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Short communication

Basic ionic liquid immobilized oxides as heterogeneous catalyst for biodiesel synthesis from waste cooking oil

Jian Sun, Jingyi Yang *, Shaoping Li, Xinru Xu

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, PR China

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ABSTRACT

The basic ionic liquid (IL) [Bmin]OH was synthesized and immobilized onto oxide surface to obtain IL/Mg-Al and IL/Mg-Al-La catalysts. The catalysts were characterized by FT-IR, XRD, EDS, BET and basic test. The results proved that the IL immobilized oxides exhibited high activity for biodiesel synthesis from waste cooking oil. The high FAME yield of 98.7% could be obtained at 338 K, 12:1 methanol to oil, 3 wt% catalyst amount and 6 h reaction time by IL/Mg-Al-La catalysts.

1. Introduction

Biodiesel has received extensive interest because of its biodegradable, nontoxic and renewable properties. The transesterification of the unrefined inedible oil even waste cooking oil is considered to be an economical method of biodiesel production [1,2]. However, the high amounts of free fatty acids in raw oil decrease the activity of common catalysts. Therefore, the modified alkali and acid catalysts [3,4], two-step transesterification process [5] and ionic liquid [6,7] were reported for biodiesel production from waste cooking oil.

Recently, ionic liquids are widely investigated as catalytic medium because of their interesting properties, such as low melting temperature, negligible vapor pressure, low toxicity, excellent thermal stability and good solubility for most organic and inorganic compounds [8]. Generally, ionic liquids were researched as catalysts or efficient solvent for biodiesel production [9,10]. Most of ionic liquids exhibited high activity and excellent stability for transesterification [11], expressly acidic ionic liquids for esterification [12,13]. Because of good miscibility, ionic liquids were mostly used as green solvent in enzymatic transesterification of vegetable oil [14,15]. However, the homogeneous transesterification in ionic liquids are restricted by high viscosity, large consumption and separation problems [16]. It was reported that ionic liquids immobilization process was an appropriate method to address above problems [17,18]. The ionic liquids immobilized catalysts could be used as heterogeneous catalysts in terms of easy separation and recovery [19]. Some researchers have reported several supports for immobilization such as magnetic nanoparticle [20], metal oxide [21], molecular sieve [22], polystyrene [23] and silica [24].

In this paper, the basic IL with imidazolium cation was synthesized and immobilized onto oxides surface for transesterification. The obtained catalysts were characterized by FT-IR, XRD, NMR, EDS, BET and basic test. The catalytic activity and recyclability in transesterification of waste cooking oil and methanol were investigated.

2. Experimental

2.1. Catalyst preparation

The basic IL [Bmin]OH with imidazolium cation and basic anion was prepared [25]. 0.5 mol 1-methylimidazole was added in a glass reactor with condenser and stirrer. When the reactor reached 333 K, 0.55 mol 1-bromobutane was added dropwise into the glass reactor. After 24 h reaction at 333 K, colorless viscous liquid was obtained. The crude product [Bmin]Br was washed with ethyl acetate and subsequently dried at 353 K in vacuum oven for 12 h. Methylene chloride solution containing sodium hydroxide was mixed with above intermediate [Bmin]Br under constant stirring at 293 K for 12 h. The target product 1-butyl-3-methylimidazolium hydroxide ([Bmin]OH) was obtained after separation, washing and drying processes. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.58 (s, 1H), 6.36 (d, $J = 7.5$ Hz, 1H), 6.26 (d, $J = 7.5$ Hz, 1H), 5.01 (t, $J = 7.7$ Hz, 2H), 3.29 (s, 3H), 2.93 (bs, 1H), 2.01 (p, $J = 7.8$ Hz, 2H), 1.35 (h, $J = 7.9$ Hz, 2H), 0.87 (t, $J = 8.0$ Hz, 3H). IR: 3424, 3156, 3086, 2977, 2930, 2884, 1574, 1457, 1410, 1338, 1160 cm^{-1}.

