Efficient Production of Biodiesel from Esterification of Lauric Acid Catalyzed by Ammonium and Silver Co-Doped Phosphotungstic Acid Embedded in a Zirconium Metal–Organic Framework Nanocomposite

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ABSTRACT: A novel solid acid nanocatalyst (Ag1(NH4)2PW12O40/UIo-66) comprising ammonium and silver co-doped H3PW12O40 and zirconium-based metal–organic frameworks (UIo-66) was synthesized and characterized by Fourier transform infrared spectroscopy, N2 adsorption/desorption, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and ammonia temperature-programmed desorption. The catalytic activity was evaluated for the synthesis of biodiesel via esterification of lauric acid and methanol. The effect of the operating parameters including the molar ratio of lauric acid to methanol, catalyst amount, and reaction temperature and time on the lauric acid conversion was also investigated to obtain optimum reaction conditions. Also, the composite (Ag1(NH4)2PW12O40/UIo-66) was recyclable and reused up to six cycles. Kinetics of the lauric acid esterification has been assumed to be of a pseudo-first order, and the results showed that the activation energy for the esterification process was found to be 35.2 kJ/mol.

1. INTRODUCTION

Nowadays, with the inadequacy of fossil oil resources, the increasing price of energy imports, and rising environmental concerns,1−5 biodiesel has gained increasing attention as a potential renewable alternative to fossil diesel, which can be obtained by the esterification/transesterification of free fatty acids (FFAs), vegetable oils (edible and non-edible oil), animal fats, algal oils, or waste oils with alcohols in the presence of an acid/basic catalyst.6 In an industrial biodiesel production process, heterogeneous catalysts such as sodium hydroxide, sodium methoxide, potassium hydroxide, hydrochloric acid, and sulfuric acid are typically employed to catalyze the esterification/transesterification reaction owing to their high activity and low cost.7 However, these homogeneous catalysts are non-recoverable and induce equipment corrosion and environmental concerns related to the final product purification with multiple washing steps, which limit their industrial application.8,9 Thus, the study of a heterogeneous solid catalyst is preferred, which can be easily separated and recycled from the reaction mixture; also, simple purification of the product and reduced purification costs have recently become a current area of potential interest.10,11 Of note, a variety of heterogeneous solid acid catalysts, such as heteropolyacids,12 carbon-based solid acids,13 metal oxides,14 zeolites,15 cation exchange resins,16 and graphene oxide,17 have been evaluated as alternative catalysts for biodiesel production. Among them, heteropolyacids are widely considered as a potential replacement for the homogeneous catalysts.

Currently, the heteropolyacids have been studied owing to its strong Brønsted acidity being stronger than the conventional acid catalysts such as sulfuric acid and acidic resins.18 However, it should be noted that bulk heteropolyacids are easily soluble into reaction media that leads to serious catalyst deactivation. Moreover, the heteropolyacids have low specific surface areas.19 To overcome these shortcomings, two strategies have been developed recently: (1) The partial/full substitution of protons by large monovalent ions and (2) embedding them into supports were attempted.20,21 Our group is also working in the field of further modification and solidification of heteropolyacids, and we have established the use of the co-doped heteropolyacids as solid acid catalysts for biodiesel production from oleic acid.22
Very recently, metal–organic frameworks (MOFs) have attracted enormous attention as a promising solid support because of their structural versatility, very high surface areas, and good thermal stability. 25,26 In this regard, the encapsulation of heteropolyacids into MOFs can be achieved as promising heterogeneous catalysts for organic reactions. 25,26 Therefore, in this work, we attempt to synthesize the encapsulation of ammonium and silver co-doped H3PW12O40 onto the zirconium-based metal–organic frameworks (UiO-66) using a one-pot solvothermal method. The as-prepared Ag1(NH4)2PW12O40/UiO-66 nanocomposite was investigated for the production of biodiesel from lauric acid. Moreover, the characterization of the synthesized nanocatalyst was done using Fourier transform infrared spectroscopy (FT-IR), N2 adsorption/desorption, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric (TG) and ammonia temperature-programmed desorption (NH3-TPD) techniques. The esterification parameters, such as the molar ratio of lauric acid to methanol, catalyst amount, and reaction temperature and time, were studied regarding the conversion to methyl laurate. Additionally, the reusability of the composite was also investigated to evaluate the stability of the catalyst in the present study. Finally, the reaction kinetics of methyl esterification was researched.

