experiments.

2.4.2 Simultaneous esterification and transesterification of Jatropha curcas crude oil

The simultaneous esterification and transesterification reaction was carried out in stainless steel high-pressure autoclave reactor with stirring. A prescribed amount of JCCO, methanol and catalyst were placed in the reactor, and the resulting mixture was heated at 180°C under autogeneous pressure (1.0 – 1.2 MPa). After the reaction, the catalytic system was cool down to room temperature and the products were extracted. The fatty acid methyl ester (FAME) content of the samples were determined by gas chromatography (Agilent 6890GC) equipped with a flame ionization detector. A GC method based on external standards was adopted to analyze the FAME content of the biodiesels. The FAME yield could be calculated using our previously reported technique²¹.

3 Results and discussion

3.1 Activities of different heterogeneous acid catalysts

Different catalysts were performed under identical reaction conditions to identify the most promising mixed-metal-oxide catalysts for the esterification reaction. The best catalyst was selected on the basis of maximum conversion rates. The experimental results are shown in Table 1. From this table it was seen that the Al-W-SA and Ti-W-SA showed low activities, with methyl oleate conversion conversion below 45% and JCCO esterification conversion below 30%. However, when molybdenum were introduced into the catalyst, the catalytic activity of the formed heterogeneous acid catalyst was improved in the esterification reaction, probably because of the presence of strong acid sites on the surface of the catalyst, and Ti-Mo-SA was the best among the other catalysts tested. On the basis of the above results, the Ti-Mo-SA catalyst showed potential for use as a heterogeneous acid catalyst and therefore was selected for the transesterification reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Methyl oleate conversion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>JCCO esterification conversion (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No cat.</td>
<td>19.1</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;W&lt;sub&gt;1&lt;/sub&gt;–SA</td>
<td>39.6</td>
<td>28.8</td>
</tr>
<tr>
<td>3</td>
<td>Ti&lt;sub&gt;3&lt;/sub&gt;W&lt;sub&gt;1&lt;/sub&gt;–SA</td>
<td>44.8</td>
<td>28.0</td>
</tr>
<tr>
<td>4</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;Mo&lt;sub&gt;3&lt;/sub&gt;–SA</td>
<td>83.7</td>
<td>82.9</td>
</tr>
<tr>
<td>5</td>
<td>Ti&lt;sub&gt;2&lt;/sub&gt;Mo&lt;sub&gt;3&lt;/sub&gt;–SA</td>
<td>91.4</td>
<td>87.8</td>
</tr>
<tr>
<td>6</td>
<td>Zr&lt;sub&gt;2&lt;/sub&gt;Mo&lt;sub&gt;3&lt;/sub&gt;–SA</td>
<td>80.0</td>
<td>83.6</td>
</tr>
<tr>
<td>7</td>
<td>Ti&lt;sub&gt;2&lt;/sub&gt;Mo&lt;sub&gt;3&lt;/sub&gt;–P123</td>
<td>84.9</td>
<td>82.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> Oleic acid conversion (%) = \(\frac{\text{Initial acid value} - \text{final acid value}}{\text{Initial acid value}}\) × 100, reaction conditions: oleic acid / methanol molar ratio = 1:10; catalyst amount = 3 wt. %; reaction temperature = 180°C; reaction time = 60 min.

<sup>b</sup> Reaction conditions: oil / methanol molar ratio = 1:20; catalyst amount = 3 wt. %; reaction temperature = 180°C; reaction time = 60 min.

Table 1  Catalytic activities of different modified catalysts.

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chosen for the subsequent study.

