

Esterification of oleic acid to biodiesel over a 12-phosphotungstic acid-based solid catalyst

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Abstract: A 12-phosphotungstic acid (PTA)-based esterification catalyst was prepared by modifying PTA with 1,2,3-triazaole-4,5-dicarboxylic acid (TDA). The obtained TDA-PTA sample was characterized with XRD, IR, SEM, TG and potentiometric titration techniques, and its catalytic properties for esterification of oleic acid with methanol were studied. In addition, the effects of reaction conditions, including catalyst amount, oleic acid/alcohol molar ratio, reaction time and reaction temperature, on its catalytic performance were investigated. After modification with TDA, although the Keggin structure of PTA is kept and the sample shows strong acidity, the particle morphology changes to regular spheres. In particular, the sample exhibits high catalytic activity and stability in esterification of oleic acid with methanol. The modification of PTA by TDA effectively prevents PTA from dissolving in the reaction mixture, and thus, the TDA-PTA can be recycled at least six runs without severe loss of catalytic activity, showing that it is a good heterogeneous catalyst for esterification.

Key words: heteropoly acid; solid acid; catalysis; esterification; oleic acid

Catalyst can greatly accelerate the reaction and promote selective formation of target product. Different types of reactions need different catalysts. In many heterogeneous reactions, phase-transfer catalysts are required. Heterogeneous catalyst can be easily separated from reaction mixture, and may be reused. Thus, it makes the homogeneous organic reactions environmentally benign and economically feasible. Therefore, it attracts many persons' interest from both academic and industrial fields^[1,2].

The esterification of free fatty acid with alcohol is one of the most typical and direct way to synthesize biodiesel, which is an alternative to fossil fuels^[3–5]. For the esterification, the key issue is to select a highly active and stable catalyst. In terms of the reaction mechanism, feasible catalysts mainly include enzymes, alkalis, acids and so on^[5–8]. However, enzymes are not widely used because of its high cost. Alkali easily reacts with grease, losing the catalyst^[6–8]. For acid such as sulfuric acid, although it gives high product yield, its homogeneous feature and strong acidity cause serious corrosion of equipment and it difficult to be recycled^[9–11]. Comprehensively considered, heterogeneous acid catalyst would be the most appropriate choice for esterification reactions^[12].

In this context, heteropoly acids (HPAs) with Keggin structure have drawn much attention in some fields because of its strong acidity and high thermal stability^[13,14]. However, HPAs have low surface area and are difficult to be separated from polar solutions^[5,15]. Thus, many heterogeneous HPAs-based catalysts have been developed through “immobilization” or “solidification”^[16]. The HPAs can be supported on molecular sieves and high-surface area materials, e.g. SBA-15, SiO₂ and ZrO₂^[17–19]. The proton in HPAs can be partially or totally substituted by other cations such as K⁺, Cs⁺ and Ag⁺ to give HPAs salts^[5,15]. In addition, some ionic liquid (ILs)-based HPAs have been demonstrated to be powerful for the esterification^[16,20].

All the above-mentioned HPAs-based heterogeneous catalysts effectively compensate the disadvantages of parent HPAs. For example, its surface area was increased, and it became easily separated from the reaction mixture and could be reused. Later, heterocyclic-modified HPAs were prepared. It was found that the complex was well maintained in the catalyst in polar reaction system such as epoxidation system^[15]. In such reaction systems, heterocycles play an important role in not only decrease of the solubility of HPAs in polar solutions but also increase of the catalytic activity and

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selectivity. This may be attributed to the strong electronic interaction between heterocycles and terminal tungsten-oxygen on HPAs^[15].

In our previous work, a heterogeneous PTA-based complex was prepared by reacting PTA with picolinic acid in water solution. The obtained sample has a higher surface area than PTA and can be recycled after being filtered out from the reaction mixture. However, the thermal stability decreases. Therefore, 1,2,3-triazole-4,5-dicarboxylic acid was selected here to modify PTA, and the obtained material not only maintains the advantages of picolinic acid-modified PTA, but also shows high thermal stability. Moreover, it exhibits excellent catalytic activity for esterification of free fatty acid with short-chain alcohols, which is a key step for synthesis of biodiesel.

