Codoped Phosphotungstate as an Efficient Heterogeneous Catalyst for the Synthesis of n-Butyl Oleate

Xi Zhou,* Peng He, and Chao Zhang

ABSTRACT: A quaternary ammonium and titanium codoped phosphotungstate (QA0.5Ti0.5H0.5PW) catalyst was prepared by the ion exchange method and used as a solid acid catalyst for the synthesis of n-butyl oleate. The catalyst was characterized by Fourier transform infrared, elemental analyzer, energy-dispersive X-ray spectrometry, Brunauer−Emmett−Teller, scanning electron microscopy, and Hammett indicator methods. QA0.5Ti0.5H0.5PW showed a higher catalytic activity than other phosphotungstate solid acid catalysts reported by literature, and the esterification rate reached 99% under optimized conditions. Moreover, QA0.5Ti0.5H0.5PW exhibited well reusability. An esterification rate of 90.1% was still obtained in the eighth run.

INTRODUCTION

As an important fine chemical product, n-butyl oleate can be used as a hard plasticizer for the processing of polyvinyl chloride and neoprene, as well as a lubricant, waterproofing agent, and fatliquor for animal leather. In the traditional process, concentrated sulfuric acid was used as catalyst for the synthesis of n-butyl oleate. The catalyst was characterized by Fourier transform infrared, elemental analyzer, energy-dispersive X-ray spectrometry, Brunauer−Emmett−Teller, scanning electron microscopy, and Hammett indicator methods. QA0.5Ti0.5H0.5PW showed a higher catalytic activity than other phosphotungstate solid acid catalysts reported by literature, and the esterification rate reached 99% under optimized conditions. Moreover, QA0.5Ti0.5H0.5PW exhibited well reusability. An esterification rate of 90.1% was still obtained in the eighth run.

A large number of efficient solid acid catalysts, such as solid superacids, carbon solid acid, cation exchange resin, and heteropoly acids (HPAs), have also been reported for the synthesis of oleate. Among them, HPAs have the advantages of strong acidity and being environment-friendly. However, their application suffers from high solubility in polar solvents and a small specific surface area (<10 m²/g). Insoluble salts of HPAs which have a relatively high specific surface area could be prepared by substituting partial H⁺ in HPAs with NH₄⁺, K⁺, Cs⁺, or Ag⁺. There are more reports on simple salts of HPAs catalysts based on only one type of cation (excluding H⁺), but fewer studies on oleic acid esterification catalyzed by mixed salts of HPA catalysts with different cations. Santos et al. found that (NH₄)₂Cs₀.5H₀.5PW prepared by NH₄⁺ and Cs⁺-codoped phosphotungstic acid (HPW) had a higher specific surface area (46.1 m²/g), and showed a higher catalytic activity to the methyl esterification of oleic acid. In a previous study, our group found that (NH₄)₀.5Ag₀.5H₂PW exhibits excellent catalytic property for the esterification of levulinic acid with n-butanol. It showed a higher catalytic activity than simple salts of HPW such as (NH₄)₁H₂PW and Ag₁H₂PW. Subsequently, it was also reported that the conversion rate of oleic acid is close to 100% using Ag₁(NH₄)₂PW as the catalyst for the methyl esterification of oleic acid.

Although the above codoped HPW catalysts showed a high catalytic activity for esterification, their large-scale application suffers from high cost of Cs and Ag. In addition, these catalysts have poor affinity with long-chain fatty acids as the molecular structure of the catalyst does not contain a lipophilic group. On the basis of our previous research, a quaternary ammonium and titanium codoped HPW (QA0.5Ti0.5H0.5PW) was prepared by the ion exchange method and used as a heterogeneous...
catalyst for the synthesis of n-butyl oleate. The results showed that QA0.5Ti0.5H0.5PW without a precious metal ingredient exhibited an excellent catalytic property.

■ RESULTS AND DISCUSSION

Catalyst Characterization. Detecting by elemental analyzer and X-ray fluorescence (XRF), the calculated/detected element content of QA0.5Ti0.5H0.5PW is as follows: C (3.75%/3.63%), Ti (0.79%/0.72%), W (72.46%/73.86%). According to the results, the test values of the element content of QA0.5Ti0.5H0.5PW were similar to the calculated values, which were consistent with the results reported in previous literature.26–28

The structure of QA0.5Ti0.5H0.5PW was characterized by Fourier transform infrared (FT-IR), and the result is shown in Figure 1. The characteristic absorption peaks of the Keggin structure appeared at 1080, 982, 890, and 793 cm−1, which are attributed to ν2P–O−, ν3W–O−, ν4W–O−, and ν5W–O−, respectively. The characteristic absorption peaks at 1623 and 1473 cm−1 were attributed to the telescopic vibration peaks of C−C and C−N bonds, indicating that [C16H33N(CH3)3]1+ was successfully introduced into the molecular structure of QA0.5Ti0.5H0.5PW.

