Facile Synthesis of Ferric-Modified Phosphomolybdic Acid Composite Catalysts for Biodiesel Production with Response Surface Optimization

Qiuyun Zhang,*†‡ Caiyan Yue,** Quanlin Pu,** Tingting Yang,** Zhongfu Wu,** and Yutao Zhang*†‡

†School of Chemistry and Chemical Engineering and ‡Engineering Technology Center of Control and Remediation of Soil Contamination of Provincial Science & Technology Bureau, Anshun University, Anshun 561000, Guizhou, China

ABSTRACT: An attempt has been made to optimize the preparation of biodiesel from the transesterification of oleic acid with methanol over iron(III)-doped phosphomolybdic acid (H3PMo) catalysts. The prepared doped H3PMo salts were characterized using powder X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The detailed characterization results demonstrated that the doped H3PMo salts have a strong interaction between the iron(III) ions and metal oxygen cluster, well preserving a typical Keggin structure of heteropolyacids and possessing good thermal stability. The effect of esterification reaction parameters was investigated and optimized using single-factor experiments method in combination with response surface methodology (RSM). The doped catalyst exhibited good catalytic activity, affording the oleic acid conversion of 89.2% with single factor optimization and 95.1% with RSM. More importantly, the catalyst was simply separated by decantation and exhibited good stability, with the oleic acid conversion of 70.2% after three consecutive cycles. Besides, this catalyst can also catalyze the esterification of other free fatty acids. Therefore, the doped H3PMo catalyst is a promising candidate for eco-friendly production of biodiesel in industry.

1. INTRODUCTION

The gradual depletion of the traditional fossil fuels increases the environmental pollution and global warming, so more and more attention is being paid to develop renewable fuels (e.g., biodiesel and biofuel).1 Biodiesel production from plant oils, animal fats, waste cooking oils, or free fatty acids (FFAs) is regarded as a renewable green fuel owing to its clean, nontoxic, and nonrecyclability associated with product separation and purification, leading to the increase in biodiesel production cost and relevant issues.12,13 Instead, solid-acid catalysts can overcome these drawbacks in esterification, such as mixed-metal oxides,14,15 zeolites,16 metal complexes,17 and sulfonic acid functionalized solid acid.18 Unfortunately, they suffered from some drawbacks of low acidity, weak interaction between active component and support, complicated preparation process, and poor mass transfer. Heteropolyacids (HPAs) of the Keggin series, in particular H3PW12O40 (H3PW), H3PMo12O40 (H3PMo), and H5SiW12O40 (H5SiW), have drawn significant attention as promising eco-friendly catalysts applied for various organic transformations such as esterification, transesterification, dehydration, etherification, oxidation, and acetylation reactions due to their strong acidity, thermostability, and good oxidizing ability.19,20 However, HPAs is easily soluble in most of the organic solvents, which restrains the catalyst recycling and product purification. Very recently, the exchange of protons of HPAs with various cations (e.g., K+, Ag+, Cu2+, Mn2+) resulting in the formation of insoluble salts could be an effective strategy for the use of HPAs as solid-acid catalysts in green chemistry. Li et al.22 have reported the optimization of the biodiesel preparation process from Eruca sativa Gars vegetable oil catalyzed by Cs2.5H0.5PW12O40 heteropolyacid salt. The

Received: April 11, 2019
Accepted: May 9, 2019
Published: May 22, 2019
heteropolyacid salt shows an excellent catalytic activity for environmental biodiesel production with a high yield of 99%. Interestingly, the Cs$_2.5$H$_{0.5}$PW$_{12}$O$_{40}$ heteropolyacid salt can be reused for six cycles. Su et al.$^{23}$ reported that microwave-assisted the preparation of biodiesel from yellow horn oil using Cs$_2.5$H$_{0.5}$PW$_{12}$O$_{40}$ catalyst, and a high conversion yield (96%) could be achieved. In our previous study, Ag$^+$-, NH$_4^+$-, and Cu$^{2+}$-doped HPAs were successfully used as efficient catalysts in esterification reaction.$^{24,25}$ As far as we know, the use of iron(III)-doped phosphomolybdic acid (H$_3$PMo) as a catalyst in esterification reaction for the production of biodiesel is still lacking.

