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Full Length Article

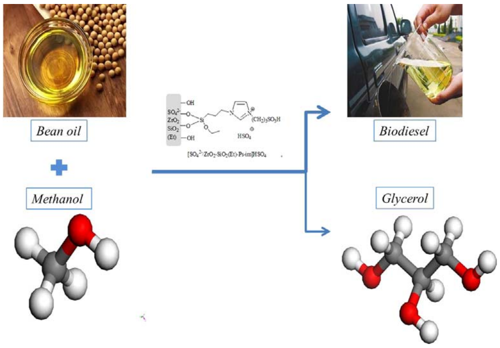
Ionic liquid on the acidic organic-inorganic hybrid mesoporous material with good acid-water resistance for biodiesel production

Mingming Fan*, Hui Liu, Pingbo Zhang*

School of Chemical and Material Engineering, Jiangnan University, Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, Wuxi 214122, China

GRAPHICAL ABSTRACT

The immobilized catalyst SO_4^{2-}/ZrO_2-SiO_2(Et)-IL with double-acid acitive sites behaved better in the transesterification for biodiesel production. Not only the ionic liquid of catalysts which provided Brønsted acid sites, but also the supporter which contained Brønsted and Lewis acid sites made joint efforts to the efficiency of the reaction.



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ABSTRACT

Different amounts of acidic ionic liquid sulfonic acid functionalized imidazolium hydrogen sulfate ([Ps-im] HSO_4) were immobilized on the acidic organic-inorganic hybrid mesoporous material SO_4^{2-}/ZrO_2-SiO_2(Et) by the chemical grafting. The structure of the catalyst was characterized by FT-IR, XRD, N_2 absorption–desorption measurement, XPS and TG. The results showed that the ethane-bridge organosilica moieties were incorporated into the framework of SO_4^{2-}/ZrO_2, enhancing the acidity of SO_4^{2-}/ZrO_2-SiO_2(Et) with respect to SO_4^{2-}/ZrO_2. Meanwhile, the ionic liquid was successfully immobilized onto the acidic mesoporous materials SO_4^{2-}/ZrO_2-SiO_2(Et) and with the increase of ionic liquid loading, the BET surface areas and the pore volumes decreased and the average pore diameters increased. SO_4^{2-}/ZrO_2-SiO_2(Et)-IL-*i* were very efficient in the transesterification of soybean oil with methanol and gave an approximate 99% biodiesel yield when the reaction was carried out at 150 °C with a 5 wt% catalyst amount at 18:1 methanol/oil molar ratio for 3.0 h. And they not only own the abilities of water and acid resistance, but also maintain satisfactory catalytic activity after five runs.

1. Introduction

Biodiesel, as a promising biomass energy to replace conventional fossil fuels, has a prefect market prospect because of its environmental-friendliness and renewable biomass capacity [1,2]. Biodiesel is a mixture of C_{12}-C_{22} fatty acid monoalkyl esters which are prepared from acid- or base-catalyzed transesterification of animal fats or plant oils with a short-chain alcohol, such as methanol, ethanol or other alcohols

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* Corresponding authors.
E-mail addresses: fanmm2000@126.com (M. Fan), pingbozhang@126.com (P. Zhang).

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[3,4]. Biodiesel had many good properties superior to petroleum-derived diesel such as environment protection properties. Biodiesel was a biodegradable and environmentally beneficially that can be used in diesel engines and heating systems with low harmful emission. And it could also give a substantial improvement in fuel lubricity, reducing wear on fuel injection components and raising engine life etc [5]. Therefore, biodiesel would replace the petroleum-based fuel gradually. For example, Europe produced more than 2.7 million tones biodiesel in 2003 and planed to make the about 20% total diesel market come true in 2020 [6]. Currently, biodiesel produced from edible oil feedstock contributed more than 95% of total biodiesel production, rapeseed oil (84%), sunflower oil (13%) and others (3%), which inevitably raised many problems, such as food versus fuel crisis, soil resources destruction etc. Thus, non-edible oils resources were gaining more and more worldwide attention [7].