In addition, the surface topography of the catalyst was characterized by scanning electron microscopy (SEM). As shown in Figure 2, the particle size of QA0.5Ti0.5H0.5PW was smaller than that of Ti0.625H0.5PW, and the particle aggregation of Ti0.625H0.5PW was more serious than that of QA0.5Ti0.5H0.5PW. According to the results of SEM and Brunauer–Emmett–Teller (BET) characterization (Table 1), the introduction of quaternary ammonium cations could improve the dispersion and specific surface area of phosphotungstate. The acid strength and density of QA2.5H0.5PW, Ti0.625H0.5PW, and QA0.5Ti0.5H0.5PW were also tested by the method of Hammet indicators. As shown in Table 1, the surface acid strengths of QA0.5Ti0.5H0.5PW and Ti0.625H0.5PW are both in the range of −13.75 to −14.52, which is slightly stronger than that of QA2.5H0.5PW. However, the surface acid density of QA0.5Ti0.5H0.5PW is higher than that of Ti0.625H0.5PW, which may be due to the higher specific surface area and pore volume of the former.

Catalyst Activity Test. The effect of the catalyst on the synthesis of n-butyl oleate was investigated in the presence of the 1.2% (based on the mass of oleic acid) catalyst at 140 °C within 1 h. As shown in Table 2, the esterification rate was only 19.7% without the catalyst. The esterification rate reached 87.5, 89.2, and 92.9% using (NH4)2C6H5O7·H2O·PW, (NH4)2Ag·PW, and (NH4)2Al·PW as the catalyst, respectively. It means that above three mixed salts of HPW exhibited high catalytic activity. Among them, (NH4)2Al·PW exhibited the highest catalytic activity with a 91.9% esterification rate.

| catalyst | esterification rate (%) | TOF (h−1) |
|----------|-------------------------|-----------|
| QA0.5Ti0.5H0.5PW | 19.7 | |
| (NH4)2C6H5O7·H2O·PW | 87.5 | 72.9 |
| (NH4)2Ag·PW | 89.2 | 74.3 |
| (NH4)2Al·PW | 92.9 | 77.4 |
| QA0.5Ti0.5H0.5PW | 91.9 | 76.6 |
| QA2.5H0.5PW | 96.4 | 80.3 |
| QA1Ti0.5PW | 76.6 | 66.3 |

**Reaction conditions:** n(butanol)/n(oleic acid) = 2:1, catalyst amount: 1.2% (based on the mass of oleic acid), 140 °C, 1 h. *Gram of oleic acid converted per gram of catalyst in 1 h.

Table 1. Acid Strength and Acidity of the Catalyst

| catalyst | \( S_{\text{BET}} \) (m²/g) | pore volume (cm³/g) | \( H_0 \) | acid density (mmol/g) |
|----------|---------------------------|---------------------|----------|---------------------|
| QA0.5Ti0.5H0.5PW | 36 | 0.039 | −13.75 < \( H_0 \) < −12.70 | 1.83 |
| Ti0.625H0.5PW | 23 | 0.022 | −14.52 < \( H_0 \) < −13.75 | 1.96 |
| QA0.5Ti0.5H0.5PW | 29 | 0.027 | −14.52 < \( H_0 \) < −13.75 | 2.13 |

Figure 1. FT-IR spectrum of QA0.5Ti0.5H0.5PW.

Figure 2. SEM micrographs of Ti0.625H0.5PW (a) and QA0.5Ti0.5H0.5PW (b).
However, its affinity with oleic acid is poor as there is no good lipophilic group in its molecular structure. In order to further enhance the catalytic activity, QA_{0.5}Ti_{0.5}H_{0.5}PW was prepared by replacing NH_4^+ with [C_{18}H_{33}N(CH_3)_3]^+ in the molecular structure of (NH_4)_3(Ti_{0.5}H_{0.5})PW to introduce a strong lipophilic group. The results showed that QA_{0.5}Ti_{0.5}H_{0.5}PW exhibited a higher catalytic activity than (NH_4)_3(Ti_{0.5}H_{0.5})PW owing to its better affinity with the raw material. The esterification rate reached 96.4% with a 80.3 h\(^{-1}\) TOF value in the presence of QA_{0.5}Ti_{0.5}H_{0.5}PW. It means that the catalytic activity of QA_{0.5}Ti_{0.5}H_{0.5}PW is even higher than that of previous reported mixed salts of HPW such as (NH_4)_2 Cs_{0.5} H_{0.5} PW, (NH_4)_2 Ag_{1} PW, or (NH_4)_3 Ag_{0.5} H_{0.5} PW.\(^{26-28}\)

