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Catalytic performance of a novel amphiphilic alkaline ionic liquid for biodiesel production: Influence of basicity and conductivity

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ABSTRACT

Three novel alkaline guanidine ionic liquids as amphiphilic catalysts have been successfully synthesized for two-phase transesterification, which can efficiently improve the catalytic activity for the synthesis of biodiesel. They were characterized by a series of techniques including ^{1}H NMR, thermal stability, electronegativity (DFT calculation), basicity and conductivity. It was demonstrated that 1,1,3,3-trimethyl-2-octyl-guanidine hydroxide(IL3) exhibited better catalytic activity compared with other base guanidine ionic liquid catalysts, which was related to the better basicity and electronegativity of the ILs. The experimental results indicated that catalytic performance was relative to both enough alkaline center and conductivity of ionic liquid catalysts, but the former was a main factor in the catalytic system. The catalytic performance also revealed that optimum catalyst dosage was about 6 wt.%, the appropriate reaction temperature was about 55 °C, the optimum n(Methanol)/n(Soybean Oil) for the biodiesel synthesis was about 15:1 and the suitable reaction time was 4 h on the basis of biodiesel yield of 97%. In addition, the reaction mechanism of the amphiphilic catalyst was illuminated by the interaction between the methoxyl group and the carbonyl group of the triglyceride after activating for two-phase transesterification.

1. Introduction

For the growing shortage of non-renewable resources such as fossil fuels, alternative renewable energy sources have recently attracted significant attention [1,2]. Biodiesel (fatty acid methyl esters) is an attractive alternative due to its renewability, biodegradability and non-toxicity, which is produced by transesterification of triglycerides and methanol [3,4]. And it also has better lubricity, which could be mixed with petroleum diesel [5–7]. Hence, biodiesel has gained more attention recently.

The development of novel catalysts is the key of the field in order to improve the yield of biodiesel. Traditional homogeneous catalysts were harmful to production equipments and environment, such as strong acid (H_2SO_4) or alkali (NaOH, KOH). Several new heterogeneous catalyst systems had been developed for biodiesel synthesis, such as solid base catalysts KOH/Al_2O_3 and KOH/NaY [8], cinder supported K_2CO_3 [9], KOH/bentonite [10], modified CaO catalysts [11], KF/CaO [12], KF/CaO–MgO [13] and so on; solid acid catalysts $Al(HSO_4)_3$ [14], glucose starch mixture composed of $CS_{0.073}O_{0.541}$ [15], $Mg_{1-x}Zn_{1+x}O_2$ [16] and so on.

Recent years, the ionic liquids (ILs) have been used as catalysts with high-density active sites, so they are widely used in the transesterification. ILs can be divided into different categories depending on the acid-base property, including acidic ionic liquids and basic ionic liquids. Recently, the acidic ionic liquids have been widely applied in the synthesis of biodiesel. For example, Long-chain Brønsted acid ionic liquid was used as catalyst for synthesis of biodiesel [17,18], Ammonium, pyridinium, imidazolium, and phosphonium-based Lewis and Brønsted acid sites ionic liquids have been found extensive applications in biodiesel fields [19–25]. Although acidic ionic liquids have good catalytic activity, its reaction condition is rigorous. Higher temperature and pressure for acid ionic liquids is necessary, which limits the development of the industry. However, less research has been done on basic ionic liquids. Because the reaction condition of basic ionic liquids is relatively mild, basic ionic liquids have been gradually concerned by researches. Xiao et al. used superhydrophobic porous solid basic ionic liquids as catalysts for transesterification [26]. However, most reports were mainly based on the investigation of activity and

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optimization of reaction conditions. To the best our knowledge, no studies have been reported on the influence of alkalinity and conductivity on catalytic activity.

In this study, the influence of alkalinity and conductivity on catalytic activity was demonstrated. We successfully developed several basic ionic liquid catalysts based on 1, 1, 3, 3-Tetramethylguanidine (TMG) prepared for biodiesel production. For alkali active center of ionic liquid, the differences of several catalysts was investigated by the alkalinity and electronegativity analysis. The impact of electronegativity about the modified group was compared through the calculation with Gaussian software. Then the optimum condition of the better catalyst for biodiesel synthesis from soybean oil was investigated. We put forward the feasible reaction mechanism based on the amphipathicity of the ionic liquids.