1 Experimental

1.1 Catalyst preparation

All the used chemicals are of A.R. grade, and were used as received without further pretreatment. 1,2,3-Triazole-4,5-dicarboxylic acid (TDA) and 12-phosphotungstic acid (PTA) were purchased from Camolai Trading Company and Aladdin Industrial Corporation, respectively. At room temperature, TDA aqueous solution (0.002 mol TDA in 10 mL distilled water) was slowly dropped into the PTA solution (0.002 mol PTA in 25 mL distilled water) under vigorous stirring condition. After that, it was continuously stirred for 12 h. Finally, the white precipitate was filtered and dried at 100°C. The obtained sample was designed as TDA-PTA.

1.2 Catalyst characterization

Powder XRD patterns in the 2θ range of 5°–60° were recorded at speed of 4(°)/min on an X-ray diffractometer (Bruker AXS GmbH, D8 Advance) at a step size of 0.04°.

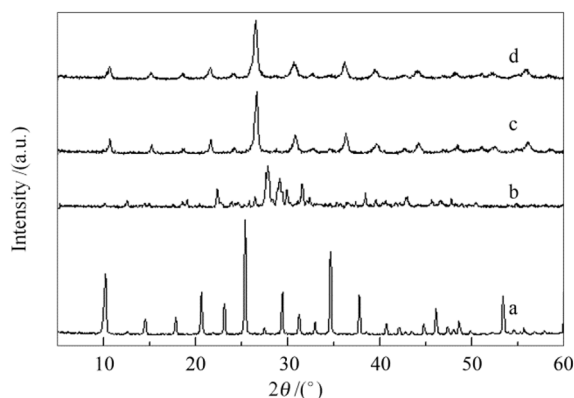


Fig. 1 XRD patterns of PTA (a), TDA (b), TDA-PTA (c) and used TDA-PTA (d)

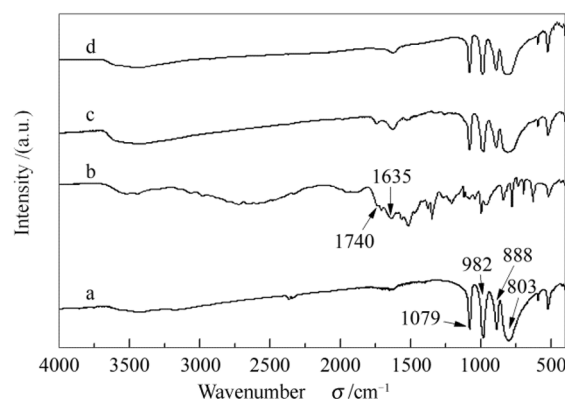


Fig. 2 FT-IR spectra of PTA (a), TDA (b), TDA-PTA (c) and used TDA-PTA (d)

Fourier transform infrared (FT-IR) spectrum of the sample was obtained in the range of 4000–400 cm^{-1} on a FT-IR spectrometer (Thermo Nicolet Corp., 6700) using KBr method.

The acidity of the sample in methanol solution was measured by the potentiometric titration method using a pH composite electrode. The sample (0.05 g) was suspended in methanol (15 mL) and agitated for 1 h. Then, the suspension was titrated with a solution of 0.05 mol/L *n*-butylamine in acetonitrile.

TG analyses were performed on a thermogravimetric analyzer (Netzsch-Gerätebau GmbH, STA449). About 5 mg solid sample was heated to 600°C at the rate of 10°C/min.

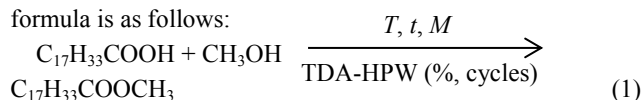
The sample morphology was investigated by a scanning electron microscope (SEM, JEOL Ltd., JSM6380LV).

The particle size distribution of the sample was measured in a DTS0012 polystyrol/polystyrene küvetten cuvette (10 mm × 10 mm × 45 mm) by a nano-particle size analyzer (Malvern Instruments Ltd., Zetasizer Nano ZSP). Before measured, the sample was ultrasonically dispersed in ethanol.

The Brunauer-Emmett-Teller (BET) surface area was measured using a physical adsorption instrument (Micromeritics Instrument Corp., ASAP2010) at –196°C. Prior to the measurement, the sample was degassed at 100°C for 3 h under high vacuum condition.

1.3 Catalytic test

The catalytic properties of the TDA-PTA for esterification was carried out in a 25 mL gas-tight batch reactor equipped with a magnetic stirrer and an oil bath for controlling the reaction temperature. In a typical batch, 0.07 g TDA-PTA (5% of oleic acid), 5 mmol oleic acid (1.41 g) and 40 mmol methanol (1.28 g) were added in the reactor. The reaction formula is as follows:



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