The supports were prepared from hydrotalcite precursors according to our previous work [26]. The [Bmim]OH (1.50 g) and support (5.00 g) were mixed together in 50 mL dry toluene solution. The mixture was

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* Corresponding author.
E-mail address: jyyang@ecust.edu.cn (J. Yang).

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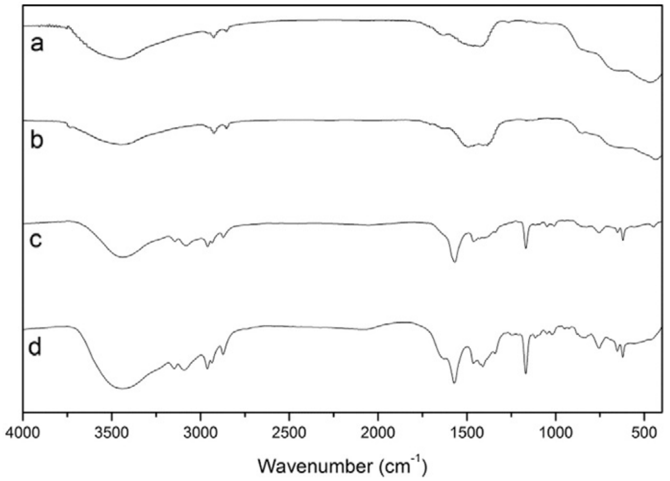

Fig. 1. FT-IR spectra of Mg-Al (a), Mg-Al-La (b), IL/Mg-Al (c) and IL/Mg-Al-La (d) catalysts.

stirred at room temperature and refluxed under nitrogen protection for 24 h. After filtration, the mixture was washed with ethyl acetate several times and dried at 353 K in vacuum oven for 12 h to obtain IL immobilized catalysts IL/Mg-Al and IL/Mg-Al-La samples.

2.2. Characterization method of catalyst

Fourier transform infrared (FT-IR) spectra were measured by Nicolet Magna-IR 550 instrument using KBr pellet technique and recorded in a range of 4000–400 cm^{-1}. ^{1}H NMR spectrum was determined by Bruker Avance 500 spectrometer using TMS as internal standard and CDCl$_3$ as the solvent. X-ray diffraction (XRD) patterns were carried out on Rigaku D/max 2550 VB/PC diffractometer operating with CuKα radiation($\lambda = 1.5406$ Å), at 100 mA, 45 kV, 2 θ scanning range 10–80° and a step size of 0.02° (2 θ). Surface elemental compositions of catalysts were determined by Edax Falcon energy dispersive spectrometer (EDS). Surface area and pore size distribution of catalysts were measured by BET method and BJH method on Micromeritics ASAP-2400. The basic strength of catalysts was qualitatively assessed using Hammett indicators by matching color change. The used Hammett indicators included bromthymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.8$), 2.4-dinitroaniline ($H\_ = 15.0$) and4-nitroaniline($H\_ = 18.4$). The basicity of catalysts was measured using Hammett indicator-benzene-carboxylic acid titration [27].

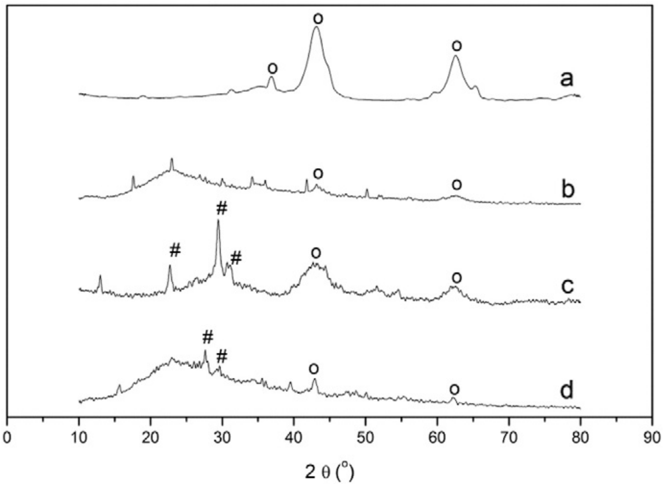

Fig. 2. XRD patterns of Mg-Al (a), IL/Mg-Al (b), Mg-Al-La (c) and IL/Mg-Al-La (d) catalysts.

