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Heterogenization of ionic liquid based on mesoporous material as magnetically recyclable catalyst for biodiesel production

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ABSTRACT

To develop green and reusable catalysts for the biodiesel preparation, a novel magnetically separable nanocatalyst was fabricated by covalent bonding of 3-sulfopropyl-1-(3-propyltrimethoxysilane) imidazolium hydrogen sulfate ([SO_3H-PIM-TMSP]HSO_4) on mesoporous silica modified Fe_3O_4 nanoparticle. The catalyst possessed uniform core-shell structure with magnetic response core and Brønsted ionic liquid functionalized mesoporous silica shell. The multifunctional catalyst also exhibited appealing physicochemical features like high specific surface area, mesoporous channel, magnetic response, and fine catalytic activity in esterification of oleic acid with alcohol. Under mind conditions, the conversion of oleic acid was up to 93.5%. The catalyst exhibited recyclable property based on magnetism and the separation of the catalyst would be simply using external magnetic field without obvious mass loss, allowing a clean biodiesel product.

1. Introduction

Biodiesel has been a modern and technological area due to the relevance to environmental benefits and the increasing in the petroleum price. As an alternative diesel fuel derived from vegetable oils, animal fats, and microalgae etc., biodiesel is biodegradable, renewable, and nontoxic, having low emission profiles [1,2]. Generally, both of the transesterification of triglycerides (TGs) with alkaline catalysts and esterification of free fatty acids (FFAs) with acidic catalysts can be applied to prepare biodiesel. But alkaline catalysts require anhydrous conditions and feed stocks with low levels of FFAs to avoid saponification [3]. In that situation, many approaches involving acid catalysis have been developed [4]. Specially, heterogeneous acid catalysts have played the important role for green and recyclable catalysts [5,6].

Recently, ionic liquid has become a new eco-benign approach toward modern chemistry, having found applications in a wide range of areas, including catalysis, synthesis, analysis, and gas absorption, etc., [7], especially those functionalized with Lewis and/or Brønsted acid sites [8,9]. The ionic liquid, with the properties of flexibility, non-volatility, non-corrosivity, and immiscibility with many organic solvents, can afford higher yields and selectivities with potential application in replacing conventionally homogeneous/heterogeneous acid catalysts [10]. It has been reported that esterification of oleic acid can be catalyzed by functionalized ionic liquid with satisfied yield [11,12]. However, several drawbacks like unsuitable viscosity, tedious separation procedures, and large dosage in catalysis, hamper their widespread applications. As separation and recycle of catalysts are critically required to reduce the cost of catalysts as well as to avoid the generation of waste, it requires the heterogenization of ionic liquid [13]. Based on the facts that the chemical and structural versatility of ionic liquid make them potential guest molecule candidates for the post-functionalization of solid materials [14], supported ionic liquid (SIL) is prepared by immobilizing IL on solid material [15,16]. The supported ionic liquid has better performance in many fields, with the merits of both homogeneous ionic liquid and heterogeneous solid materials [17,18].

To develop efficient and recyclable catalysts, nano-magnetite has been developed as a new support with the properties of easy synthesis and functionalization, facile separation by magnetic force [19,20]. At the same time, ordered mesoporous materials have been widely used in adsorption, separation, catalysis, etc., due to the unique properties and functionalities [21]. Thus the introduction of magnetic nanoparticles in mesoporous materials realizes the combination of ionic liquid heterogenization with techniques

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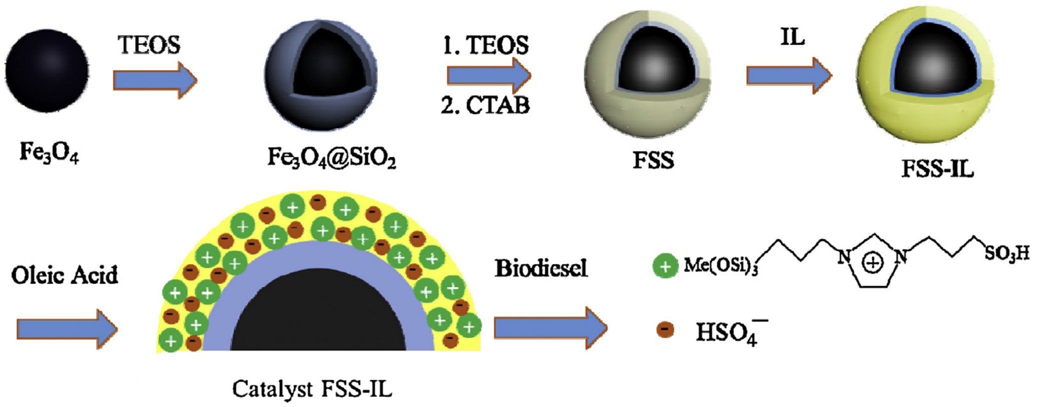

Fig. 1. The schematic representation of the synthetic route of FSS–IL and the application in esterification of oleic acid for biodiesel production.

for magnetic separation [22,23]. Magnetite-supported ionic liquid catalysts are an important and growing arena in heterogeneous catalysis, having been successfully applied in numerous important reactions [24,25].