3.2 Characterization of the catalyst

3.2.1 TG-DSC analysis of the catalyst

TG analyses were carried out to provide information on the decomposition of the samples, and also to help determine a more accurate calcination temperature for the catalyst precursors. Figure 1 displays TG-DSC curves of stearic acid modified Ti₇Mo₃ catalyst precursors. With the increase of temperature from room temperature to 300°C, the sample with large weight loss could be mainly assigned to desorption of water from the framework and evaporation of surplus carboxylic acids, corresponding to a strong endothermic peak in DSC curve. Corresponding to the weight loss stage between 300°C and 500°C, a remarkable exothermic peak could be observed in DSC curve. This might be attributed to the decomposition of carboxylic acid-metal complexes in the samples. After 600°C, there was no weight loss in the TG profile and also no observed change in the DSC profiles, indicating no phase transition happened in the structure of the sample, the residue at 600°C corresponds essentially to Ti–Mo oxides, as indicated by the XRD patterns. On the basis of these results, the modified catalyst precursors at 600°C have been well treated with the aim to evaporate surplus carboxylic acids and decompose carboxylic acid-metal complexes. Hence, the calcination temperature for the modified catalyst precursors is 600°C.

3.2.2 Power XRD

The X-ray diffractograms of modified Ti₁₀–₅Moₙ catalysts are presented in Fig. 2. It was noticeable that all samples exhibited typical crystalline anatase phase with the characteristic peaks at about 25°, 27°, 35°, 48° and 55° (based on JCPDS files 01-083-2243), the crystallite size of sample can be calculated by Scherrer equation, Using the strong diffraction peak (2θ = 25°), the average crystallite size was calculated as 21.5, 17.5, 17.4, 15.1, 14.4, 13.4 nm from Ti₇Mo₃ to Ti₃Mo₅, respectively, it was indicated that the addition of Mo-rich to samples leads to a sharp decrease in crystallite size. Moreover, with increasing the Mo content, the crystalline anatase phase was completely swallowed and instead, because of Ti⁴⁺(0.068 nm) and Mo⁵⁺(0.062 nm) having slightly smaller radius. Instead, oxygen vacancies were formed, which might influence the adsorptive and catalytic properties of the system, in agreement with earlier studies. On the other hand, crystalline MoO₃ (based on JCPDS files 47-1320) was observed on the XRD patterns of n = 2–5 and the intensity of these peaks increases with Mo-loading.

3.2.3 FT-IR

The FT-IR spectra of modified Ti₁₀–₅Moₙ (n = 0–5) catalysts were carried out using KBr pellets. The spectrograms as a function of Mo-rich samples with n = 0–5 are shown in Fig. 3. In FT-IR spectra, 800–1200 cm⁻¹ region is interesting as in this region characteristic bands due molybdenum...
species can be detected. From Fig. 3, with increasing Mo content \( n = 4-5 \), the strong sharp peak appears around 993 cm\(^{-1}\), 860 cm\(^{-1}\) and 585 cm\(^{-1}\), which might be attributed to the vibration of the MoO\(_3\) bulk phase, the Mo–O–Mo or O–Mo–O antisymmetric vibration and OMo\(_3\) vibration mode, respectively, according to previous literatures. The FT-IR spectra also revealed the presence of an amorphous structure in samples with \( n = 0-3 \), though the Ti\(_7\)Mo\(_3\) catalyst was detected some weak sharp peaks around 500–1000 cm\(^{-1}\) by crystalline MoO\(_3\), and it can be deduced that amorphous MoO\(_3\) is well dispersed on surface of Ti\(_7\)Mo\(_3\) catalyst.

3.2.4 Nitrogen adsorption–desorption

The textural properties of modified Ti\(_{10-n}\)Mon \( (n = 0-5) \) Ti–Mo metal oxides were analyzed by N\(_2\) adsorption–desorption isotherms (Fig. 4) and pore-size distribution (Fig. S1). All of the samples presented in Fig. 4 showed type IV isotherms with type H2 hysteresis loops at a relative pressure \( (P/P_0) \) of 0.7–1.0 except for Ti\(_7\)Mo\(_3\) catalyst, representative of mesoporous materials, when Mo-rich catalysts with \( n = 4-5 \), the type IV isotherms is gradually destroyed, this probably because of formed non-mesoporous structures with crystallized molybdenum oxide on the catalyst surface to blockage porous, which corresponds well with the FT-IR results. Besides, the pore size distributions of these catalysts were shown in Fig. S1, the corresponding pore size distribution curves performed narrow distribution around 20.0 nm. The textural properties of above samples were summarized in Table 2, the pore size of mesoporous Ti–Mo samples decreases from 28.2 nm to 12.5 nm as the samples with \( n \) values from 0 to 2. In contrast, pore volume and surface area gradually increase within this range. However, the pore size up to maximum for the Ti\(_7\)Mo\(_3\) catalyst with \( n = 3 \). The pore size, pore volume and surface area began to decrease as further increase of Mo-rich in samples, which may be ascribed to the large density of molybdenum oxide (4.692 g cm\(^{-3}\)) and high proportion of Mo introduction that inhibit the shrinkage of the mesoporous framework during calcinations.

