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Immobilized phosphotungstic acid based ionic liquid: Application for heterogeneous esterification of palmitic acid

Yongqiang Wang[a], Dan Zhao[a], Lulu Wang[a], Xianqin Wang[a], Lujun Li[a], Zhongpeng Xing[b], Na Ji[a], Shejiang Liu[a], Hui Ding[a,*]

[a] School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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ABSTRACT

For biodiesel production from waste oils, the esterification pretreatment process is now recognized as one of the most important approaches to convert free fatty acids for improving the quality of waste oils. In this paper, before immobilizing, three environmentally friendly acid ionic liquids were selected to conduct the immobilization. 1-(3-sulfonate)-propyl-3-allylimidazolium hydrogen sulfate, trifluoromethanesulfonate and dihydrogen phosphotungstate ionic liquids were prepared and characterized by NMR. All the three ionic liquids had the capacity to catalyze esterification of palmitic acid with yields of more than 98%. Therefore, the ionic liquids were supported on functionalized SBA-15 by thiol-ene click reaction. The immobilized ionic liquids were characterized by SEM, FTIR, NMR, XRF, and BET. Because of the strong acidity of phosphotungstic acid and the high loading rate (41.2%), 1-(3-sulfonate)-propyl-3-allylimidazolium phosphotungstate supported ionic liquid was proved to possess the highest catalytic performance which gave a 88.1% esterification yield after 8 h when the reaction temperature, methanol to acid molar ratio and catalyst dosage were 65 °C, 9 and 15 wt%, respectively. In addition, the supported ionic liquid could be reused for 5 times without significant deactivation.

1. Introduction

The environmental and energy issues caused by excessive combustion of fossil fuels have aroused widely attentions among researchers, and the renewable resources such as sunlight, wind and biomass are encouraged to be developed [1]. Among the renewable resources, biodiesel is a mixture of different kind of fatty acid esters, and can be employed as substitute for traditional diesel [2]. Compared with fossil fuels, biodiesel is renewable and producing less CO and particulate matter [3–5]. Therefore, application of biofuels which contain certain amount of biodiesel can be regarded as a crucial solution to tackle with the environmental and energy issues.

Transesterification of triglyceride catalyzed by base or acid catalysts is the most important reaction to prepare biodiesel [6]. Besides, waste oils with high acid value which contain large amount of free fatty acids (FFA) are promising raw materials to produce biodiesel because of the low cost [7,8]. Normally, base catalysts are more efficient than acid catalysts for transesterification. However, while base catalysts are directly employed to waste oils with high acid value, the fatty acid salts have to be removed for biodiesel purification [9]. Thus, great efforts directed towards the development of acid catalysts have been made to catalyze esterification and transesterification simultaneously. Unfortunately, homogeneous acid catalysts such as sulphuric acid suffer problems of equipment corrosion, harmful waste emission and inconvenient recycling [10,11]. While solid acid catalyzed transesterification always requires a high reaction temperature and pressure, an esterification pretreatment was proposed to convert the free fatty acids before conducting the alkali-catalyzed transesterification [12].

Therefore, several novel solid acid catalysts have been developed to conduct the esterification of different fatty acids and overcome the disadvantages of traditional homogeneous acid catalysts [13,14]. For example, supported ionic liquids (SILs) [15–17] or poly(ionic liquid)s (PILs) [18,19] that inherit catalytic abilities and environmentally friendly feature from homogeneous ionic liquids [20] have been reported to perform the esterification pretreatment. And heteropolyacid (HPA) based catalysts such as heteropolytungstate salts and supported heteropolyacid catalysts have been proposed to harness the excellent catalytic performance of heteropolyacid [21]. However, the deactivation of supported HPA should be overcome to prolong their life. Therefore, immobilization conducted through stable chemical bonds is worthy of attempt to avoid the leaching or deactivation of HPA. According to the environmentally friendly feature of ionic liquids and high

* Corresponding author.
E-mail address: dinghui@tju.edu.cn (H. Ding).