In this work, we design and prepare a magnetic mesoporous material Fe_3O_4@SiO_2@mSiO_2 (FSS) supported ionic liquid [SO_3H-PIM-TMSP]HSO_4 (IL) catalyst, defined as FSS–IL, for biodiesel production. Magnetic mesoporous support FSS is fabricated with super magnetic Fe_3O_4 nanoparticle as core and silica layers as shells. The inner silica layer of FSS acts as the surface protector and the outer mesoporous silica shell works as the support, which benefits the diffusion of guest molecules and improves mass transfer. The catalyst is systematically characterized and applied in heterogeneous catalytic esterification of oleic acid, allowing a clean biodiesel product and easy catalyst removal from the reaction mixture under magnetic force.

2. Material and methods

2.1. Material and instruments

Ethylene glycol, ethanol, imidazole, sulfuric acid, anhydrous $FeCl_3$, toluene, 1,3-propane sultone, cetyltrimethylammonium bromide (CTAB), sodium acetate anhydrous, sodium citrate, ethyl silicate (TEOS), γ-chloropropyltrimethoxysilane (CPMS), oleic acid (85%), diethyl ether, ammonium hydroxide were commercially available and were used without further purification unless otherwise stated.

Scanning electron microscopy (SEM) images were gained by a S4800 Field-emission scanning electron Microscope (HITACHI, Japan). Transmission electron microscopy (TEM) images were taken with a JEM-2100 (HR) (JEOL, Japan), and the samples were daubed onto carbon film supported on copper grids for analysis. X-ray diffraction (XRD) patterns were recorded on a Smartlab diffractometer (RIGAKU, Japan). Fourier-transform infrared (FT-IR) spectra were measured by a Nicolet-6700 spectrometer (Thermo Fisher Scientific, United States) using anhydrous KBr as dispersing agent. N_2 adsorption–desorption measurements were carried out on a Micromeritics ASAP 2020 system model instrument. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) algorithm. The mesoporous pore size distribution was obtained through the Barrett–Joyner–Halenda (BJH) theory. The magnetic hysteresis loops were measured by a lakeshore 7407 vibrating sample magnetometer (China Trend Limited, China).

2.2. Catalyst preparation

Brønsted ionic liquid 1-(propyl-3-sulfonate)-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate [SO_3H-PIM-TMSP][HSO_4] was prepared referring to the previous published article [26]: imidazole (0.05 mol) was dissolved in ethanol and equimolar sodium ethylate was added afterwards. The reaction was carried out at 348 K for 12 h. 3-Chloropropyltrimethoxysilane (0.05 mol) was added dropwise and the mixture was stirred for another 12 h in N_2 atmosphere. After the generated sodium chloride was removed, 1,3-propane sultone (0.05 mol) was added and stirred at 323 K for 12 h. Sulfuric acid (0.05 mol) was added, reacting at the same temperature for 6 h. [SO_3H-PIM-TMSP][HSO_4] was achieved by washing with diethyl ether and drying under vacuum.

The magnetic Fe_3O_4 microspheres were synthesized by a solvothermal reaction [27]. By the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the mixture of water, ethanol and ammonia, individual Fe_3O_4 microsphere was coated with uniform silica layer, generating Fe_3O_4@SiO_2 microsphere. With TEOS as silica source and cetyltrimethylammonium bromide (CTAB) as structure-directing agent, a CTAB/silica composite layer was formed on the surface of Fe_3O_4@SiO_2 microsphere. Magnetic FSS mesoporous microspheres were gained after CTAB was removed [28].

The catalyst FSS–IL was prepared as following. IL (1.5 g) and FSS (1.0 g) was dissolved in dry toluene (50 ml). The mixture was heated to reflux for 24 h in N_2 atmosphere. FSS–IL catalyst was obtained after washing with diethyl ether and drying in vacuum at 323 K for 8 h. The total synthetic route of FSS–IL was represented in Fig. 1.

2.3. Catalytic activity measurement

Biodiesel production from oleic acid with alcohol was carried out with FSS–IL as catalyst. In a typical run, oleic acid (10 mmol), alcohol (60 mmol), and catalyst (0.2 g) were added in a flask (50 ml) and kept under 373 K for 4 h. When the reaction was finished, a magnet was put at the bottom of the reaction flask and the catalyst would be totally adsorbed to the magnet. The upper layer was dumped out for analysis and the yield of biodiesel was calculated based on oleic acid referring to previous publication [11]. The left catalyst was washed with acetone for three times, setting in vacuum at 323 K for 6 h for recycling experiment. The recovered catalyst was also weighted by electronic balance ($d = 0.0001$ g) for calculating catalyst mass loss data.

3. Results and discussion

3.1. Catalyst characterization

According to the SEM/TEM images, the FSS particle (Fig. 2a) exhibited good monodispersity and uniform spherical morphology.