Moreover, various parameters such as reaction time and temperature, the molar ratio of feedstock to methanol, and the catalyst dosage affecting the conversion are noteworthy. Compared to unplanned approaches, the response surface methodology (RSM) helps researchers gain a better insight into the interactions among experimental variables, offering an optimization process and also saving research time and costs.$^{26}$ Therefore, in the present work, we focus on the design of iron(III)-modified H$_3$PMo catalysts used for the production of biodiesel in the esterification reaction, and the modified catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermogravimetric (TG), and scanning electron microscopy (SEM). Various esterification reaction variables were optimized by single-factor experiments and response surface experiments. Meanwhile, esterification of different free fatty acids with methanol is also studied to validate the compatibility of the doped H$_3$PMo catalysts. Finally, the reusability of the doped catalyst was also profoundly investigated.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Catalyst. The powder XRD patterns of pristine H$_3$PMo, Fe$_{1/3}$H$_2$PMo, Fe$_{2/3}$H$_2$PMo, and Fe$_1$PMo are shown in Figure 1a. The pristine H$_3$PMo shows principal diffraction 2θ angles at 7.6, 8.8, 25.9, 26.7, 28.0, 32.2, and 35.0°, which can be attributed to a body-centered cubic secondary structure of Keggin anions.$^{27,28}$ When iron(III) ions were added, the diffractograms of Fe$_{1/3}$H$_2$PMo, Fe$_{2/3}$H$_2$PMo, and Fe$_1$PMo show diffraction lines that belong to those of triclinic symmetry for the crystal lattice. Besides, these samples also exhibited some new strong peaks around at 20.0 and 33.0° associated with iron species$^{29-31}$ implying that the heteropolyacid salt was formed, and Villabrille et al. also found the same characteristic peaks for the iron-doped heteropolyacid.$^{32}$

The FT-IR spectra of pristine H$_3$PMo, Fe$_{1/3}$H$_2$PMo, Fe$_{2/3}$H$_2$PMo, and Fe$_1$PMo are displayed in Figure 1b. The peaks of the Keggin structure were clearly observed at approximately 1064 cm$^{-1}$ (P=O in the central PO$_4$ tetrahedron), 963 cm$^{-1}$ (Mo=O in the MoO$_6$ octahedron), 874 cm$^{-1}$ (Mo=O$_3$−Mo bridge, O$_3$: corner-sharing oxygen), and 788 cm$^{-1}$ (Mo=O$_3$−Mo bridge, O$_3$: edge-sharing oxygen) in all samples, indicating that the Keggin structure was well preserved in doped samples. Moreover, for the Fe$_1$PMo sample, its characteristic peaks of Keggin structure were weaker than those of the Fe$_{1/3}$H$_2$PMo and Fe$_{2/3}$H$_2$PMo samples, this surprising result may be because the iron(III) ions fully substituted the acidic protons of phosphomolybdic acid that has a strong interaction between the iron(III) ions and metal oxygen cluster.$^{28,33}$ Therefore, the FT-IR results revealed that a good Keggin structure retention was achieved after the iron-doped heteropoly cage structure.

![Figure 1](image_url). (a) Powder XRD patterns and (b) FT-IR spectra of iron(III)-doped H$_3$PMo.

![Figure 2](image_url). (a) TG profile of Fe$_1$PMo catalyst. SEM images of (b) pristine H$_3$PMo and (c) Fe$_1$PMo catalyst.
On the other hand, the catalytic data for the Fe$_{1/3}$H$_2$PMo, Fe$_{2/3}$H$_2$PMo, and Fe$_1$PMo catalysts in the esterification are evaluated. Each reaction was performed with 10:1 of methanol-to-oleic acid molar ratio, and 5 wt% of the catalyst at 70 °C for 3 h. The results showed the conversion was 87.5, 89.8, and 89.2% with the Fe$_{1/3}$H$_2$PMo, Fe$_{2/3}$H$_2$PMo, and Fe$_1$PMo catalysts, respectively, implying the iron(III) cations that fully or partially substituted H$_3$PMo have better catalytic performance, with no significant difference in the esterification rate. Thus, based on the powder XRD and FT-IR, as well as catalytic activity of various catalysts, the Fe$_1$PMo solid-acid catalyst prepared by a simple and convenient method was selected for the subsequent study.

TG analysis was used to test the stability of the catalysts. It is demonstrated that the Fe$_1$PMo catalyst was thermally stable in the air up to 800 °C, as presented in Figure 2a. A slight weight loss (13.1%) due to the vaporization of physically adsorbed water and thermal decomposition of constitutional water (H$_2$O$^+$) from Fe$_1$PMo in the range of 40−400 °C was also observed. Then, no additional weight loss of Fe$_1$PMo catalyst was observed at the temperature of >400 °C, presumably due to the high thermal stability of the Keggin structure similar to that of other heteropolyacid-based solid-acid catalysts.

SEM images of pristine H$_3$PMo and Fe$_1$PMo catalyst are given in Figure 2b,c. There was significant morphological difference between the two samples. The images exhibited that the pristine phosphomolybdic acid has a large irregular shape and the surface morphology is rough. For the Fe$_1$PMo catalyst, the phosphomolybdic acid after doping with iron(III) ions acquired a multilayered laminar structure morphology but exhibited cubic shapes and some cracks. Thus, from the above observation, the changing surface morphology of the Fe$_1$PMo catalyst was probably due to the exchange of protons with iron(III) ions, which is consistent with previous reports.