2. MATERIALS AND METHODS

2.1. Chemicals. Silver nitrate, ammonium carbonate, hydrate phosphotungstic acid (H3PW12O40), zirconium(IV) chloride, terephthalic acid, lauric acid, and methanol (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without prior purification.

2.2. Catalyst Preparation. The encapsulation of ammonium and silver co-doped H3PW12O40 onto the zirconium-based metal–organic frameworks was realized by a convenient one-pot hydrothermal method. 27 First, the Ag1(NH4)2PW12O40 sample was also synthesized according to the procedure reported in our previous work. 22 Second, the prepared Ag1(NH4)2PW12O40 solid, terephthalic acid (2 mmol), and zirconium(IV) chloride (2.2 mmol) were added together into 18 mL of N,N-dimethylformamide (DMF) under vigorous stirring at room temperature for 3 h. Consequently, the prepared mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and aged at 120 °C for 6 h. After cooling to room temperature, the precipitate was isolated by centrifugation and washed with DMF and ethanol. Finally, the product was dried overnight at 80 °C, which was denoted as Ag1(NH4)2PW12O40/UiO-66. Following these steps, the UiO-66 sample without addition of ammonium and silver co-doped H3PW12O40 was obtained.

2.3. Characterization. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer spectrum100 spectrophotometer. The crystallinity of the samples was analyzed by powder X-ray diffraction (XRD) using a Bruker D8 advance diffractometer with Cu Kα radiation (1.5418 Å), and the patterns were recorded in the 2θ range of 5–70°. N2 adsorption/desorption isotherms were conducted on a Quantachrome instrument (Quantachrome Instruments, Boynton Beach, USA). The sample morphology was examined using a scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopy (TEM; FEI Tecnai G2 20, accelerating voltage of 200 kV). The acidic properties of samples were examined via an NH3-TPD (Micrometrics AutoChem II 2920) instrument. Thermogravimetric (TG) analysis was carried out using a NETZSCH/STA 409 PC Luxx simultaneous thermal analyzer at a heating rate of 5 °C/min.

2.4. Reaction Procedure. The esterification of lauric acid with methanol was carried out in a 50 mL stainless steel high-pressure autoclave reactor at 110–160 °C under magnetic stirring. Typically, about 3 g of the lauric acid was mixed with the required quantity of the catalyst and different volumes of methanol. The temperature was controlled by a silicone oil bath. At the end of the reaction, the autoclave reactor was cooled and opened, and the mixture was centrifuged to separate the solid catalyst. The water and residual methanol were removed by using the rotary evaporator. Subsequently, the conversions were calculated precisely via the ISO 660-2009 standard in accordance with the reduction of the acid value of lauric acid after the reaction.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst. 3.1.1. Fourier Transform Infrared Spectrometer (FT-IR). The FT-IR spectra of H3PW12O40, UiO-66, Ag1(NH4)2PW12O40, and Ag1(NH4)2PW12O40/UiO-66 samples in the region between 450 and 2400 cm−1 are demonstrated in Figure 1. The peaks at 1080, 982, 889, and 801 cm−1 are assigned to the particular stretching vibrations of P–O, W–O, W–O−, W, and W–O−–W, respectively, referring to the existence of the Keggin structure. 28 Interestingly, these characteristic bands were also found in the spectra of Ag1(NH4)2PW12O40 and Ag1(NH4)2PW12O40/UiO-66, implying that the Keggin structures were retained. However, the marginal shift of four characteristic peaks in Ag1(NH4)2PW12O40 and Ag1(NH4)2PW12O40/UiO-66 samples may be due to the replacement of larger Ag+ and NH4+ ions with smaller H+, and the co-doped salts incorporated the pores of UiO-66, further confirming that the co-doped salts has been successfully incorporated into the matrix cavities. Additionally, the bands that appeared at 1660, 1538, 1397, 745, 667, and 553 cm−1 in UiO-66 and Ag1(NH4)2PW12O40/UiO-66 composites were assigned to the C==O stretching vibrations of BDC carboxylic acid, the O–C–O asymmetric and symmetric stretching of the BDC ligand, O–H and C–H vibration in the BDC ligand, and...
the Zr–(OC) asymmetric stretch, respectively. Similar results were reported by Tang et al.29 These results revealed that the structures of UiO-66 and the Keggin structures were retained in the composite Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66.

