



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Efficient and reusable polyoxometalate-based sulfonated ionic liquid catalysts for palmitic acid esterification to biodiesel

Xiao-Xiang Han^{a,*}, Yan-Fei He^a, Chin-Te Hung^b, Li-Li Liu^b, Shing-Jong Huang^c, Shang-Bin Liu^b^a Department of Applied Chemistry, Zhejiang Gongshang University, Hangzhou 310035, China^b Institute of Atomic and Molecular Sciences, Academic Sinica, Taipei 10617, Taiwan^c Instrumentation Center, National Taiwan University, Taipei 10617, Taiwan

HIGHLIGHTS

- Several polyoxometalate-based sulfonated ionic liquid catalysts were synthesized and characterized.
- Significant operating parameters in biodiesel production were studied and optimized by RSM.
- Better superacidity and lower molecular transport resistance of catalysts were responsible for superior catalytic efficiency.
- The catalyst presented high efficiency, convenient recovery and steady reuse.

ARTICLE INFO

Article history:

Received 20 December 2012

Received in revised form

10 March 2013

Accepted 28 August 2013

Available online 6 September 2013

Keywords:

Polyoxometalate

Phosphotungstic acid

Fuel

Catalytic activation

Reaction engineering

Optimization

ABSTRACT

Fabrication of polyoxometalate-based sulfonated ionic liquid catalysts was achieved by combining phosphotungstic acid (HPW) and SO₃H-functionalized zwitterion ionic complex. The obtained composite materials were well characterized by FT-IR, TG, ¹H NMR, ¹³C NMR and ³¹P MAS-NMR and investigated their performance as catalyst for esterification reactions of palmitic acid to biodiesel. Response surface methodology (RSM) was applied to optimize esterification of palmitic acid with ethanol by [MIM-PSH]_{2.0}HPW₁₂O₄₀. The effects of various reaction conditions, including ethanol/acid molar ratio, the amount of ionic liquid and reaction time were addressed by Box–Behnken experimental design (BBD). The variance (ANOVA) analysis showed that the reaction time and amount of catalyst were the most significant parameters. And the effect of interaction between the ethanol/acid molar ratio and reaction time was also the most significant parameter affecting the conversion of palmitic acid. The coefficient of determination of this model was 0.9754. The optimum reaction conditions were established as follows: ethanol/acid molar ratio of 13, amount of catalyst of 7%, reaction time of 5 h at 80 °C and got a maximum yield of biodiesel of 91.8%. The [MIM-PSH]_{2.0}HPW₁₂O₄₀ ionic liquid could be reused six times without noticeable drop in activity. Under optimum conditions, catalysts showed a superior catalytic efficiency and reusability due to better superacidity and lower molecular transport resistance.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Esters from esterification have gained more attention due to their wide applications in plasticizers, plastic derivatives, perfumes and flavor chemicals. Furthermore, they can also be used as the precursors for agrochemicals, fine chemicals and pharmaceuticals (Yadav and Thathagar, 2002; Alípio et al., 2009). The most important and valuable product obtained by esterification of long chain fatty acids is biodiesel (Anastasia et al., 2010; Bruno et al.,

2012), which has several advantages, such as biodegradability, low viscosity, good miscibility with fossil diesel under any proportions as fuels for conventional diesel engines without further modifications.

Esterification of free fatty acids (FFAs) to alkyl esters in the presence of a catalyst is a route to improve biodiesel production from high FFA oils. The esterification was conventionally carried out by mineral acids, such as H₂SO₄, HF and H₃PO₄ as the homogeneous acid catalysts with a high conversion rate. However, additional neutralization and separation steps are mandatory (Haas et al., 2003). Other issues such as corrosiveness, unfavorable byproducts, environmental hazards, and the difficulty in catalyst recovery and reuse (He et al., 2008) also obscure the large-scale

* Corresponding author. Tel.: +86 571 88071024x7581.

E-mail addresses: hxx74@126.com, han-xx74@163.com (X.-X. Han).

production of biodiesels using homogeneous acid catalysts from high FFA oils. The extensive attempts to search desirable heterogeneous acid catalysts as replacements for liquid acids in such reactions still encountered problems of product selectivity, environmental safety, spent catalyst disposal and catalyst recyclability (Feng et al., 2010; Kouzu et al., 2008).

Ionic liquids (ILs) could be regarded as green solvents/catalysts substituting the conventional counterparts for their adjustable physical and chemical properties, good thermal stability and reusability (Chowdhury et al., 2007; Wu et al., 2012). Heteropolyacids (HPAs) mentioned in this study also have been used in numerous organic reactions as catalysts due to their unique redox and acidic properties (Dai et al., 2010). However, their low surface areas ($< 10 \text{ m}^2/\text{g}$) highly reduce the efficiency of interior active sites during reactions. This drawback can be improved by dispersion of HPAs on porous solid carriers and better catalytic performances in heterogeneous reaction applications have been reported (Nazmul and Sung, 2012; Alsalmeh et al., 2008; Xiang et al., 2011). Nevertheless the novel organic–inorganic hybrid design of HPAs–base catalysts to further improve the high mass transfer resistance is still favorable (Misono, 2005). In this context, the novel heteropolyacid–base IL salts have been proposed as the catalysts for esterification and promising results were reported (Leng et al., 2009a; Zhang et al., 2009).