### 2.2. Single-Factor Experiments for Esterification

#### 2.2.1. Effect of Methanol-to-Oleic Acid Molar Ratio

Since the esterification of oleic acid with methanol is reversible, excess methanol is significant to shift the equilibrium toward the product side, thus improving the substrate conversion rate. In Figure 3a, it is shown that the conversion of oleic acid is raised from 44.5 to 89.2% with the changing molar ratio of methanol to oleic acid from 2:1 to 10:1. This is because more amount of methanol could not only promote the dispersion of the catalyst but also consolidate forward reaction. However, further increase in the molar ratio of methanol to oleic acid to 18:1 makes no difference in increasing the oleic acid conversion for the limited equilibrium of esterification, and similar result was also found by Ezebor et al. Taking energy consumption and operating cost into account, 10:1 was chosen as the optimum molar ratio for methanol to oleic acid.

#### 2.2.2. Effect of Catalyst Dosage

The relationship between catalyst dosage and oleic acid conversion is shown in Figure 3b. As exhibited in Figure 3b, the oleic acid conversion is slower without adding a catalyst, and 51.6% conversion was obtained with the addition of catalyst in the dosage of 0.5 wt%. When the catalyst dosage was increased from 1 to 5 wt%, the conversion was gradually increased from 68.2 to 89.2%. This reason for this phenomenon was that more catalyst could offer more active sites to activate the substrate. However, the oleic acid conversion does not further increase if the catalyst
dosage keeps increasing to 6 wt % because of the equilibrium limit. Meanwhile, a large catalyst dosage might lead to the dispersion of active centers and worsen the partial coverage, and similar results were reported by Wan et al. Therefore, we selected 5 wt % as the optimal catalyst dosage for the following studies.

2.2.3. Effect of Reaction Temperature. Esterification of oleic acid with methanol is the endothermic reaction, which could increase the conversion rate through raising the temperature. As exhibited in Figure 3c, low temperature severely hampers the esterification reaction and the conversion is 60.3% at 20 °C. Then, an increase of the reaction temperature from 30 to 70 °C distinctly heightens the oleic acid conversion from 67.7 to 89.2%. If the reaction temperature is further increased, the large amount of liquid methanol vaporized will reduce the methanol concentration in the reaction system, probably resulting in an unfavorable effect on conversion. Therefore, the optimum temperature can be set at 70 °C.

2.2.4. Effect of Reaction Time. The effect of reaction time on the oleic acid conversion was also studied, and the results are exhibited in Figure 3d. It can be seen from Figure 3d that the oleic acid conversion increases from 58.6 to 89.2% with the increment of reaction time from 0.5 to 3 h. However, there was no obvious increase in the conversion when the time was above 3 h, and the oleic acid conversion of 90.8% is obtained in 7 h. Therefore, the reaction time of 3 h was found to be optimum when taking the production cost into account.

2.3. Statistical Analysis for Optimization of Fe₅PMo Catalyst for Esterification. 2.3.1. Experimental Design and Evaluation. The preliminary single-parameter studies imply that catalyst dosage, molar ratio of methanol to oleic acid, and reaction time are significant variables for biodiesel production. The effect of the three variables was investigated by RSM, and a 3-level–3-factor Box–Behnken Design including seventeen experiments were performed by a second-order response surface. A second-order polynomial model (eq 1) was correlated with independent variables as follows

\[ C_{\text{conversion}} = \beta_0 + \sum \beta_i x_i + \sum \beta_{i2} x_i^2 + \sum \beta_{ij} x_i x_j \]  

(1)

where \( C_{\text{conversion}} \) is the oleic acid conversion to biodiesel, \( \beta_0 \) is the intercept term, \( \beta_i \) is the linear coefficient, \( \beta_{ij} \) is the quadratic coefficient, \( \beta_{ij} \) is the interactive coefficient, and \( x_i, x_j \) are the coded independent variables (the reaction conditions).

The minimum and maximum values of the Box–Behnken Design process variables are shown in Table 1. The Box–Behnken Design for the three process variables \( X_1, X_2, \) and \( X_3 \) with the experimental results and predicted responses based on this RSM model are given in Table 2. The quadratic model, describing the relationships between the predicted response variable (conversion of methyl oleate at 70 °C) and the reaction conditions, was selected for an in-depth statistical study. On the basis of the results, the quadratic regression model of the experimental data (eqs 2 and 3) for the oleic acid conversion is given below

\[ C_{\text{conversion}} = 90.44 + 3.58X_1 + 0.91X_2 + 7.76X_3 + 0.17X_1X_2 + 1.02X_1X_3 - 1.05X_2X_3 - 2.45X_1^2 + 0.83X_2^2 - 6.02X_3^2 \]  

(2)

\[ C_{\text{conversion}} = 9.59625 + 14.98250X_1 - 3.62750X_2 + 9.74687X_3 + 0.17500X_1X_2 + 0.25625X_1X_3 - 0.26250X_2X_3 - 2.44500X_1^2 + 0.83000X_2^2 - 3.7625X_3^2 \]  

(3)

