Homogeneous borotungstic acid and heterogeneous micellar borotungstic acid catalysts for biodiesel production by esterification of free fatty acid

CrossMark

Zhong Sun [a,1], *Xixin Duan* [a,1], *Jing Zhao* [a,1], *Xiaohong Wang* [a,*], *Zijiang Jiang* [b,**]

[a] *Key Lab of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun 130024, PR China*
[b] *Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*

ARTICLE INFO

ABSTRACT

A highly negatively charged borotungstic acid $H_5BW_{12}O_{40}$ had been tested as homogeneous catalyst in esterification. Compared with common used $H_3PW_{12}O_{40}$, it displayed a higher conversion (98.7%) and excellent efficiency (96.2%) due to its high amount of protons in methanol. In order to overcome the drawbacks of homogeneous heteropolyacid $H_5BW_{12}O_{40}$, a Brønsted-surfactant-combined $(C_{16}TA)H_4BW_{12}O_{40}$ ($C_{16}TA$ = cetyltrimethyl ammonium) had been fabricated with strong acidity and nano-size micellar structure resulting in enhanced activity and stability during the reaction, which exhibited consistent activity during recycling in esterification reaction.

1. Introduction

With the problem of the shortness of fossil fuels and the environmental pollution becoming more and more serious, the development of alternative clean energy has attracted much attention. Fatty acid alkyl esters (FAAEs) named as biodiesel is a green and potential alternative fuel due to its biodegradability and renewability [1]. The routine procedure for producing biodiesel is esterificating free fatty acids (FFAs) and transesterificating triglycerides such as vegetable oil or animal fats [2–4] with short chain alcohols such as methanol. Esterification of FFAs is a key procedure for producing biodiesel, because the existence of FFAs in feedstocks influences the performance of the base catalysts [5,6]. As an advantageous alternative method, heterogeneous acid-catalyzed

processes can be applied to produce biodiesel directly from low-cost raw materials and high amount of FFAs. Fatty acids should be previously converted into FAAEs through esterification with short chain alcohols by acid catalysts. By now, many approaches involving acid catalysis have been developed [7,8]. Among these, heteropolyacids (HPAs) and their salts have been reported as promising catalysts for esterification reactions [9–12]. Many heteropolyacids such as Keggin-type HPAs $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ are strong Brønsted acids and of great interest as acid catalysts, which had been applied in esterification and transesterification reactions [13]. However, the acid catalytic activity of $H_3PW_{12}O_{40}$ was not high enough to efficiently convert FFAs into biodiesel. It is known that the acidic catalytic activity depends on the dissociation of protons in HPAs. In this concept, borotungstic acid $H_5BW_{12}O_{40}$ (HBW) has attracted much attention in acidic catalytic reactions due to its highly negative charges with five protons in saccharification of cellulose [14]. To the best of our knowledge, there is no study on the catalytic performance of $H_5BW_{12}O_{40}$ in esterification reaction. As the continuation of our work, we tried our best to study the catalytic activity of Keggin-type heteropolyacids $H_5BW_{12}O_{40}$ in order to develop a new HPA species for further application. Meanwhile, $H_5BW_{12}O_{40}$ is homogeneous existed the separating problems in esterification facing. Therefore, we used the surfactant hexadecyltrimethylammonium bromide (CTAB) as building blocks to fabricate a Brønsted-surfactant-combined heteropolyacid $(C_{16}TA)H_4BW_{12}O_{40}$. $(C_{16}TA)H_4BW_{12}O_{40}$ displayed a hydrophilic head $H_4BW_{12}O_{40}$ and hydrophobic tail $C_{16}TA$, which could act as a heterogeneous acidic catalyst and also provide hydrophobic surroundings resulting in high catalytic activity and more water-tolerance in esterification of FFAs. So far, there is no report in the literature on the application of Brønsted-surfactant-combined HBW in esterification reactions. A series of borotungstic acids and borotungstates had been prepared and were tested for esterification of FFAs with methanol, focusing on the different conversion of FFAs with homogeneous and heterogeneous catalysts. Our results suggest that the HPAs with different components give different FFA conversions corresponding to their acidic strengths in methanol. $H_5BW_{12}O_{40}$ can make a significant enhancement in the conversion of FFAs compared to $H_3PW_{12}O_{40}$. Moreover, the fabrication of Brønsted-surfactant-combined HBW results in highly efficient heterogeneous catalysts in esterification reactions compared to homogeneous $H_5BW_{12}O_{40}$.

2. Methods

2.1. Material and reagent

All chemicals were obtained from commercial suppliers. They were of AR grade and used without further purification.

2.2. Preparation of catalysts

$K_5BW_{12}O_{40}$ was prepared according to Ref [15]. The pure $H_5BW_{12}O_{40}$ was prepared by H^+ replacement of K^+ using cation exchange resins and was recrystallized twice by water with 57 wt % mass yield, and was identified by IR spectroscopy and ICP-AES. $(C_{16}TA)H_4BW_{12}O_{40}$ was prepared as following: (20 cm^{-3}, 1 mol $\cdot$ m^{-3}) hexadecyltrimethylammonium bromide (CTAB) aqueous solution was added into (20 cm^{-3}, mol $\cdot$ m^{-3}) $H_5BW_{12}O_{40}$ solution with stirring. Immediately the white precipitate formed and collected by filtration then calcined at 100 °C for 3 h. The crude product was purified by recrystallized with CH_3CN, then the mass yield of the obtained $(C_{16}TA)H_4BW_{12}O_{40}$ was about 50 wt%.

FTIR spectra (4000–500 cm^{-1}) were recorded in KBr 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 Kα 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. ^{11}B NMR spectra was recorded on a Bruker AVANCE III 400 MB spectrometer equipped with a 4 mm standard bore CPMAS probe head whose X channel was tuned to 162 and 100.62 MHz, respectively. The CMC of $(C_{16}TA)H_4BW_{12}O_{40}$ was determined by break points of two nearly straight-line portions of the specific conductivity versus concentration plot [16].

In order to determine the acid strength of the HPAs, the Hammett constants (H_0) in methanol was studied. The color intensity of the mixture was measured in a Cary 500 UV/Vis/NIR spectrophotometer at 380 nm [21].

2.3. Esterification reaction

The esterification of palmitic acid with methanol was carried out in a 100 cm^3 three-necked round bottomed flask with mechanical stirring at atmospheric pressure and 338 K. In a typical experiment, 5.12 g of palmitic acid, 7.9 cm^3 of anhydrous methanol and catalyst in it were vigorously stirred and refluxed for the some time. For homogeneous $H_5BW_{12}O_{40}$, after the reaction, the mixture was rotary evaporated at 50 °C to separate the excessive methanol, then the mixture formed two phases. The upper layer was methyl esters of palmitic acid and the lower layer was the catalyst with small amount of water. Then the upper layer was evaporated by water bath in 60 °C. For the heterogeneous $(C_{16}TA)H_4BW_{12}O_{40}$, after the reaction the catalyst was decanted at the bottom of the reactor and separated from the mixture by centrifugation, and washed with methanol to remove the polar compounds. Then product was dried in the air for reuse. The conversion of ester was calculated by measuring the acid value of the product and the yield was detected by gas chromatography (GC).

The yield of monoester was determined on Shimazu GC-14C fitted with an HP-INNOWAX capillary column and flame ionization detector and HP-INNOWAX capillary column (30 m × 0.32 mm; 0.50 μm film). 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.