3.1.2. X-ray Powder Diffraction (XRD). Figure S1 shows the XRD patterns of H$_3$PW$_{12}$O$_{40}$ and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$. The diffraction peaks of the Keggin structure at 9.1, 20.3, 25.8, 27.5, 28.7, 31.6, and 35.9° were clear, and the data agree well with those by Raveendra et al.30 Of note, the four similar diffraction peaks (10.6, 21.3, 26.2, and 30.4°) were observed with a marginal shift toward higher 2θ values due to a contracted unit cell.31,32 Figure 2 shows the XRD patterns of UiO-66 and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66, and the diffraction patterns of the composites similar to that of UiO-66 indicated that Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$ did not disturb the crystallization of the UiO-66 structures. However, the intensity of the peaks in Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 was lower than that of UiO-66, and the diffraction pattern of Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$ was undetectable in the composite, implying the uniform distribution of the co-doped salts, which is consistent with previous reports.33,34

3.1.3. N$_2$ Adsorption/Desorption Analysis of the Catalysts. The N$_2$ adsorption/desorption isotherms and corresponding pore size distribution curves of the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$ and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 samples are illustrated in Figure 3a and 3b, respectively. The isotherms of two samples had type I/IV isotherms according to the IUPAC classification, indicating the combination of the mesoporous and microporous cavities.35,36 Besides, this also implies that the incorporation of salts species into the UiO-66 matrix had no influence on the porosity of UiO-66. The structure parameters (specific surface area, pore size, and pore volume) of the samples are shown in Table 1. Based on a comparison, the structure parameters of the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 sample were lower than those of the UiO-66 sample, which might be due to the cavities of UiO-66 partly occupied by the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$ salts. These results are similar to the results observed from XRD and FT-IR, as well as previous literature studies.37

3.1.4. Scanning Electron Microscopy (SEM) Analysis. The morphologies of the synthesized UiO-66, Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$, and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 were studied by SEM images, as illustrated in Figure 4a–c. For the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$ sample, it exhibited the small particles with the size of around 500 nm (Figure 4a). Meanwhile, the UiO-66 sample has an irregular near-cubic crystallite morphology with the size of nearly 200 nm (Figure 4b). After the encapsulation process of the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$, the Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 composite with a layered-sheet morphology was observed. It may be attributed to a strong guest molecule and matrix interaction, resulting in improved activity and stability. Meanwhile, it still retained the original structure of UiO-66, which is closely related to its excellent physical properties.

![Figure 2. XRD patterns of UiO-66 and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66.](image)

![Figure 3. (a) N$_2$ adsorption/desorption isotherms and (b) pore size distribution of UiO-66 and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66.](image)

### Table 1. Nitrogen Physical Adsorption Data of UiO-66 and Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66

| entry | sample type | surface area (m$^2$/g) | average Pore size (nm) | pore volume (cm$^3$/g) |
|-------|-------------|------------------------|-----------------------|------------------------|
| 1     | UiO-66      | 667.2                  | 2.58                  | 0.431                  |
| 2     | Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 | 554.7                  | 2.42                  | 0.335                  |
3.1.5. Transmission Electron Microscopy (TEM) Analysis. TEM was also used to further analyze the morphology and structure of the catalyst. Figure 5a–c shows the TEM images of UiO-66 and Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66. UiO-66 presents near-cubic crystal morphology. In contrast, TEM images of the Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66 also exhibited similar morphology, and the crystalline size is around 200 nm, suggesting that the encapsulation of co-doped salts did not significantly affect the original structure, further confirming the excellent stability of the UiO-66 matrix. These results were also in good agreement with the N₂ adsorption/desorption and SEM analysis results.