2.3.2. Model Regression and Analysis. The analysis of variance (ANOVA) for the statistical significance of the model is shown in Table 3. From Table 3, the high value of \( R^2 \) of 0.9894 for the response implied that the model explained that about 98% of the experimental data were compatible with the predicted data. The regression coefficient of the predicted \( R^2 \) was 0.8846 (>0.80), and the adjusted \( R^2 \) was 0.9758 was achieved; the actual conversion was in reasonable agreement with the predicted conversion. It has been summarized from the data that the model was precise and reliable. The result of oleic acid conversion shows the \( F \)-value of 72.65, and a very low probability value (<0.0001) indicated that this model was statistically significant. The \( F \)-value of the “lack of fit” was 2.44, indicating that the model was not significant. Besides, the \( p \)-value of \( X_1, X_2, X_3, \) and \( X_4 \) terms had significant effects on the oleic acid conversion. Other model terms were not significant. Based on the above analysis, \( X_1, X_2, \) and \( X_3 \) have positive effects, whereas the other variables have negative effects.

2.3.3. Interactions among Variables. Three-dimensional response surface plots (Figure 4a–c) show the interaction effect of the process-independent variables with their response. Figure 4a shows the combined effect of the amount of catalyst and the reaction time on methyl oleate conversion. Based on Figure 4a and as expected, the oleic acid conversion was found

| standard order | \( X_1 \) | \( X_2 \) | \( X_3 \) | conversion (%) |
|---------------|-----|-----|-----|--------------|
|              |     |     |     | experimental | predicted |
| 1            | −1  | −1  | 0   | 84.70        | 84.51      |
| 2            | 1   | −1  | 0   | 91.60        | 91.31      |
| 3            | −1  | 1   | 0   | 85.70        | 85.99      |
| 4            | 1   | 1   | 0   | 93.30        | 93.49      |
| 5            | −1  | 0   | −1  | 72.50        | 71.66      |
| 6            | 1   | 0   | −1  | 77.50        | 76.76      |
| 7            | −1  | 0   | 1   | 84.40        | 85.14      |
| 8            | 1   | 0   | 1   | 93.50        | 94.34      |
| 9            | 0   | −1  | −1  | 74.50        | 75.53      |
| 10           | 0   | 1   | −1  | 78.90        | 79.45      |
| 11           | 0   | −1  | 1   | 93.70        | 93.15      |
| 12           | 0   | 1   | 1   | 93.90        | 92.88      |
| 13           | 0   | 0   | 0   | 90.60        | 90.44      |
| 14           | 0   | 0   | 0   | 90.40        | 90.44      |
| 15           | 0   | 0   | 0   | 89.30        | 90.44      |
| 16           | 0   | 0   | 0   | 90.20        | 90.44      |
| 17           | 0   | 0   | 0   | 91.70        | 90.44      |

Table 1. Variables and Experimental Design Levels for Response Surface

| variable                        | levels |
|---------------------------------|--------|
| reaction time (h)               | X₁     |
| catalyst dosage (wt %)          | X₂     |
| molar ratio of methanol to oleic acid | X₃     |

Table 2. Experimental and Predicted the Oleic Acid Conversion Using RSM Box–Behnken Design
to decrease with increasing reaction time at a constant catalyst amount because of the reversibility of the esterification reaction, and these also clearly demonstrated that the effect of reaction time on oleic acid conversion was more than the catalyst dosage. Moreover, the interaction between the molar ratio (methanol to oleic acid) and reaction time on the conversion is given in Figure 4b. According to Figure 4b, an increase in both methanol to oleic acid molar ratio and reaction time at 4.0 wt % Fe1PMo catalyst results in the increase of methyl oleate conversion, implying the time and molar ratio had a positive influence on oleic acid conversion. However, a slight decrease in the conversion with the rise in methanol to oleic acid molar ratio was also observed because excess methanol led to a relative reduction in the active sites of the catalyst. Figure 4c exhibits the interaction of methanol to oleic acid molar ratio and catalyst dosage on methyl oleate conversion. It was also observed that changes in the amount of methanol affect the oleic acid conversion at a constant catalyst dosage. Nonetheless, excess methanol was inadvisable because of the resulting dilution of the catalyst and oleic acid.

### 2.3.4. Optimum Reaction Conditions

Optimization of the esterification process to maximize oleic acid conversion was performed using the Design-Expert software. Meanwhile, based on various factors' influence on the design issues such as Table 3. Analysis of ANOVA for Response Surface Second-Order Model

| source      | sum of squares | df | mean square | F-value | probability (P) > F |
|-------------|----------------|----|-------------|---------|---------------------|
| model       | 785.04         | 9  | 87.23       | 72.65   | <0.0001 significant |
| X1          | 102.25         | 1  | 102.25      | 85.16   | <0.0001             |
| X2          | 6.66           | 1  | 6.66        | 5.55    | 0.0507              |
| X3          | 482.05         | 1  | 482.05      | 401.49  | <0.0001             |
| X1X2        | 4.20           | 1  | 4.20        | 3.50    | 0.1035              |
| X1X3        | 4.41           | 1  | 4.41        | 3.67    | 0.0968              |
| X22         | 25.17          | 1  | 25.17       | 20.96   | 0.0025              |
| X32         | 2.90           | 1  | 2.90        | 2.42    | 0.1641              |
| X1^2        | 152.59         | 1  | 152.59      | 127.09  | <0.0001             |
| residual    | 8.40           | 7  | 1.20        |         |                     |
| lack of fit | 5.43           | 3  | 1.81        | 2.44    | 0.2047 not significant |
| pure error  | 2.97           | 4  | 0.74        |         |                     |
| cor total   | 793.44         | 16 |             |         |                     |