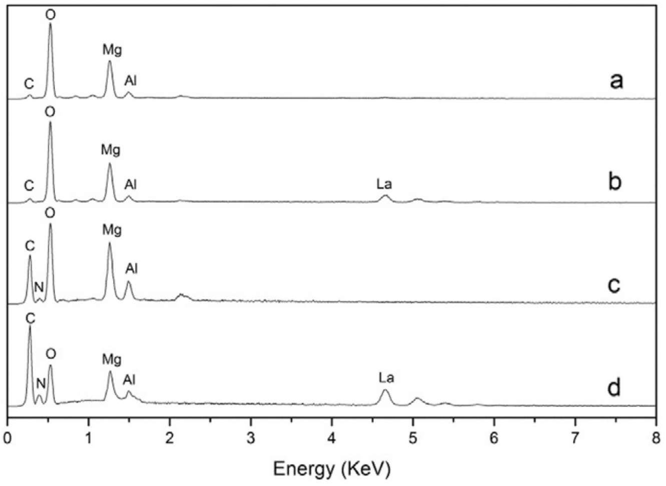

Fig. 3. EDS spectra of Mg-Al (a), Mg-Al-La (b), IL/Mg-Al (c) and IL/Mg-Al-La (d) catalysts.

2.3. Transesterification procedures

A certain amount of raw oil, anhydrous methanol and catalysts were added to a glass reactor with condenser and magnetic stirring. After a certain reaction time, the product was filtered and stratified. The upper layer product was extracted, weighed and analyzed by gas chromatograph (Jinghe GC-7860), equipped with phenyl-methyl-polysiloxane capillary column, flame ionization detector according to EN 14103. A known amount of methyl heptadecanoate was added as internal standard to determine the fatty acid methyl ester (FAME) in products. The absolute difference between two independent single test results was less than 1.6%.

3. Results and discussion

3.1. Catalyst characterization

The FT-IR spectra of Mg-Al, Mg-Al-La, IL/Mg-Al and IL/Mg-Al-La catalysts are shown in Fig. 1. For oxide supports, the broad band at 3470 cm^{-1} could be assigned to ν_{OH} stretching vibration of hydroxyl group attached to metal cations. The bands at 1430 cm^{-1} could be attributed to C—O bonds in carbonates [27]. For IL immobilized catalysts, the characteristic bands of [Bmim]OH appeared in the spectrums of IL/Mg-Al and IL/Mg-Al-La catalysts. The broad band at 3440 cm^{-1} could be assigned to the ν_{OH} stretching vibration of functionalized basic hydroxyl group. The bands at 3150 and 3090 cm^{-1} could be ascribed to stretching vibration of unsaturated C—H bonds in imidazole ring. The bands at 2960, 2930 and 2880 cm^{-1} could be ascribed to stretching vibration of saturated C—H bonds in branch chain. The sharp bands at 1570, 1460, 1410, 1340 and 1160 cm^{-1} corresponded to C═N bonds and C—C bonds of imidazole ring [17,20]. The result indicated that the homogeneous IL was successfully immobilized onto the supports surface.

The XRD patterns of Mg-Al, Mg-Al-La, IL/Mg-Al and IL/Mg-Al-La catalysts are shown in Fig. 2. The support Mg-Al oxide (a) displayed the

Table 1
Textural characterization of catalysts.

Samples	BET surface area (m^2/g)	Pore size (nm)
Mg-Al	82	21.9
Mg-Al-La	53	21.0
IL/Mg-Al	36	17.5
IL/Mg-Al-La	30	13.3