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reaction activity of HPA, covalent combination of ionic liquids and HPA was conducted to combine their advantages for esterification pretreatment.

In the present work, 1-(3-sulfonate)-propyl-3-allylimidazolium hydrogen sulfate (IL-1), trifluoromethanesulfonate (IL-2) and dihydrogen phosphotungstate (IL-3) ionic liquids were firstly prepared and characterized by NMR. And a task-specific immobilized ionic liquid catalyst (SIL-3) was prepared by supporting dihydrogen phosphotungstate ionic liquid (IL-3) onto SBA-15 through covalent bonds. Besides, the catalytic activities of supported IL-1 (SIL-1) and IL-2 (SIL-2) were compared with the performance of SIL-3. Afterwards, ^{31}P NMR, FTIR, BET, SEM and XRF were employed to characterize the support and catalysts. And the effects of some reaction conditions on biodiesel or esterification yield were also investigated.

2. Experiment

2.1. Materials

Methyl palmitate standard was purchased from Innochem Scientific & Technology Co. (Beijing, China), and the purity was 99% according to the manufacturer. 1-allylimidazole, trifluoromethanesulfonic acid and palmitic acid (purity 98%) were purchased from SiCheng Chemical Co. (Jiaxing, China). 1,3-propanesultone and phosphotungstic acid (PTA) were analytical grade and obtained from HWRK Chemical Co. (Beijing, China) and Molbase Biotechnology Co. (Shanghai, China), respectively. 3-mercaptopropyltrimethoxysilane (KH-590, purity 97%), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO–PPO–PEO) block copolymers (P123, purity 98%, average M.W. 5800) and ethyl orthosilicate (TEOS, purity 98%) were purchased from J&K Scientific Co. (Beijing, China). All other solvents and chemicals were purchased from Jiangtian Chemical Reagents Co. (Tianjin, China) and were analytical grade.

2.2. Preparation approaches

SBA-15 was prepared according to the approach reported in the literature [22,23]. For modification of SBA-15 support, 2 g of SBA-15 was firstly dispersed in toluene, and 1 g of KH-590 was slowly added to the suspension. Then, the suspension was stirred at 110 °C for 8 h in N_2 atmosphere. After the modification, the mixture was filtered and the modified SBA-15 was washed three times with ethanol to remove the residual solvent and KH-590. Finally, the obtained white solid was dried at 60 °C under vacuum for 12 h to form thiol-group functionalized SBA-15 (SBA-SH).

For preparation of ionic liquids, a two-step method was employed. 1-allylimidazole (0.1 mol) was firstly dissolved in acetonitrile (100 ml) which was placed in an ice bath, and 1,3-propanesultone (0.1 mol) was slowly added to the solution. Then, the solution was stirred at 40 °C for 24 h in N_2 atmosphere, and the produced white solid was collected and washed three times with acetonitrile to remove the unreacted materials. The solid was dried at 60 °C under vacuum for 12 h to form 1-(3-sulfonate)-propyl-3-allylimidazolium zwitterion. A stoichiometric amount of concentrated sulfuric acid or trifluoromethanesulfonic acid was slowly added to the zwitterion. The mixture was heated gradually to 80 °C and magnetically stirred for 24 h to form yellow viscous ionic liquid (IL-1 or IL-2). And the obtained hot ionic liquid was washed three times with diethyl ether and dried at 40 °C under vacuum for 12 h.

Preparation of 1-(3-sulfonate)-propyl-3-allylimidazolium dihydrogen phosphotungstate (IL-3) was slightly different from the method stated above. A stoichiometric amount of PTA was mixed with the zwitterion (2 mmol) and dissolved in 10 ml of water. The solution was stirred at 80 °C for 24 h and dried at 60 °C under vacuum for 12 h to remove water. Finally, the obtained silvery solid (IL-3) was washed three times with diethyl ether and dried at 40 °C under vacuum for 3 h.