In this study, we synthesized and characterized a series of Keggin tungstophosphoric acid (TPAs)–base IL salts prepared via combining TPA with propane sulfonated IL with different composition ratios. Furthermore, the catalytic activities of these materials for the esterification of palmitic acid to biodiesel were also investigated and the optimum conditions were established using response surface methodology (RSM).

2. Methods

2.1. Preparation and characterization of organic TPA salt catalysts

The organic TPAs ionic liquids were synthesized in the laboratory following the procedure described in literature (Zhang et al., 2009; Leng et al., 2009b) and the detailed preparations were as follows: methylimidazole (8.2 g, 0.10 mol) and 1,3-propanesultone (12.2 g, 0.10 mol) were dissolved in ethyl acetate (30 mL) under ice bath and stirred at 50°C for 2 h. After solidification, the zwitterion 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS) was formed and washed by ethyl acetate for three times, then dried under vacuum.

The zwitterion MIM-PS was added to the aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 12\text{H}_2\text{O}$. The mixture was stirred at 90°C for 24 h. The final product was obtained after removing the water and washing the solid by diethyl ether. Then the solid was dried under vacuum. A series of organic TPA salts were obtained and named as $[\text{MIM-PSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ in which x meant the molar ratio of PS/TPA changing from 1.0 to 3. All the chemicals were analytical pure and were used without further purification unless otherwise stated.

2.2. Characterizations of catalysts

FT-IR spectra for samples in KBr disks were recorded on Bruker IFS28 spectrometer. Thermogravimetric and differential thermogravimetric (TG-DTG) curves were obtained on a TG209 (NETZSCH) thermal analyzer. Samples were heated from room temperature to 600°C at a heating rate of $10 \text{ K}/\text{min}$ under flowing air. The catalysts were measured by ^1H and ^{13}C NMR spectroscopy using Bruker AV500 spectrometer in D_2O . Solid-state ^{31}P NMR experiments were carried out on a Bruker AVANCE III 500 spectrometer using a 4-mm double-resonance MAS probe head.

The Larmor frequencies for ^{31}P is 202.46 MHz. Spectra were acquired using a single-pulse sequence under a sample spinning rate of 12 kHz. The excitation pulse for ^{31}P was $1.5 (\pi/6)$ and the recycle delay was 10.0 s. The chemical shifts of P were referenced to a 85% phosphoric acid solution as 0 ppm.

The acid properties of various catalysts were characterized by solid-state ^{31}P NMR of adsorbed trimethylphosphine oxide (TMPO). Prior to the adsorption of TMPO probe molecule, catalyst was first subjected to a thorough dehydration treatment at 120°C for 12 h under vacuum ($< 10^{-5}$ Torr). Subsequently, a known amount of TMPO dissolved in anhydrous CH_2Cl_2 was introduced into a vessel containing the dehydrated solid sample in a N_2 glove box, followed by removal of the CH_2Cl_2 solvent by evacuation at 50°C . To ensure a uniform adsorption of adsorbate probe molecules in the pores/channels of the porous adsorbents, the sealed sample vessel was further subjected to thermal treatment at 120°C for at least 24 h. Finally, the sealed sample vessel was placed in a N_2 glove box where the TMPO-loaded sample was transferred into a MAS rotor and then sealed by a gas-tight Kel-F cap.

2.3. Catalytic testing

The esterification reactions were carried out in a 100 mL three-necked flask equipped with a dropping funnel including 3 A mesoporous molecular sieves for removing the water of system with reflux condenser. The procedure was as follows: palmitic acid (7.68 g, 0.03 mol), ethanol (16.56 g, 0.36 mol) and catalyst (0.46 g) were added. The reaction mixture was heated to reflux (about 80°C) for desired time in the oil bath. The mixture was then cooled to the room temperature and the catalyst was separated from the mixture. The catalyst was washed by diethyl ether for reuse. Chemical analysis of the products was performed by gas chromatography (Agilent 6890N GC), equipped with a FID detector and HP-5 capillary column. Reactants and products were identified by comparison with authentic samples. Methyl laurate was used as internal standard. The final acidity was determined by titration with sodium hydroxide.

The conversion of palmitic acid was calculated by the formula:

$$\text{Conversion} = (1 - a_1/a_2) \times 100\%$$

where a_1 was the initial acidity of the mixture and a_2 was the acidity of the mixture at the end of experiment.

2.4. Experimental design and mathematical model

The optimum conditions for the synthesis of ethyl palmitate using loaded TPAs ionic liquid as catalyst were determined by means of response surface methodology. A Box–Behnken experimental design (BBD) (Kok et al., 2010; Han and Zhou, 2011) was chosen to value the relationship between yield of biodiesel with reactant ratio, amount of ionic liquid and time. 17 sets of experiments (12 factorial points and 5 center points) were performed according to a 3^3 Box–Behnken experimental design. The three variables were tested at the three levels by associated plus signs (+1) with high levels, zero (0) indicating center value and minus signs (−1) with low levels. The coded values of these factors were obtained according to Eq. (1) as follows:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (1)$$

where x_i was the independent variable coded value, X_i was the independent variable real value, X_0 was the independent variable real value at the center point, and ΔX_i was (variable at high level – variable at low level)/2. The independent variables and their levels, real values were presented in Table 1a.

Download English Version:

<https://daneshyari.com/en/article/6591444>

Download Persian Version:

<https://daneshyari.com/article/6591444>

[Daneshyari.com](https://daneshyari.com)