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Short Communication

A Brønsted–Lewis-surfactant-combined heteropolyacid as an environmental benign catalyst for esterification reaction

Jing Zhao ^a, Hongyu Guan ^a, Wei Shi ^a, Mingxing Cheng ^a, Xiaohong Wang ^{a,*}, Shiwu Li ^{b,*}

^a Key Lab of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun 130024, PR China
 ^b Traffic College, Jilin University, Changchun 130025, PR China

A R T I C L E I N F O

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1. Introduction

Fatty acid alkyl ester (FAAE), which is called biodiesel, is well known as green energy resource and renewable liquid fuel instead of fossil fuel. Biodiesel is produced from transesterification of vegetable oil or animal fats and esterification of free fatty acids (FFA) with short chain alcohols such as methanol using a chemical method [1–3]. Waste cooking oil is a cheap starting material that can help in improving the economic feasibility of biodiesel [4]. However, biodiesel from such low quality oils is unsuitable for base catalysts because of the FFA and water content. Fatty acids could be converted into FAAE by esterification with short chain alcohols in the presence of acid catalysts, which is also an important process for biodiesel. Among the acid catalysts, heteropolyacids (HPAs) represent promising catalysts for esterification reaction [5–10].

Among the HPA catalysts, $H_3PW_{12}O_{40}$ (HPW) as a Brønsted acid has higher strength than H_2SO_4 [11]. Metal salts of $PW_{12}O_{40}^{3-}$ potentially show the Lewis acidity originating from the metal cations as the electron pair acceptors as well as Brønsted acidity of protons [12]. Therefore, Lewis acidic HPAs could be introduced by modular grafting Lewis cations onto the phosphotungstic backbone [13]. As a continuation of our work, we designed a Brønsted–Lewissurfactant-combined heteropolyacid ($C_{16}TA$) $H_4TiPW_{11}O_{40}$, which was used in esterification of fatty acids. It is known that this kind of complexes could not only act as acid catalysts, but also surfactants in the organic reactions. It had been reported that Lewis acid/

ABSTRACT

A Brønsted–Lewis-surfactant-combined heteropolyacid (HPA) catalyst ($C_{16}TA$) $H_4TiPW_{11}O_{40}$ ($C_{16}TA$ = cetyl-trimethyl ammonium) had been designed and used as a water-tolerantly heterogeneous catalyst in esterification of free fatty acid with a higher conversion (94.7%) and excellent efficiency (91.8% yield) due to its acidic properties and structures. This micellar polyoxometalate catalyst was stable during the reaction and can be recycled by a simple separation process.

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surfactant cerium trisdodecylsulfate could be used as a catalyst for transesterification and esterification [14]. The advantages of these catalysts are: (1) concentrating the substrate molecules around the catalysts through the interaction between lipophilic tail and ester molecules. Meanwhile, methanol molecules could be absorbed by HPAs through hydrogen bonds; (2) providing hydrophobic surroundings for separation the water molecules from the catalyst. This catalyst exhibits some water-tolerant property available for the esterification reaction. By now, there are no reports in the literature on the application of Brønsted–Lewis-surfactant-combined heteropolyacids in esterification reactions.

2. Methods

2.1. Material and reagent

All chemicals were obtained from commercial suppliers. They were of AR grade and used without further purification. $Na_7PW_{11}O_{39}$ was synthesized according to the Ref. [15].

2.2. Preparation of catalysts

1 mL solution of Ti(SO₄)₂ (6 mmol in 2 M H₂SO₄) was added to Na₇PW₁₁O₃₉ (6 mmol) aqueous solution (20 mL). Adjusting the pH to 5.6 by adding NaHCO₃, the product of K₅TiPW₁₁O₄₀ was precipitated by adding excess of KCl. Then separated by filtration and recrystallized for three times. And K⁺ was replaced by H⁺ using cation exchange resins. A certain amount of hexadecyltrimethylammonium bromide was added into the above solution with stirring. Immediately the white precipitate formed and collected by filtration

^{*} Corresponding authors. Fax: +86 431 85099759. E-mail address: wangxh665@nenu.edu.cn (X. Wang).

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then calcined at 100 °C for 3 h. The yield of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was 50%.