Under the same reaction conditions, QA_{0.5}Ti_{0.5}H_{0.5}PW also exhibited a higher catalytic activity than QA_{0.5}H_{0.5}PW and Ti_{0.5}H_{0.5}PW prepared by single [C_{18}H_{33}N(CH_3)_3]^+ or Ti^{4+} doped HPW, which is consistent with the results reported in the literature.\(^{26-28}\) According to the results of surface acid strength and a density test (Table 1), QA_{0.5}Ti_{0.5}H_{0.5}PW exhibited a stronger surface acid strength than QA_{2.5}H_{0.5}PW, and showed a higher surface area and acid density than Ti_{0.5}H_{0.5}PW, which may be one of the reasons for its higher catalytic activity.

In addition, QA_{0.5}Ti_{0.5}PW and QA_{0.5}Ti_{0.625}PW were prepared by exchanging all H^+ of HPW to [C_{18}H_{33}N(CH_3)_3]^+ and Ti^{4+}. According to the results in Table 2, the esterification rate was only 72.5 and 79.6% using QA_{1}Ti_{0.5}PW and QA_{0.5}Ti_{0.625}PW as catalysts for the synthesis of n-butyl oleate, respectively. It indicated that the retention of partial H^+ in the molecular structure of QA_{0.5}Ti_{0.5}H_{0.5}PW has an important influence on its catalytic activity, which is consistent with the results reported in the literature.\(^{26-28}\) According to the results reported in the previous literature,\(^{21-28}\) partial H^+ in the molecular structure of HPW can be replaced by other cations (such as NH_4^+, K^+, Cs^+, or Ag^+), and a Lewis acid site can be introduced into the catalyst surface, whereas retaining a partial H^+ is conducive to maintaining its Bronsted acid site. Therefore, the type and quantity of doped cations have a significant influence on the specific surface area, surface acid density, and surface acid quantity of phosphotungstate.

**Effect of Reaction Conditions on the Esterification Rate.** The effect of catalyst amount on the synthesis of n-butyl oleate using QA_{0.5}Ti_{0.5}H_{0.5}PW as the catalyst was investigated, and the result is shown in Figure 3. The esterification rate was only 19.7% without a catalyst, which indicated that a catalyst has a remarkable effect on the transformation of oleic acid to n-butyl oleate. An esterification rate of 73.1% was obtained with 0.4% (based on the mass of oleic acid) QA_{0.5}Ti_{0.5}H_{0.5}PW as the catalyst. The esterification rate increased from 73.1 to 96.4% with increasing of the catalyst amount to 1.5%.

As shown in Figure 4, the reaction temperature also played an important role in the esterification of oleic acid with n-butanol. The esterification rate increased quickly from 83.6 to 96.4% with a rising temperature from 120 to 140 °C. Then, the esterification rate decreased to 87.8% with further rising of the temperature to 140 °C. It is beneficial to the esterification reaction to improve the reaction temperature appropriately as esterification is an exothermic reaction. However, an exorbitant temperature can cause low boiling n-butanol to vaporize, resulting in a relatively low concentration of n-butanol in the liquid reaction system.

Esterification reactions are usually tested under an excess of alcohol to achieve higher yields. Herein, the effect of material ratio on the synthesis of n-butyl oleate was studied using QA_{0.5}Ti_{0.5}H_{0.5}PW as the catalyst. According to the results of Figure 5, the esterification rate increased from 87.2 to 97.9% with raising the molar ratio of n-butanol to oleic acid from 1.6 to 2.8.
to 2.4. However, the esterification rate decreased to 95.7% with further increasing the material ratio to 2.8. This may be due to the lower reaction temperature resulting by the high concentration of n-butanol with a low boiling point (117 °C) in the reaction system.

In order to find out the detailed progress of the reaction, the effect of reaction time on the synthesis of n-butyl oleate was also investigated. As shown in Figure 6, the esterification rate had no viewable change during the first four runs. Then, the esterification rate slowly decreased in the next four runs. An esterification rate of 90.1% was still obtained in the eighth run detected by an element analyzer. According to the reports in the literature, this should be caused by the residual oleic acid or butyl oleate on the catalyst surface or pore. It may be the reason why the activity of the catalyst decreased slightly in the later stage.