Note: $R^2_{red} = 0.8846$, $R^2_{adj} = 0.9758$, $R^2 = 0.9894$.

Figure 4. Three-dimensional response surface plots for the esterification of oleic acid with methanol with varying reaction parameters using Fe1PMo catalyst: effect of reaction time and the catalyst dosage (a); effect of molar ratio of methanol to oleic acid and the reaction time (b); and effect of molar ratio of methanol to oleic acid and the catalyst dosage (c).

Figure 5. Reuse of the catalyst (a). Reaction conditions: molar ratio of methanol to oleic acid = 10:1, reaction temperature = 70 °C, catalyst dosage = 5 wt %, and reaction time = 3 h. The comparison of FT-IR spectra of fresh catalyst and reused catalyst (b).
energy consumption, the operating and circulation costs, the assurance safety devices, etc.43 The optimum conditions were found to be 3.9 h, 5.0 wt % of catalyst, and 12.54 molar ratio of methanol to oleic acid, and these optimum conditions were validated by the triplication of the experiments. The results showed that the predicted and experimental values of oleic acid conversion were found to be 95.99 and 95.1%, respectively, indicating they were close to each other.

2.4. Reusability. The reusability and stability studies of heterogeneous catalyst are of great significance. To test the catalyst, the oleic acid esterification reaction was conducted under optimal conditions: reaction temperature of 70 °C, the molar ratio of methanol to oleic acid of 10:1, catalyst dosage of 5 wt %, and reaction time of 3 h. After the first production cycle, the catalyst was simply separated by decantation and subjected to direct reuse in a new oleic acid esterification reaction cycle for five times, and the results are exhibited in Figure 5a. As presented in Figure 5a, the catalyst keeps its activity for the third use (89.2% in first reuse versus 70.2% in third reuse). However, with continuous increment of reuse cycles, the oleic acid conversion drops sharply. After five cycles, only 41.5% conversion is obtained. Meanwhile, different variations are observed in the FT-IR spectra between the fresh catalyst and the fifth reused catalyst in Figure 5b, indicating that the significant decrease in oleic acid conversion in the fifth cycle compared to that in the first cycle can be mainly attributed to the change in the Keggin structure of the catalyst. This might occur due to the loss of catalyst and the blockage of the channel during each cycle. Thus, from the above observation, the Fe1PMo catalyst can show good stability during esterification.

2.5. Catalytic Activity of Fe1PMo for the Esterification of Other Substrates. Esterification of different free fatty acids (high free fatty acid, nonedible oils) with methanol was performed over Fe1PMo to test the generality of this doped catalyst. The conversion of lauric acid, myristic acid, palmitic acid, and stearic acid was 92.4, 89.1, 92.7, and 90.9% respectively, indicating they were close to each other.

4.2. Preparation of Iron(III)-Doped H3PMo Solid-Acid Catalyst. Iron(III)-doped phosphomolybdic acid catalyst was prepared according to the previous literature,25,33,44 with slight modifications. Briefly, various calculated amounts of phosphomolybdic acid and iron(III) chloride were dissolved in distilled water. Then, the aqueous solution of iron(III) chloride was slowly added to the solution of phosphomolybdic acid under vigorous stirring at room temperature for over 1 h. Subsequently, the mixture was heated at 70 °C for 3 h and finally dried under vacuum at 110 °C for 12 h to obtain the product as doped catalysts; these as-prepared catalysts are designated as Fe1/3H2PMo, Fe2/3H2PMo, and Fe1PMo according to the following equations

\[
FeCl_3 + H_3PMo_{12}O_{40} \rightarrow Fe_{x/3}H_{3-x}PW_{12}O_{40} + xHCl \\
= 1, 2, 3
\] (4)

4.3. Characterization of the Catalyst. The XRD patterns of the catalysts were obtained using a Rigaku D/max 2000 ultima plus diffractometer (monochromatic nickel filter, Cu Kα radiation) and a step scan technique at 2θ angles of 5°–80°. The FT-IR spectra were scanned on a PerkinElmer spectrum 100 using the KBr disk technique (4000–400 cm⁻¹). TG analysis was carried out with a Netzsch STA 449F3 instrument in dry air at a heating rate of 10 °C/min. The surface morphology of the catalyst was studied using a JEOL-6701F scanning electron microscope at 10.0 kV.