2. Experimental

2.1. Materials and equipment

1,1,3,3-Tetramethylguanidine (98%), bromopropylene (98%), 1-Bromopropane (≥98%), 1-Bromooctane (≥98%), Ethyl Alcohol, Acetonitrile, Potassium Hydroxide were purchased from Sinopharm Chemical Reagent Co, Ltd (SCRC) and used as received. Soybean oil was obtained from the local market. These ILs were prepared as indicated in Scheme 1. Transesterification reaction was carried out in the presence of ILs according to Scheme 2. The structure of the IL was verified by ^{1}H NMR spectroscopy (Bruker AVANCE III 400 MHz) (Scheme 3). The electrical conductivity was investigated by the conductivity meter (DD-307, Shanghai Leici analysis instrument factory). The thermal stability was studied by the thermogravimetric analyzer (TGA/DSC1/1100 SF, Switzerland Mettler Toledo Company). Samples between 5 mg and 10 mg were heated from 25 to 500 °C under N_2 atmosphere and constant heating at 10 °C/min. The geometries and the electronegativity were calculated at density functional theory (DFT) level on a personal computer using Gaussian-03 package using B3LYP/6-31G (d, p) basis set (Fig. 1).

2.2. Catalyst preparation and characterization

IL was prepared by the following reported method with minor modification [27]. Bromopropylene (0.025 mol, 3.03 g) was slowly added into a solution of 1, 1, 3, 3-Tetramethylguanidine (0.02 mol, 2.30 g) in acetonitrile (25 ml) in a stand-up flask, and stirred at 60 °C for 24 h. The mixture was then cooled down to room temperature. Functionalized guanidinium bromides were acquired after washing with ether and drying in vacuum at room temperature for one day, to obtain ionic liquid precursor Guanidine bromine salt.

Compound 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H, N–H), 6.16–5.47 (m, 1H, =CH$^-$), 5.34 (d, 2H, =CH_2), 3.86 (d, J = 18.9 Hz, 2H, –$CH_2$$^-$), 3.09 (s, 12H, –$CH_3$).

Compound 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H, N–H), 3.10 (t, 2H, –$CH_2$$^-$), 2.99 (s, 12H, –$CH_3$), 1.65 (m, 2H, –$CH_2$$^-$), 0.82 (t, 3H, –$CH_3$).

Compound 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H, N–H), 3.13 (t, 2H, CH_2–N=C), 3.02 (s, 12H, CH_3–N), 1.67 (m, 2H, CH_2–CH_2–N=C), 1.22 (m, 10H, CH_2–CH_2), 0.80 (m, 3H, CH_3–CH_2).

Then, KOH (0.02 mol, 1.12 g) was added into a solution of Guanidine bromine salt in Ethanol (25 ml) in a stand-up flask and stirred at room temperature for 24 h. After that the white solid KBr was filtered to get pale yellow solution and the solvent was evaporated under vacuum to leave the yellow IL1.

According to the above method, IL2 and IL3 were also synthesized.

2.3. Catalytic tests and biodiesel analytical methods

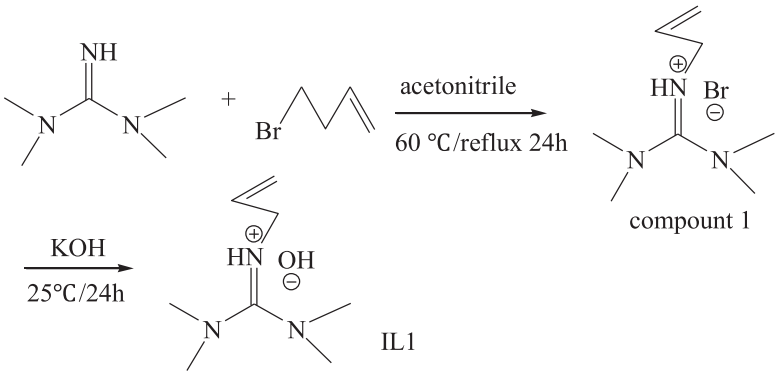
Dehydrated soybean oil (8.71 g), methanol (4.80 g), and IL catalyst (0.5226 g, 6wt% oil) were mixed in 50 mL stand-up flask and heated to 55 °C for 4 h under stirring with a constant speed. After the reaction, the reaction mixture was then cooled to room temperature and two phases were formed.

The samples were analyzed by an FULI GC9790 gas chromatograph, equipped with a flame ionization detector (FID) and SE-54 capillary column. Nitrogen was used as carrier gas. The oven program was set to an initial temperature of 50 °C (held for 4 min), increasing to 220 °C at a rate of 15 °C min^{-1}, after increasing to 260 °C at a rate of 5 °C min^{-1}, where the temperature was held for 3 min. The temperatures of injector and interface were both held constant at 300 °C. The internal standard method was used with methyl salicylate as internal standard for determinating the yield of biodiesel.

3. Results and discussion

3.1. Preliminary properties of soybean oil

The soybean oil was analyzed at the preliminary stage before the transesterification reaction, the results exhibited saponification index = 193.68 mg KOH/g, acid value = 0.49 mg KOH/g. The experimental calculation showed average molecular weight = 871.16 g/mol, density = 0.921 g/mL and viscosity = 62.0 mm^2/s at 25 °C [28,29].



Scheme 1. Synthesis of IL1.