3.1.6. Thermogravimetric (TG) Analysis. The results of the TG analysis of the Ag₁(NH₄)₂PW₁₂O₄₀ and Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66 samples are shown in Figure 6. As expressed in Figure 6, for the Ag₁(NH₄)₂PW₁₂O₄₀ sample, the first mass loss occurred at 40–270 °C, which indicated the loss of surface-adsorbed water from the catalyst and bonded water from the crystal hydrates, the second mass loss of 2.7 wt % (between 300 and 600 °C) may belong to the separation of NH₃ molecules from Ag₁(NH₄)₂PW₁₂O₄₀ and the crystallization of constitutive oxides, which are in good agreement with previous results. In comparison with the Ag₁(NH₄)₂PW₁₂O₄₀ sample, the Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66 has two clear loss stages at 40–300 and 300–580 °C. The first mass loss stage of 20.3 wt % is attributed to the loss of desorbed water from the sample surface, Ag₁(NH₄)₂PW₁₂O₄₀ crystallization, water, and solvent molecules. Another weight loss of about 18.5 wt % is attributed to the departure of constitutive water molecules of the Ag₁(NH₄)₂PW₁₂O₄₀ the portion of thermal decomposition of the organic ligand, and the framework structure of UiO-66. According to previous reports, UiO-66 was mainly decomposed at 50–600 °C (58% mass loss), and ~42% of the starting weight remained after the decomposition. Therefore, the incorporation of Ag₁(NH₄)₂PW₁₂O₄₀ obviously improves the stability of the composite, probably because of the strong interaction of Ag₁(NH₄)₂PW₁₂O₄₀ with the framework structure. Finally, the Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66 sample is stable up to 300 °C.
which indicates good thermal stability to catalyze the esterification reaction.

3.1.7. Ammonia Temperature-Programmed Desorption (NH3-TPD) Analysis. The NH3-TPD profile of the Ag1(NH4)2PW12O40/UiO-66 material is displayed in Figure 7. It can be observed that the catalyst displayed two desorption peaks in the low-temperature region and medium-temperature region. The low-temperature desorption peak (<150 °C) can be assigned to weak acid sites, with the acid concentration of about 1.5 mmol/g. Importantly, the medium-temperature peak from 150 to 300 °C is attributed to NH3 desorption from moderately acidic sites with the acid concentration of about 11.7 mmol/g. Such results therefore showed that the Ag1(NH4)2PW12O40/UiO-66 nanocatalyst has a relatively higher acidity and will subsequently be advantageous for esterification reaction.

3.2. Influence of Esterification Parameters on the Lauric Acid Conversion. The catalytic activity of the Ag1(NH4)2PW12O40/UiO-66 nanocatalyst was evaluated in the esterification of lauric acid with methanol, and the influence of reaction conditions including the molar ratio of lauric acid to methanol, catalyst amount, reaction temperature, and reaction time was investigated (Figure 8).

As the esterification reaction was an equilibrium-limited reaction, an excess amount of methanol used could shift the reaction equilibrium toward the right. The molar ratio of lauric acid to methanol varied from 1:3 to 1:18, and the conversions obtained are shown in Figure 8a. The lauric acid conversion increased rapidly from 46.2% to 75.6% as the molar ratio of lauric acid to methanol increased from 1:3 to 1:15. Further increasing the molar ratio led to a slight decrease of the lauric acid conversion probably because excess methanol makes the lauric acid and catalyst become too dilute.40 Hence, the molar ratio of 1:15 was selected for achieving high conversions.

The effect of the amount of catalyst on lauric acid conversion was also investigated (see Figure 8b). The catalyst amount was varied in the range of 1–12 wt % (based on lauric acid). As depicted in Figure 8b, with an increase in the amount of catalyst, conversion of lauric acid also increases, and the conversion of lauric acid could reach 75.6% in 10 wt %. The conversion slightly increases when the catalyst amount continued to extend. Therefore, the appropriate catalyst amount was selected as 10 wt %.

Figure 8c showed the relationship between lauric acid conversion and reaction temperature. The reaction temperature was varied within a range from 110 to 160 °C. It can be seen from Figure 8c that there was a gradual increase in the lauric acid conversion upon increasing reaction temperature from 110 to 150 °C. However, a slight decrease in the lauric acid conversion was observed with rising the reaction temperature beyond 150 °C, probably because too high reaction temperature had little effect since a mass of methanol turned into vapor. Accordingly, the reaction temperature of 150 °C was selected for the production of biodiesel catalyzed by the Ag1(NH4)2PW12O40/UiO-66 nanocatalyst.