The modification and immobilization process was presented in Fig. 1. Specifically, to 10 ml of methanol with a temperature of about 40 °C, IL-1, IL-2 (6 mmol) or IL-3 (2 mmol) was dissolved. And then, SBA-SH (2 g) was dispersed in the solution. The thiol-ene reaction was conducted by thermal initiation at 60 °C for 12 h, and AIBN was employed as initiator with a dosage of 0.12 mmol. Afterwards, the suspension was filtered and the obtained solid was washed three times with methanol. And supported ionic liquids SIL-1, SIL-2 and SIL-3 were obtained by drying the precipitate at 60 °C under vacuum for 3 h.

Meanwhile, SBA@IL-3 was also prepared by impregnation according to the approach reported in the literature [24] with an immobilization rate of about 40%. And a difference was that the support employed in the present work was the modified SBA-SH for comparing with SIL-3.

2.3. Characterization methods

Surface areas were calculated through the BET equation and conducted by multi-point BET method. Fourier transform infrared (FT-IR) spectra were obtained using a Bruker ALPHA FT-IR spectrometer. Scanning electron microscopy (SEM) images were obtained on a Hitachi S4800 scanning electron microscope. Main elements contents of the catalysts were determined by X ray fluorescence (XRF) spectrometry on a Bruker S4 Pioneer instrument. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were acquired with a Bruker AVANCE III 500 MHz spectrometer. ^{31}P CP-MAS NMR spectra were recorded on Varian Infinity-plus 300 MHz spectrometer.

2.4. Biodiesel preparation over ILs and SILs catalysts

A round-bottom flask, an attached reflux condenser and a magnetic stirrer were used to conduct the esterification of palmitic acid with methanol, and the diagram of the facility was presented in the supporting information. A water bath kettle was employed to heat the reaction system while the temperature of water bath was stably controlled by a thermocouple. And the stirring rate was maintained at 800 r/min. Catalyst, palmitic acid and methanol were added to the flask successively, and the reaction temperature was maintained at 65 °C for a controlled reaction time.

After the reaction and centrifugation, the lower layer was collected while ILs were employed as catalysts, and the upper layer was analyzed by gas chromatography. For esterification catalyzed by SILs, catalysts were separated from the mixture through centrifugation for recycling. And the reaction products were analyzed by Lunan GC-2060 gas chromatography with a PC-88 capillary column (length: 60 m, internal diameter: 0.25 mm, film thickness: 0.20 μm). In addition, internal standard method was employed to analyze the products precisely while dimethyl carbonate (DMC) was selected to be the internal standard.

3. Results and discussion

3.1. Characterizations

^{1}H NMR and ^{13}C NMR spectra were commonly used approaches to analyze molecular structures of ionic liquids and prove that ionic liquids were successfully prepared. Besides, ^{31}P NMR spectra were also conducted to investigate IL-3 and PTA. The NMR data were listed as follows.

Zwitterion: ^{1}H NMR (400 MHz, CD_3OD) δ: 2.27–2.41 (m, J = 7.2 Hz 2H), 2.83 (t, J = 7.6 Hz, 2H), 4.46 (t, J = 7.2 Hz, 2H), 4.84–4.91 (d, J = 6.3 Hz 2H), 5.4–5.52 (m, J = 9.2, 1.0 Hz, 2H), 6.04–6.19 (m, J = 6.7 Hz, 1H), 7.63 (t, 1H), 7.74 (t, J = 1.8 Hz 1H), 9.04 (s, J = 1.8 Hz 1H). ^{13}C NMR (400 MHz, CD_3OD) δ: 25.68, 47.39, 47.94, 51.48, 120.54, 122.43, 122.61, 130.60, 136.31.

IL-1: ^{1}H NMR (400 MHz, CD_3OD) δ: 2.29–2.44 (m, J = 7.2 Hz 2H), 2.90 (t, J = 7.6 Hz, 2H), 4.47 (t, J = 7.2 Hz, 2H), 4.87–4.93 (d, J = 6.3 Hz 2H), 5.39–5.51 (m, J = 9.2, 1.0 Hz, 2H), 5.82 (s, 2H),