3.2.5 NH\(_3\)-TPD

To study the acid strength and acidic properties, NH\(_3\)-TPD was employed on modified Ti\(_{10-n}\)Mon \( (n = 0-5) \) metal oxides and the acid strength was evaluated via NH\(_3\)-TPD based on desorption temperatures. In Fig. 5, these entire samples exhibited a stronger NH\(_3\) desorption peaks centered at around 150°C, representative of the weak acid sites. As a comparison, the Ti\(_{10}\)Mo\(_0\) catalyst possessed much weaker acid sites. Surprisingly, additional sharp peaks were detected around 650°C when increasing the Mo content, confirming the presence of strong acid sites. Moreover, the peak for Ti\(_7\)Mo\(_3\) catalyst was much broader than that of Ti\(_9\)Mo\(_1\) and Ti\(_8\)Mo\(_2\) catalyst, and no peak was observed for the Ti\(_6\)Mo\(_4\) and Ti\(_5\)Mo\(_5\) catalyst. On the other hand, the NH\(_3\)-TPD curves also revealed the presence of a broad main peak at 450°C, it is indicated that samples with \( n = 2-5 \) exhibited the medium strong acid sites. The acid concentrations were calculated according to the amount of adsorbed NH\(_3\) in Table 1, and Ti\(_7\)Mo\(_3\) and Ti\(_8\)Mo\(_2\) are demonstrated to show the lowest (0.25 mmol/g).

Table 2 Textural parameters and acid concentrations of Ti\(_{10-n}\)Mo\(_n\) \( (n = 0-5) \).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample type</th>
<th>Surface area ( \left( \text{m}^2\text{g}^{-1} \right) )</th>
<th>Average Pore size (nm)</th>
<th>Pore volume ( \left( \text{cm}^3\text{g}^{-1} \right) )</th>
<th>Acid concentratione ( \left( \text{mmol/g} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti(_{10})Mo(_0)</td>
<td>21.1</td>
<td>28.2</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>Ti(_{9})Mo(_1)</td>
<td>49.4</td>
<td>21.7</td>
<td>0.27</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>Ti(_{8})Mo(_2)</td>
<td>65.7</td>
<td>12.5</td>
<td>0.21</td>
<td>0.61</td>
</tr>
<tr>
<td>4</td>
<td>Ti(_{7})Mo(_3)</td>
<td>33.0</td>
<td>29.0</td>
<td>0.24</td>
<td>0.78</td>
</tr>
<tr>
<td>5</td>
<td>Ti(_{6})Mo(_4)</td>
<td>27.8</td>
<td>28.8</td>
<td>0.20</td>
<td>0.64</td>
</tr>
<tr>
<td>6</td>
<td>Ti(_{5})Mo(_5)</td>
<td>25.6</td>
<td>26.8</td>
<td>0.17</td>
<td>0.49</td>
</tr>
</tbody>
</table>

\(^e\) Determined by adsorption and TPD of NH\(_3\), acid concentrations were calculated according to the amount of adsorbed NH\(_3\).
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3.2.6 SEM

SEM was further employed to elucidate further morphological and compositional data of modified Ti_{10-}Mo_{n} (n = 0–5) metal oxide catalysts. The SEM images of modified Ti_{10-}Mo_{n} (n = 0–5) are shown in Fig. 6. For the Ti_{10}Mo_{0} catalyst, the small particles are aggregated in irregular shapes. With increasing Mo content (n = 1–3), the particle diameters of the catalysts tend to become smaller and exhibit to a loose honeycombed structure. When Mo-rich catalysts with n = 4–5, the particles were some aggregated with framework partially collapsed.