4.4. Procedure for Esterification. The catalytic activity of the prepared catalysts was tested through the esterification of oleic acid (other free fatty acids and oils). Esterification reaction of certain amounts of oleic acid, methanol, and Fe1PMo catalyst was performed in a 100 mL single-necked glass flask immersed in a thermostatic oil bath equipped with a reflux condenser and mechanical stirrer; no inert atmosphere was used and all reactions occurred in contact with air and at ambient pressure. After esterification, the used catalyst was simply separated from the liquid phase by decantation and methanol was then removed by reduced pressure distillation to purify the product. The acid value of the product was tested using the national standard method ISO 660-2009, and the conversion was calculated using eq 5. All data presented are averages of at least duplicate experiments.

\[
\text{conversion(\%)} = \frac{AV_1 - AV_2}{AV_1} \times 100\%
\] (5)

where AV1 is the acid value of raw materials and AV2 is the acid value of the catalyzed product.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: sci_qyzhang@126.com (Q.Z.).

*E-mail: zyt0516@126.com (Y.Z.).

ORCID®

Qiuyun Zhang: 0000-0002-3905-962X
Funding
This work was financially supported by the technical talent support program of Guizhou education department (No. KY [2018]069), the joint science and technology funds of Guizhou S&T department, Anshun city people’s government and Anshun university (No. LH [2016]7278), the creative research groups support program of Guizhou education department (No. KY [2017]049), the construction projects of innovation platform from S&T bureau in Anshun (No. [2016]-4), and the youth growth S&T personnel foundation of Guizhou education department (KY [2016]272).

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Lee, A. F.; Bennett, J. A.; Manayil, J. C.; Wilson, K. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. Chem. Soc. Rev. 2014, 43, 7887−7916.

(2) Sharma, R. K.; Saxena, M.; O’Neill, C. A.; Ramos, H. A. R.; Griekenow, K. Synthesis of rhizopus arrhizus lipase nanoparticles for biodiesel production. ACS Omega 2018, 3, 18203−18213.

(3) Mierczynski, P.; Chalupka, K. A.; Maniukiewicz, W.; Kubicki, J.; Szyknowska, M. I.; Maniecki, J. P. SrAl2O4 spinel phase as active phase of transesterification of rapeseed oil. Appl. Catal., B 2015, 164, 176−183.

(4) Sales, E. A.; Ghirardi, M. L.; Jörquera, O. Subcritical ethyl biodiesel production from wet animal fat and vegetable oils: A net energy ratio analysis. Energy Convers. Manage. 2016, 141, 216−223.

(5) Olutoye, M. A.; Wong, S. W.; Chin, L. H.; Amani, H.; Asif, M.; Hameed, B. H. Synthesis of fatty acid methyl esters via the transesterification of waste cooking oil with methanol using a barium-modified montmorillonite K10 catalyst. Renewable Energy 2016, 86, 392−398.

(6) Costarrasa, L.; Leiva-Candia, D. E.; Cubero-Atienza, A. J.; Ruiz, J. J.; Dorado, M. P. Optimization of the transesterification of waste cooking oil with Mg-Al hydrotalcite using response surface methodology. Energies 2018, 11, 302−310.

(7) Nunez, R. S.; Altino, F. M.; Meneghetti, M. R.; Meneghetti, S. M. P. New mechanistic approaches for fatty acid methyl ester production reactions in the presence of Sn (IV) catalysts. Catal. Today 2016, 289, 121−126.

(8) Chen, G. Y.; Liu, J.; Yao, J. G.; Qi, Y.; Yan, B. B. Biodiesel production from waste cooking oil in a kìnketically fluidized bed reactor using whole-cell biocatalysts. Energy Convers. Manage. 2017, 138, 556−564.

(9) Onojie, S. E.; Iyuke, S. E.; Igbafe, A. I.; Daramola, M. O. Transesterification of rubber seed oil to biodiesel over a calcined waste rubber seed shell catalyst: Modeling and optimization of process variables. Energy Fuels 2017, 31, 6109−6119.

(10) Wu, L.; Wei, T. Y.; Lin, Z. J.; Zou, Y.; Tong, Z. F.; Sun, J. H. Bentonite-enhanced biodiesel production by NaOH-catalyzed transesterification: Process optimization and kinetics and thermodynamic analysis. Fuel 2016, 182, 920−927.

(11) Pan, Y.; Alam, M. A.; Wang, Z. M.; Wu, J. C.; Zhang, Y.; Yuan, Z. H. Enhanced esterification of oleic acid and methanol by deep eutectic solvent assisted Amberlyst heterogeneous catalyst. Bioresour. Technol. 2016, 220, 543−548.

(12) Liu, P. D.; Truong, H. T.; Luu, B. V.; Pham, L. N.; Imamura, K.; Takenaka, N.; Maeda, Y. Production of biodiesel from Vietnamese Jatropha curcas oil by a co-solvent method. Bioresour. Technol. 2014, 173, 309−316.