Of the various raw materials for the synthesis of biodiesel, the low-cost feedstocks, such as waste oil and non-edible, are widely used in industry [8,9]. However, less-expensive feedstocks contain high percentage of water or free fatty acid and may be a major hindrance to produce biodiesel catalyzed by an alkali, due to the hydrolysis and saponification reactions will reduce the yield of biodiesel and increase the costs of purification [10,11]. Generally, the problems can be circumvented by refining the raw materials, but the higher costs come with it. Acid catalysts, including homogeneous and heterogeneous, can catalyze the esterification of free fatty acid and transesterification of triglycerides simultaneously and are insensitive to water. Therefore, acid catalysts can be more suitable for the production of biodiesel from waste oils. Traditionally homogeneous acid catalysts (p-toluene sulfonic acid, sulfonic acid etc.) are widely applied in industrial production of biodiesel because of their high catalytic activity and the cheap price [12–15]. Environmental pollution, corrosiveness and difficult recovery are the disadvantages of these catalysts. The use of heterogeneous acid catalysts eliminates corrosion while solving environmental and recovery problems, although the process is much slower due to the large mass-transfer resistance and rapid deactivation from coking [16–18]. Hence, new types of heterogeneous acid catalysts with efficient and low-cost appear to be an area worthy of investigation.

Supported ionic liquids catalysts (SILs), with catalytic amount of ionic liquids immobilized on the surface of solid carriers, combine the merits of homogeneous catalysts that the ionic liquid films on carriers provide high catalytic activity and heterogeneous catalysts in terms of their recovery and easy separation, which are considered as promising green catalysts [12,19,20]. Impregnation, sol-gel and grafting are usually applied to fix ionic liquids on the solid supporters. And the supported ionic liquids catalysts which prepared by grafting own the properties of high thermal stability and excellent catalytic activity, and can avoid ionic liquids washing away efficiently. The common carriers are inorganic carriers (silica gel, SBA-15, etc.) and organic carriers (phenolic resin, PDVB, etc.) [20–24].

The surface of organic carriers possess many active groups which can hold more ionic liquids on it, but the mechanical strength, thermal stability and structure of the pore are poor [24,25]. Inorganic carriers such as silicon-containing mesoporous materials have the advantage of excellent pore structure and strong mechanical strength, but the number of functional groups is limited and leads to the low loading of ionic liquid as well as low catalytic activity [22,26]. In order to compensate for the shortcomings of their, the organic-inorganic hybrid mesoporous material (SO_4^{2-}/ZrO_2-SiO_2(Et)) with acidic active sites is prepared by incorporating organic functional into structure of inorganic siliceous mesoporous material. The acidic sites of the material can make up the defect of less active groups on the inorganic silicon material and the organic-inorganic components are good for the contact between the hydrophilic reactant (alcohols) and the hydrophobic reactant (oils). Acidic ionic liquid functionalized on the material can obtain SILs with high efficiency and excellent structure.

In this work, The SILs with double-acid active sites, namely Brønsted and Lewis acid sites, were synthesized by immobilization of different dosage of acid ionic liquid sulfonic acid functionalized imidazolium hydrogen sulfate ([Ps-im]HSO_4) onto the acidic mesoporous material SO_4^{2-}/ZrO_2-SiO_2(Et) which was prepared by a one-step co-condensation technique combined with hydrothermal treatment. Characterization methods were applied to analyze the structure and properties of the catalysts. The catalytic activities were investigated by the transesterification of soybean oil with methanol for biodiesel production as the probe reaction.