3.2.7 TEM

The particle size enlargements and morphologies for modified Ti_{10}Mo_{0} catalyst is also clearly seen in TEM images (Fig. S3). As seen from TEM figures, it can be observed that discernible pores were present at the surface of the mesoporous catalyst (Fig. S3a). In addition, the pore properties were investigated using high-resolution TEM (Fig. S3b), the pores can be seen as black spots, with a wormhole framework can be observed on the sample surface. These results are well consistent with the N\textsubscript{2} adsorption–desorption isotherms and SEM analysis.

3.3 Effect of Ti/Mo molar ratio

The esterification of JCCO and oleic acid with methanol was chosen as the model reaction to evaluate the catalytic performance of the various modified Ti/Mo molar ratio catalysts. As shown in Fig. 7, the conversion after 60 min reaction differed significantly among various Ti/Mo molar ratio catalysts. Ti_{10}Mo_{0} gave the lowest conversion, whereas Ti_{7}Mo_{3} achieved the highest conversion. The catalytic activity increased in the order of Ti_{10}Mo_{0} < Ti_{9}Mo_{1} < Ti_{8}Mo_{2} < Ti_{7}Mo_{3} < Ti_{6}Mo_{4} < Ti_{5}Mo_{5}, which is in good agreement with the trend of surface acid site density. Clearly, the good cor-
relation between the catalytic activity and the surface acid site density of various Ti/Mo molar ratio catalysts points to the importance of catalyst acidity in the esterification reaction, which is in good agreement with the characterization of NH₃-TPD. Therefore, more in-depth study on the catalytic activity of modified Ti₇Mo₃ was investigated to the esterification of JCCO with methanol.

3.4 Catalytic activity of modified Ti₇Mo₃ for esterification of FFAs in JCCO

3.4.1 Effect of methanol to oil molar ratio

The methanol and oil ratio is one of the most significant factors that influence the reaction process. The esterification reaction requires one moles of alcohol and one mole of FFAs to give one moles of esters and one mole of water. Since esterification is a kind of reversible reaction, excess alcohol may favor the product side to increase the conversion. To evaluate the influence of molar ratio of oil to methanol on the catalytic activity, the molar ratios of oil to methanol varied from 1:10–1:30 were employed. As depicted in Fig. 8a, the conversion was increased with increasing the ratio up to 1:20 (87.8% conversion). However, a slight increase in the conversion was observed when the ratio was increased beyond 1:20. Taking into account of the excessive methanol that brings about difficulties in the heating and elimination process in order, the optimal molar ratio of *Jatropha curcas* crude oil to methanol is found to be 1:20.

3.4.2 Effect of catalyst dosage of conversion

The effect of the catalyst dosage on the conversion of low-grade JCCO esterification was investigated with Ti₇Mo₃ mixed oxide catalyst by varying catalyst dosages from 0 to 5 wt.%. As indicated in Fig. 8b, when the catalyst dosage was increased from 0–3 wt.%, correspondingly, conversion was gradually increased and a maximum conversion of 87.8% was attained at 3 wt.%. However, further increase in the amount of catalyst, a decreased conversion was observed, probably because the slurry (mixture of solid catalyst and reactants) was too viscous. From the result, 3 wt.% of catalyst was chosen as the optimum catalyst dosage.

3.4.3 Effect of reaction time

Figure 8c shows the effect of reaction time on esterification conversion at 30, 45, 60, 75 and 90 min. From the results it can be seen that the conversion increased from 46.9% to 87.8% with reaction time increasing from 30 min to 60 min. However, the conversion increased slightly to 91.2% and maintained constant with further increase of reaction time to 90 min. So, 60 min is sufficient in terms of shortening reaction time and reducing energy consumption.

3.4.4 Effect of reaction temperature

The effect of reaction temperature on the catalytic activity of Ti₇Mo₃ was studied in the temperature range from 80 to 200°C, while keeping the other experimental conditions constant. The results shown in Fig. 8d revealed that the conversion increased with an increase in temperature and it reached 87.8% at 180°C. When the reaction temperature is further increased to 200°C, the conversion only increases slightly. So, the optimum reaction temperature of 180°C was chosen in the subsequent experiments.