2.3. Esterification reaction

A 100 mL three-necked glass flask charged with cooled condenser with 5.0 g of palmitic acid, a certain amount of anhydrous methanol and catalyst in it were vigorously stirred and refluxed for the required reaction time. After reaction, the mixture was rotary evaporated at 50 °C to separate the excess of methanol. Then the mixture was left divided into two layers by centrifugation with 4000 rpm. The upper layer was methyl esters of palmitic acid and the lower layer was the catalyst with small amount of water. The conversion of ester was calculated by measuring the acid value of the product and the yield was detected by gas chromatography (GC). The catalyst was decanted at the bottom of centrifuge, which was easy to be separated, washed by methanol to remove the remaining reactants and water, then dried in air and reused for the next experiment.

2.4. Critical micelle concentration (CMC) determination

The CMC of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was determined by break points of two nearly straight-line portions of the specific conductivity versus concentration plot [16].

2.5. Analytical analyses

$$Conversion(\%) = \left(1 - \frac{\text{acid values in raw material}}{\text{acid values after esterification}}\right) \times 100\%$$

2.6. Instrument

FTIR spectra (4000–500 cm⁻¹) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. The elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. X-ray diffraction (XRD) patterns of the sample were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu K α radiation (λ =0.154178 nm). DR-UV-vis spectra (200–800 nm) were recorded on a Cary 500 UV-vis-NIR spectrophotometer. TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The yield of monoester was determined on Shimazu GC-14C fitted with a HP-INNOWAX capillary column (30 m×0.32 mm; 0.50 µm film). Acetone was used as the solvent while nitrogen was used as the carrier gas. The oven temperature was set at 220 °C and the temperature of the detector and injector were set at 250 °C and 250 °C, respectively. Methyl laurate was used as the internal standard.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1a. shows the IR spectrum of the $(C_{16}TA)H_4TiPW_{11}O_{40}$. Obviously, the characteristic bands of the Keggin structure are observed at 1075, 970, 891, and 808 cm⁻¹ corresponding to $v_{as}(P-O_a)$, $v_{as}(W-O_d)$, $v_{as}(W-O_b)$ and $v_{as}(W-O_c)$, respectively. The C–H stretching vibrational peaks at 2923 and 2853 cm⁻¹ and C–N at 1473 cm⁻¹ show the existence of $C_{16}TA$ in the catalyst. The IR spectrum shows a pronounced band at 655 cm⁻¹ which indicated a Ti–O bond.

Powder X-ray diffraction patterns were used to confirm the structure of $(C_{16}TA)H_4TiPW_{11}O_{40}$. Compared with the diffraction peaks of $H_5PW_{11}TiO_{40}$ (Fig. S1a) at $8.4^{\circ}(110)$, $23.4^{\circ}(222)$, and $29.5^{\circ}(332)$, $(C_{16}TA)H_4TiPW_{11}O_{40}$ shows the similar diffraction peaks (Fig. S1b). This result indicates the original structure of $H_5PW_{11}TiO_{40}$ being attained after forming the micelles.

(%) a 4000 3500 3000 2500 2000 1500 1000 500 Wavenumbers (cm⁻¹)

Fig. 1. The IR spectra of the $(C_{16}TA)H_4PW_{11}TiO_{40}$ before (a) and after the reaction (b).

The result of micelles tested by cryo-TEM image (Fig. 2) shows mostly single 200–300 nm particles. And the elemental analyses of ($C_{16}TA$) $H_4TiPW_{11}O_{40}$ are: W, 66.69; Ti, 1.6; P, 0.98; C, 7.35; H, 1.53; N, 0.48%, respectively. EDX measurement results suggested the molar ratio of C: P: W: Ti = 19:1:11:1.

The CMC of $(C_{16}TA)H_4TiPW_{11}O_{40}$ given in Fig. S2 showed that the CMC of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was 0.92 mM, which also confirms the formation of micelle in aqueous solution [17].

The acidity of the catalyst was studied by Hammett indicator method [18] using paranitroaniline as the indicator. The acidity of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was 0.34 mmol/g, which was lower than HPW (0.80 mmol/g) and $H_5PW_{11}TiO_{40}$ (0.97 mmol/g). The surface acidity of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was determined by pyridine adsorption infrared spectroscopy (Fig. S3). The spectrum exhibits absorption bands attributed to Brønsted (1540 cm⁻¹) and Lewis (about 1450 cm⁻¹ and 1620 cm⁻¹) acid sites, which is confirmed by the reference [19]. Actually, we observed absorption bands of Brønsted acid site at 1539 cm⁻¹ and Lewis acid sites were successfully introduced to the catalyst.



Fig. 2. The cryo-TEM image of (C₁₆TA)H₄PW₁₁TiO₄₀ micellar catalyst.