2. Experimental

2.1. Chemical reagents

Pluronic F127 ($EO_{106}PO_{60}EO_{106}$, $M_W = 12600$, where EO = $-CH_2CH_2O-$, PO = $-CH_2(CH_3)CHO-$, Sigma-Aldrich). Zr(*n*-OBu)$_4$ (80% in *n*-butanol), 1,3-Propane sultone (99%) and 1,2-bis-(triethoxysilyl)ethane (BTEE, AR) were purchased from Macklin (Shanghai) and used without further purification. Soybean oil (CP) was obtained from Macklin (Shanghai), and was analyzed before the initiation of the transesterification reaction at the preliminary stage, exhibited acid value = 0.47 mg KOH/g, saponification index = 192.75 mg KOH/g, and average molecular weight = 875.24 g/mol, viscosity = 61.8 mm^2/s and density = 0.919 g/mL at 25 °C. Soybean oil was dried by sodium sulfate before use. And other chemicals were commercially available and used without further purification unless otherwise state.

2.2. Catalysts preparation

2.2.1. Synthesis of SO_4^{2-}/ZrO_2-SiO_2(Et)

One-step co-condensation technique combined with hydrothermal treatment was applied to the preparation of SO_4^{2-}/ZrO_2-SiO_2(Et) [5,27]. P123 (1 g) was dissolved in HCl (58 mL, 2 mol·L^{-1}) under vigorous stirring at 40 °C for 1 h. After that, 1,3,5-Trimethylbenzene (4.6 mL) was added dropwise and continuous stirred for another 2 h. Subsequently, BTEE, Zr(*n*-OBu)$_4$ and $(NH_4)_2SO_4$ were added dropwise at hourly intervals. The molar ratio of Zr/Si/S in the starting material was 1/1/1.2. After homogenizing the mixture at 40 °C for 24 h, the suspension was transferred into an autoclave and aged at 100 °C for another 24 h. Finally, the product was filtered and washed with deionized water and boiling ethanol. The final product obtained after being dried at 80 °C for 12 h and denoted as SO_4^{2-}/ZrO_2-SiO_2 (Et).

2.2.2. Synthesis of SO_4^{2-}/ZrO_2-SiO_2(Et)-IL-*i*

SO_4^{2-}/ZrO_2-SiO_2(Et)-IL-*i* was synthesized in four steps, the process is shown in Scheme 1 [28]. First, (3-chloropropy)triethoxysilane was used to modify the material of SO_4^{2-}/ZrO_2-SiO_2(Et) [29]. A mixture of SO_4^{2-}/ZrO_2-SiO_2(Et) (1 g) with (3-chloropropy)triethoxysilane (0.625, 1.25, 2.5, 3.75, and 5 mmol) in dry toluene (15 mL) were prepared and stirred at 90 °C for 24 h. After that, the reaction mixture was cooled, and the product was filtered and washed with toluene, dichloromethane, and diethyl ether in turn and dried at 100 °C for 12 h to produce SO_4^{2-}/ZrO_2-SiO_2(Et)-$(CH_2)_3$Cl-*i* (*i* = 1, 2, 3, 4, 5). Second, the product obtained from the last step and imidazole (0.625, 1.25, 2.5, 3.75, and 5 mmol) were added in dry toluene (15 mL). The mixture was stirred at 90 °C for 24 h. And the product ([SO_4^{2-}/ZrO_2-SiO_2(Et)-im-*i*] (*i* = 1, 2, 3, 4, 5) was obtained after being disposed in the same way with the last step to get SO_4^{2-}/ZrO_2-SiO_2(Et)-$(CH_2)_3$Cl-*i*. Third, [SO_4^{2-}/ZrO_2-SiO_2(Et)-im-*i*] (all product obtained from the last step) was suspended in dry toluene (15 mL) and 1,3-propane sultone (0.625, 1.25, 2.5, 3.75, and 5 mmol) was added to it. The mixture was allowed to stir at 90 °C for 24 h. After the same treatment, [SO_4^{2-}/ZrO_2-SiO_2(Et)-Ps-im-*i*] (*i* = 1, 2, 3, 4, 5) was obtained. Finally, [SO_4^{2-}/ZrO_2-SiO_2(Et)-Ps-im-*i*] was suspended in dry CH_2Cl_2 (15 mL). During vigorous stirring, concentrated H_2SO_4 (98%) (0.625, 1.25, 2.5, 3.75, and 5 mmol) was added