(13) Zhou, Y. J.; Noshadi, I.; Ding, H.; Liu, J. J.; Parnas, R. S.; Clearfield, A.; Xiao, M.; Meng, Y. Z.; Sun, L. Y. Solid acid catalyst based on single-layer α-zirconium phosphate nanosheets for biodiesel production via esterification. Catalysts 2018, 8, 17−24.

(14) Zhang, Q. Y.; Li, H.; Yang, S. Facile and low-cost synthesis of mesoporous Ti-Mo bi-metal oxide catalysts for biodiesel production from esterification of free fatty acids in Jatropha curcas crude oil. J. Oleo Sci. 2018, 67, 579−588.

(15) Zhang, Q. Y.; Wei, F. F.; Ma, P. H.; Zhang, Y. T.; Wei, F. H.; Chen, H. L. Mesoporous Al-Mo oxides as an effective and stable catalyst for the synthesis of biodiesel from the esterification of free-fatty acids in non-edible oils. Waste Biomass Valorization 2018, 9, 911−918.

(16) Purova, R.; Narasimharao, K.; Ahmed, N. S. I.; Al-Thabaiti, S.; Al-Shehri, A.; Mokhtar, M.; Schwier, W. Pillared HMCM-36 zeolite catalyst for biodiesel production by esterification of palmitic acid. J. Mol. Catal. A: Chem. 2015, 406, 159−167.

(17) Zhang, Q. Y.; Wei, F. F.; Zhang, Y. T.; Wei, F. H.; Ma, P. H.; Zheng, W.; Zhao, Y. T.; et al. Biodiesel production by catalytic esterification of oleic acid over copper (II)-alginic complexes. J. Oleo Sci. 2017, 66, 491−497.

(18) Niu, S.; Ning, Y.; Lu, C.; Han, K.; Yu, H.; Zhou, Y. Esterification of oleic acid to produce biodiesel catalyzed by sulfonated activated carbon from bamboo. Energy Convers. Manage. 2018, 163, 59−65.

(19) Zhao, P. P.; Zhang, Y. Y.; Wang, Y.; Cui, H. Y.; Song, F.; Sun, X. Y.; Zhang, L. P. Conversion of glucose into S-hydroxyethylfurural catalyzed by acid-base bifunctional heteropolyacid-based ionic hybrids. Green Chem. 2018, 20, 1551−1559.

(20) Zhang, Q. Y.; Liu, X. F.; Yang, T. T.; Yue, C. Y.; Pu, Q. L.; Zhang, Y. T. Facile synthesis of polyoxometalates tethered to post FT-BTC frameworks for esterification of free fatty acids to biodiesel. RSC Adv. 2019, 9, 8113−8120.

(21) Ren, Y. S.; Bing, L.; Zhang, Z. H.; Lin, J. T. Silver-exchanged heteropolyacid catalyst (Ag3H2PW): An efficient heterogeneous catalyst for the synthesis of S-ethoxymethylfurural from S-hydroxymethylfurfural and fructose. J. Ind. Eng. Chem. 2015, 21, 1127−1131.

(22) Li, S. W.; Wang, Y. P.; Dong, S. W.; Chen, Y.; Cao, F. H.; Chai, F.; Wang, X. H. Biodiesel production from Eruca sativa gars vegetable oil and motor, emissions properties. Renewable Energy 2009, 34, 1871−1876.

(23) Su, Z.; Zu, Y. G.; Fu, Y. J.; Meng, L.; Zhang, D. Y.; Effther, T. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. Bioresour. Technol. 2010, 101, 931−936.

(24) Zhang, Q. Y.; Wei, F. F.; Li, Q.; Huang, J. S.; Feng, Y. M.; Zhang, Y. T. Mesoporous Ag(NH3)2PW15O49 heteropolyacids as effective catalysts for the esterification of oleic acid to biodiesel. RSC Adv. 2017, 7, 51090−51095.

(25) Cai, J.; Zhang, Q. Y.; Wei, F. F.; Huang, J. S.; Feng, Y. M.; Ma, H. T.; Zhang, Y. T. Preparation of copper (II) containing phosphomolybdic acid salt as catalyst for the synthesis of biodiesel by esterification. J. Oleo Sci. 2018, 67, 427−432.

(26) Yuan, X.; Liu, J.; Zeng, G.; Shi, J.; Tong, J.; Huang, G. Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. Renewable Energy 2008, 33, 1678−1684.

(27) Fournier, M.; Feumi-Jantou, C.; Rabia, C.; Hervé, G.; Launay, S. Polyoxometalate catalyst materials: X-ray thermal stability study of phosphorus-containing heteropolyacids H2PMO13−xWxO49 (M = Mo, W; x = 0−1). J. Mater. Chem. 1992, 2, 971−978.

(28) Da Silva, M. J. D.; Libertbo, N. A.; Leles, L. C. D. A.; Pereira, U. A. Fe(SiW12O43)-catalyzed glycerol acetylation: synthesis of bioadditives by using highly active Lewis acid catalyst. J. Mol. Catal. A: Chem. 2016, 422, 69−83.