3.2. Effect of catalyst

Different catalysts had been chosen to compare their activity, including H₅TiPW₁₁O₄₀, (C₁₆TA)H₄TiPW₁₁O₄₀ and H₃PW₁₂O₄₀ (Fig. 3). The catalytic activity was in the rank of $(C_{16}TA)H_4TiPW_{11}O_{40}>H_{5-}$ $TiPW_{11}O_{40} > H_3PW_{12}O_{40}$. Although $H_3PW_{12}O_{40}$ is a homogeneous and efficient acid catalyst, the separation is a problem. The acidity of H₅TiPW₁₁O₄₀ is higher than pure Brønsted acid H₃PW₁₂O₄₀ owing to its Brønsted and Lewis acidic sites. Therefore, H₅TiPW₁₁O₄₀ exhibited a higher activity than $H_3PW_{12}O_{40}$. The introduction of CTAB into H₅TiPW₁₁O₄₀ makes (C₁₆TA)H₄TiPW₁₁O₄₀ equip with amphiphilic properties and shows superior performance. The amphiphilic properties of (C₁₆TA)H₄TiPW₁₁O₄₀ could act both catalyst and surfactant to assemble miceller in methanol solvent. It is known that this kind of amphiphilic HPA catalysts could concentrate substrate molecules around the catalysts [20] through the interaction between lipophilic tail and ester molecules. Meanwhile, methanol could be absorbed by HPAs through hydrogen bonds. Therefore, the catalytic activity of $(C_{16}TA)H_4TiPW_{11}O_{40}$ was higher than $H_5TiPW_{11}O_{40}$.

In this micellar catalytic system, the catalytic activity was not significantly influenced by the lipophilic tail length. The different catalysts containing [C₁₂TA]H₄TiPW₁₁O₄₀, [C₁₄TA]H₄TiPW₁₁O₄₀, [C₁₆TA]H₄TiPW₁₁O₄₀, [C₁₆TA]H₄TiPW₁₁O₄₀ (Fig. 3). The rank of activity was [C₁₈TA]H₄TiPW₁₁O₄₀ (89.0%)~[C₁₂TA]H₄TiPW₁₁O₄₀ (90.1%)~[C₁₄TA]H₄TiPW₁₁O₄₀ (91.0%)<[C₁₆TA]H₄TiPW₁₁O₄₀ (94.7%). The length of carbon chain of palmitic acid is 16, which is similar to [C₁₆TA]⁺. Therefore, [C₁₆TA]H₄TiPW₁₁O₄₀ performed the highest activity.

It is known that the water content in feedstocks may easily cause the deactivation and lead to phase segregation. The side reaction decreased the activity of catalyst and increased the purification cost. Therefore, a water-tolerant catalyst is required.

 $(C_{16}TA)H_4TiPW_{11}O_{40}$ as a water-tolerant catalyst could easily isolate water molecules from catalysts. To investigate the effect of water, some water had been added to the mixture under the same conditions and the result was given in Fig. 4.

It can be seen that the effect of water on the catalytic activity is related to water content. When the water content was below 0.2%, the conversion was slightly reduced to 83.8%. However, the conversion was significantly reduced to 6.31% when 1% of water was added. So our catalyst is relatively more tolerant of water than other acid catalysts such as H_2SO_4 , [21] SO_4^2 –/ZrO₂. [22]

Experiments were carried out by varying the mass of the catalyst from 0.05 to 0.30 g keeping methanol/acid ratio 20:1(Fig. S4). It can



Fig. 3. Esterification of palmitic acid using different types of catalysts. Reaction conditions: molar ratio of methanol/acid/catalyst = 4856:243:1, 65 °C, 0.25 g of catalyst, 6 h.



Fig. 4. The effect of water on the catalytic activity. Reaction conditions: molar ratio of methanol/acid/catalyst = 4856:243:1, 65 °C, 0.25 g of catalyst, 6 h.

be seen that an increase in the conversion of palmitic acid from 61.7% to 94.7% when the mass of $(C_{16}TA)H_4TiPW_{11}O_{40}$ increased from 0.05 to 0.30 g and the acid–catalyst process attains the maximum conversion at 0.25 g of the catalyst. This can be attributed to an increase in the availability of the number of catalytically active site. The molar ratio of methanol/acid/catalyst was 4856:243:1. Then the catalytic reaction reaches equilibrium.