Reusability Test. The reusability of QA0.5Ti0.5H0.5PW was tested with 2 molar ratio of n-butanol to oleic acid at 140 °C in 1 h, and the results were shown in Figure 7. The esterification rate had no viewable change during the first four runs. Then, the esterification rate slowly decreased in the next four runs. An esterification rate of 90.1% was still obtained in the eighth run. According to above results, QA0.5Ti0.5H0.5PW has good reusability for the synthesis of n-butyl oleate. In addition, the loss of the catalyst was not found by detecting the content of W and Ti in the filtrate through ICP, and the Keggin structure of QA0.5Ti0.5H0.5PW was well maintained in the reuses (Figure 8), detected by FT-IR. These might be the reasons for the good reusability of QA0.5Ti0.5H0.5PW. However, compared with the fresh catalyst, the content of carbon in the catalyst increased from 3.63 to 4.19% after the eighth run detected by FT-IR. These might be the reasons for the decrease of the catalytic activity of QA0.5Ti0.5H0.5PW.

Application of Catalyst for Other Esterification. In order to verify the universality of QA0.5Ti0.5H0.5PW, the catalytic properties of QA0.5Ti0.5H0.5PW for esterification synthesis of methyl oleate, n-butyl levulinate, tributyl citrate, and n-butyl stearate were also investigated. As shown in Table 3, all esterification rates are higher than 95%, indicating that QA0.5Ti0.5H0.5PW exhibited a high catalytic activity for the above esterification reactions. The above results indicated that the high catalytic activity of QA0.5Ti0.5H0.5PW is general for esterification.

■ CONCLUSIONS

Among the investigated catalysts, QA0.5Ti0.5H0.5PW showed the highest catalytic activity for the esterification of oleic acid to n-butanol. In comparison with single cation-doped phosphotungstate, QA0.5Ti0.5H0.5PW exhibited an excellent catalytic activity owing to its strong acidity, high surface acid density, and good affinity with the raw material. The esterification rate could reach up to 99% with good reusability. Comparing with Cs⁺ (Ag⁺) and NH₄⁺ codoped phosphotungstate reported by previous literature, QA0.5Ti0.5H0.5PW had the advantages of a cheap and high catalytic activity. Moreover, the high catalytic activity of QA0.5Ti0.5H0.5PW is general for esterification. The above results provide a feasible method for the development of efficient codoped phosphotungstate catalysts.

■ EXPERIMENTAL SECTION

Preparation and Characterization of Catalysts. HPW (AR), [C₁₆H₃₅N(CH₃)₃]Cl (AR), Ti(SO₄)₂ (AR), oleic acid (AR), and n-butanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd., China.

A typical procedure for the preparation of codoped HPW catalysts is as follows: 1 mmol HPW, 0.5 mmol Ti(SO₄)₂, and 0.5 mmol [C₁₆H₃₅N(CH₃)₃]Cl were dissolved in 5 mL of water, respectively. A Ti(SO₄)₂ solution was added slowly to the HPW solution with continuous stirring at room temperature, followed by the addition of a C₁₆H₃₅N(CH₃)₃Cl solution.
solution. The resultant mixture was further stirred for 30 min and aged for 60 min. The white solid sample was separated by filtration, dried at 80 °C for 12 h, and calculated at 200 °C for 4 h in air atmosphere. The prepared catalyst was abbreviated as QA0.5Ti0.5H0.5PW.

The structure of QA0.5Ti0.5H0.5PW was characterized by FT-IR in a Nicolet 560 with KBr pellet. The content of the N element in QA0.5Ti0.5H0.5PW was measured by an elemental analyzer (EA3000), and the contents of Ti and W elements were detected by an XRF (Shimadzu EDX 720) spectrometer with a rhodium X-ray source tube. The BET surface area of the catalyst was characterized by SEM (Tescan Mira3). The catalyst was separated by 

\[ \text{esterification rate} = \frac{1 - \text{acid value after reaction}}{\text{initial acid value of the reaction}} \times 100\% \]

In order to test the reusability of phosphotungstate, the catalyst was separated by filtration, washed with methanol, dried in an oven, and used in the next run.

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### Table 3. Application of QA0.5Ti0.5H0.5PW for Other Esterification

| carboxylic acid | alcohol | n(carboxylic acid)/n(alcohol) | catalyst amount (%) | temperature (°C) | time (h) | esterification rate (%) |
|----------------|--------|-------------------------------|---------------------|-----------------|---------|------------------------|
| oleic acid     | methanol | 1:10                          | 4.5                  | 65              | 5       | 95.0                   |
| levulinic acid | n-butanol | 1:2                            | 1.5                  | 120             | 2       | 99.1                   |
| citric acid    | n-butanol | 1:4                            | 1.5                  | 150             | 3       | 97.5                   |
| stearic acid   | n-butanol | 1:2                            | 1.5                  | 140             | 1.5     | 98.6                   |

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Notes

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