3.5 Reusability

To test the reusability of the catalyst, the JCCO esterification reaction was conducted. After the first production run and the conversion analysis, the reaction mixture was kept at room temperature for an hour to allow the catalyst to settle to the bottom of the reactor, and the mixture was then removed from the reactor by simple decantation. Subsequently, the catalyst was subjected to direct reuse without any treatment; these processes were repeated for five times, and the results are listed in Fig. 9. The JCCO conversion almost kept stable (87.3% in first reuse versus 82.3% in fifth reuse). In addition, there was almost no difference in the FT-IR patterns of the fresh catalyst and the reused catalyst (Fig. S4). These results indicated that stearic acid modified Ti-Mo mixed metal oxides catalyst was stable during the esterification process without the significant loss of its catalytic activity.
Furthermore, the activity of the Ti\textsubscript{7}Mo\textsubscript{3} catalyst for simultaneous esterification and transesterification of JCCO was checked. The simultaneous esterification and transesterification reaction was carried out in the presence of 3 wt.% catalyst dosage with 1:20 of molar ratio of JCCO to methanol for 180 °C. As illustrated in Fig. 10, a FAME yield of 95.5% was attained after 5 h. When the reaction time increased to 6 h, the yield of JCCO to FAME over the catalyst was steadily and reached as high as 95.0%. By drawing on the results, it was suggested that the mesoporous catalyst also exhibited excellent catalytic activities toward the simultaneous esterification and transesterification of JCCO with methanol.

### 3.6 Catalytic activity of modified Ti\textsubscript{7}Mo\textsubscript{3} for simultaneous esterification and transesterification of JCCO

Moreover, the activity of the Ti\textsubscript{7}Mo\textsubscript{3} catalyst for simultaneous esterification and transesterification of JCCO was checked. The simultaneous esterification and transesterification reaction was carried out in the presence of 3 wt.% catalyst dosage with 1:20 of molar ratio of JCCO to methanol for 180 °C. As illustrated in Fig. 10, a FAME yield of 95.5% was attained after 5 h. When the reaction time increased to 6 h, the yield of JCCO to FAME over the catalyst was steadily and reached as high as 95.0%. By drawing on the results, it was suggested that the mesoporous catalyst also exhibited excellent catalytic activities toward the simultaneous esterification and transesterification of JCCO with methanol.

### 4 Conclusion

In conclusion, the mesoporous Ti–Mo bi-metal oxides catalysts, which were successful prepared with various Ti/ Mo ratios in the presence of low-cost stearic acid. Excellent catalytic activities could be achieved for the esterifica-
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Fig. 10  Effects of reaction time on the catalytic activities of TiMo$_3$ in simultaneous esterification and transesterification of JCCO. Reaction conditions: molar ratio of oil to methanol = 1:20, reaction temperature = 180°C; catalyst dosage = 3 wt.%. 

tion reaction in the presence of these metal oxides, giving above 87.8% of FFAs conversion in JCCO. Besides, the catalyst also exhibited high catalytic activities in the simultaneous esterification and transesterification of JCCO, and a high FAME yield of 95.5% could be obtained. The mesoporous structure, sufficient pore size and high acid intensity of the catalysts were proposed to be the reasons for their high catalytic activity. In addition, the mesoporous catalyst showed excellent reusing ability, which made it a promising catalyst in practical biodiesel production process.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21576059, 21666008), the Key Technologies R&D Program (2014BAD23B01), the youth growth S&T personnel foundation of Guizhou education department (KY[2016]272), the creative research groups support program of Guizhou education department (KY[2017]049), the joint science and technology funds of Guizhou S&T department, Anshun city people’s government and Anshun university (LH [2015]7694, LH[2016]7278).

Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.67.10.5650/jos.ess.17231

References

14) Chung, K.H.; Park, B.G. Esterification of oleic acid in

J. Oleo Sci.