3.3. Effect of the methanol/acid molar ratio

Generally, excess methanol is necessary in order to obtain a higher yield of esters [23]. Here, we selected a molar ratio of methanol/acid from 1:1 to 24:1 (Fig. S5). Obviously, the conversion reached maximum of 94.7% at the methanol/acid ratio of 20. When increasing the molar ratio continually, no further improvement was found. This may be attributed to that the high amount of methanol would decrease the relative amount of catalytic sites and the availability of acid molecules and hence to decrease the conversion of acid. As a result, methanol/acid ratio of 20 is the best option. The molar ratio of methanol/acid/catalyst was 4856:243:1.

3.4. Effect of temperature

Esterification of fatty acid is normally performed near the boiling point of the alcohol. We studied the esterification of palmitic acid at 45 °C, 50 °C, 55 °C and 65 °C in order to determine the effect of reaction temperature on the methyl ester formation (Fig. S6). It shows the temporal evaluation of the results and it can be seen that under ($C_{16}TA$)H₄TiPW₁₁O₄₀ catalyzing, the esterification of acid to fatty acid ester can be occurred at lower temperature, the conversion being 90% at temperature 50 °C. In order to obtain the highest conversion of acid, the reaction at higher temperature of 65 °C had been done. The conversion was increased to 94.7%.

3.5. Effect of reaction time

In order to research the effect of reaction time, we choose the different reaction time with methanol/acid/catalyst 4856:243:1 at 65 °C (Fig. S7). The conversion of the product increased with increasing reaction time. It was found that the conversion increased from 1 h to 6 h and reached a maximum of 94.7% at 6 h. After 6 h, the conversion did not vary significantly. Thus the optimum reaction time is 6 h.



Fig. 5. The life span of catalyst for esterification. Reaction conditions: molar ratio of methanol/acid/catalyst = 4856:243:1, 65 °C, 0.25 g of catalyst, 6 h.

3.6. Reusability of the catalyst

The catalyst was easily separated from the mixture by centrifugation, and treated with methanol to remove the polar compounds. Then was dried in the air for reusing. After six reactions cycles, there is no considerable change in the catalytic activity and the result was shown in Fig. 5. The catalyst keeps the Keggin structure which can be proved by the IR (Fig. 1b). At the end of the reaction, the catalyst decanted at the bottom of the reactor and was used one more time without any treatment. As the catalyst ($C_{16}TA$)H₄TiPW₁₁O₄₀ was able to decant from the mixture of fatty acid methyl ester and glycerin into the bottom of the reactor, so the upper phase fatty acid methyl ester did not contain any ($C_{16}TA$)H₄TiPW₁₁O₄₀ solid (This can be determined by IR spectra of the fatty acid methyl ester).

In addition, the nature of $(C_{16}TA)H_4TiPW_{11}O_{40}$ in the inversemicellar reaction system had been tested. The test had been performed as following: (C₁₆TA)H₄TiPW₁₁O₄₀ was contacted with palmitic acid at 65 °C (without methanol) during 60 min and afterwards the solid was separated from liquid phase by an ultrafiltration membrane; then, to the liquid phase, methanol was added and the reaction was monitored during 5 h at 65 °C. The conversion was only 13.6%. From the result, $(C_{16}TA)H_4TiPW_{11}O_{40}$ is confirmed as heterogeneous one. To test for leaching, the catalyst was filtered after a reaction time of 90 min (ca. 66.17% ester conversion) and the filtrate reacted further 6 h at the same temperature of 65 °C. From the results, it can be seen that the conversion only 66.84%, which shows a very slight leaching of [C₁₆TA]H₄TiPW₁₁O₄₀. The UV spectrum of the mixture exhibited two absorption bands at 222 nm and 260 nm, which are attributed to the Keggin structure. The total amount of [C₁₆TA] H₄TiPW₁₁O₄₀ leaching through six runs of the reaction reached 1.93% of the starting amount of $[C_{16}TA]H_4TiPW_{11}O_{40}$, showing that the leaching amount of $(C_{16}TA)H_4TiPW_{11}O_{40}$ is little.

4. Conclusion

In this paper, we investigated the optimum reaction conditions for $(C_{16}TA)H_4TiPW_{11}O_{40}$ catalyzing esterification of palmitic acid.

The optimum reaction parameters were found to be molar ratio of methanol/acid/catalyst 4856:243:1, 65 °C and reaction time of 6 h. The maximum conversion was 94.7% under this reaction conditions. The catalyst showed high activity because of double acid sites, amphiphilic property and water-tolerant property. This micellar HPA catalyst could be used as a heterogeneous acid catalyst for esterification of fatty acid.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2012.01.014.

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