(29) Tian, Z. P.; Wang, C. G.; Si, Z.; Ma, L. L.; Chen, L. G.; Liu, Q. Y.; Zhang, Q.; Huang, H. Y. Fischer-Tropsch synthesis to light olefins over iron-based catalysts supported on KMnO4 modified activated carbon by a facile method. Appl. Catal., A 2017, 541, 50−59.

(30) Baskar, G.; Soumiya, S. Production of biodiesel from castor oil using iron (II) doped zinc oxide nanocatalyst. Renewable Energy 2016, 98, 101−107.
(31) Ausavasukhi, A.; Sooknoi, T. Oxidation of tetrahydrofuran to butyrolactone catalyzed by iron-containing clay. *Green Chem.* 2014, 17, 435–441.

(32) Villabrille, P.; Romanelli, G.; Gassa, L.; Vázquez, P.; Cáceres, C. Synthesis and characterization of Fe- and Cu-doped molybdovanadophosphoric acids and their application in catalytic oxidation. *Appl. Catal., A* 2007, 324, 69–76.

(33) Gong, S. W.; Jing, L.; Wang, H. H.; Liu, L. J.; Zhang, Q. Biodiesel production via esterification of oleic acid catalyzed by picolinic acid modified 12-tungstophosphoric acid. *Appl. Energy* 2014, 134, 283–289.

(34) Gawade, A. B.; Tiwari, M. S.; Yadav, G. D. Biobased green process: Selective hydrogenation of 5-hydroxymethyl furfural (HMF) to 2, 5 dimethyl furan (DMF) under mild conditions using Pd-C8H5H6PW12O40/K-10 clay. *ACS Sustainable Chem. Eng.* 2016, 4, 4113–4123.

(35) Prado, R. G.; Bianchi, M. L.; Mota, E. G. D.; Brum, S. S.; Lopes, J. H.; da Silva, M. J. HPMo12O40/Agroindustry waste activated carbon-catalyzed esterification of lauric acid with methanol: A renewable catalytic support. *Waste Biomass Valorization* 2018, 9, 669–679.

(36) Wang, H. H.; Liu, L. J.; Gong, S. W. Esterification of oleic acid to biodiesel over a 12-phosphotungstic acid-based solid catalyst. *J. Fuel Chem. Technol.* 2017, 45, 303–310.

(37) Wang, C. L.; Bu, X. N.; Ma, J. W.; Liu, C.; Chou, K. C.; Wang, X. L.; Li, Q. Wells-Dawson type Cs8H6P2W18O62 based Co/Al2O3 as bifunctional catalysts for direct production of clean-gasoline fuel through Fischer-Tropsch synthesis. *Catal. Today* 2016, 274, 82–87.

(38) Zhang, Q. Y.; Li, H.; Liu, X. F.; Qin, W. T.; Zhang, Y. P.; Xue, W.; Yang, S. Modified porous Zr-Mo mixed oxides as strong acid catalysts for biodiesel production. *Energy Technol.* 2013, 1, 735–742.

(39) Lokman, I. M.; Rashid, U.; Zainal, Z.; Yunus, R.; Tafiq-Yap, Y. Microwave-assisted biodiesel production by esterification of palm fatty acid distillate. *J. Oleo Sci.* 2014, 63, 849–855.

(40) Ezebor, F.; Khairuddean, M.; Abdullah, A. Z.; Boey, P. L. Oil palm trunk and sugarcane bagasse derived heterogeneous acid catalysts for production of fatty acid methyl esters. *Energy* 2014, 70, 493–503.

(41) Wu, H.; Wu, Z. W.; Chen, W.; Guan, G. F.; Cai, Y.; Chen, C.; Li, Z.; Li, X. Q. Heterogenization of ionic liquid based on mesoporous material as magnetically recyclable catalyst for biodiesel production. *J. Mol. Catal. A: Chem.* 2015, 398, 127–132.

(42) Wang, Y. Q.; Zhao, D.; Wang, L. J.; Wang, X. Q.; Li, L. J.; Xing, Z. P.; Ji, N.; Liu, S. J.; Ding, H. Immobilized phosphotungstic acid based ionic liquid: Application for heterogeneous esterification of palm acid. *Fuel* 2018, 216, 364–370.

(43) Rashid, U.; Anwar, F.; Ansari, T. M.; Arif, M.; Ahmad, M. Optimization of alkaline transesterification of rice bran oil for biodiesel production using response surface methodology. *J. Chem. Technol. Biotechnol.* 2009, 84, 1364–1370.

(44) Zhu, S. H.; Gao, X. Q.; Dong, F.; Zhu, Y. L.; Zheng, H. Y.; Li, Y. W. Design of a highly active silver-exchanged phosphotungstic acid catalyst for glycerol esterification with acetic acid. *J. Catal.* 2013, 306, 155–163.