Figure 8d showed the effect of reaction time on lauric acid conversion. The reaction time was varied within a range from 0.5 to 5 h. As observed from Figure 8d, when the reaction time was extended to 3 h, the conversion increased to 75.6%. Further increasing of reaction time did not improve the conversions significantly as the esterification reaction approached equilibrium. Thus, the optimal reaction time was 3 h for this procedure.

3.3. Reusability of the Solid Acid Catalyst. To examine the recyclability of the Ag1(NH4)2PW12O40/UiO-66 catalyst, six cycle experiments of esterification of lauric acid with methanol were conducted. After each cycle of 3 h reaction, the catalyst was separated by centrifugation and washed with methanol and immediately used in a new esterification process. The results (Figure 9) showed that the catalyst can be reused up to four times, and the lauric acid conversion was around 70.6–75.6%. A significant drop in lauric acid conversion (54.6%) was observed while reusing the catalyst for the 6th time. The phenomenon might be due to the leaching of the active sites in the reaction mixture and the surface-bound lauric acid and methyl laurate on the catalyst, which cannot be removed with the less polar solvent.41,42 More interestingly, the results from the XRD and FT-IR characterizations for the used Ag1(NH4)2PW12O40/UiO-66 catalyst after the 6th run reaction are similar to those for the fresh catalyst, as given in Figures S2 and S3, further suggesting that the catalyst structure was maintained and confirming the good stability of the as-synthesized Ag1(NH4)2PW12O40/UiO-66 nanocatalyst.

3.4. Kinetic Studies. In this study, the esterification reaction kinetics was investigated in a range between 130 and 150 °C (see Figure S4). Meanwhile, in the presence of an excess of methanol, the esterification is a pseudo-first-order reaction as reported in previous studies.43 Thus, the rate constant (k) can be calculated as follows

$$k = \frac{-\ln(1 - \eta)}{t} \quad (1)$$

Where $k$ is the rate constant of the pseudo-first-order reaction, $\eta$ is the lauric acid conversion, and $t$ is reaction time. A graph was plotted between $-\ln(1 - \eta)$ vs time, and the slope was calculated in order to determine the pseudo-first-order rate constant ($k$) and was displayed in Figure 10a. From Figure 10a, the excellent linear nature of the plot supports the pseudo-first-order kinetic equation. Additionally, the activation energy ($E_a$) required for the esterification process was found by considering the Arrhenius equation, and the equation can be represented as
Where $A$ is the Arrhenius constant, $E_a$ is the activation energy (J/mol), $T$ is the absolute temperature (K), and $R$ is the universal gas constant. The graph of $\ln k$ vs $1/T$ (K) is represented by a linear Arrhenius temperature dependence and is shown in Figure 10b. According to the results obtained from Figure 10b, it displayed a greater value of fit ($R^2$) of 0.999, and the values of $E_a$ for the esterification of lauric acid were calculated to be 35.2 kJ/mol.

4. CONCLUSIONS

The ammonium and silver co-doped phosphotungstic acid supported on zirconium-based metal–organic frameworks (UiO-66) was successfully synthesized with the aim of being used as a nanocatalyst for biodiesel production from lauric acid. The synthesized Ag$_1$(NH$_4$)$_2$PW$_{12}$O$_{40}$/UiO-66 nanocatalyst exhibited pronounced activity for the lauric acid esterification process, which could be attributed to its large specific surface area, structure of good stability, and relatively higher acidity. Also, the catalyst was recycled and reused up to six cycles. The kinetic studies further suggested that the esterification of lauric acid in the presence of the composite catalyst follows the pseudo-first-order kinetics with an activation energy ($E_a$) of 35.2 kJ/mol. Thus, the present strategy could potentially contribute to save energy and time in

$$\ln k = \ln A - \frac{E_a}{RT}$$

(2)
the catalyst green synthesis and hold a significant promise for the production of biodiesel.

- ASSOCIATED CONTENT
- Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00375.
  H3PW12O40 and Ag1(NH4)2PW12O40 sample characterized by XRD, the fresh and reused (after the 6th run) Ag1(NH4)2PW12O40/Uio-66 catalysts characterized by XRD and FT-IR, and the esterification of lauric acid with methanol carried out in a range between 130 and 150 °C (PDF)

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- Notes
  The authors declare no competing financial interest.

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