

Available at www.sciencedirect.com<http://www.elsevier.com/locate/biombioe>

Preparation, characterization and application of heterogeneous solid base catalyst for biodiesel production from soybean oil

Yihuai Li^a, Fengxian Qiu^{a,*}, Dongya Yang^a, Xiaohua Li^b, Ping Sun^b

^aSchool of Chemistry and Chemical Engineering, Jiangsu University, Xuefu Road 301, 212013 Zhenjiang, PR China

^bJiangsu Provincial Key Laboratory of Power Machinery and Application of Clean Energy, 212013 Zhenjiang, PR China

ARTICLE INFO

Article history:

Received 24 September 2010

Received in revised form

22 February 2011

Accepted 4 March 2011

Available online 24 March 2011

Keywords:

Heterogeneous catalyst

Transesterification

Biodiesel

Potassium hydroxide

Neodymium oxide

ABSTRACT

A solid base catalyst was prepared by neodymium oxide loaded with potassium hydroxide and investigated for transesterification of soybean oil with methanol to biodiesel. After loading KOH of 30 wt.% on neodymium oxide followed by calcination at 600 °C, the catalyst gave the highest basicity and the best catalytic activity for this reaction. The obtained catalyst was characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA), N₂ adsorption–desorption measurements and the Hammett indicator method. The catalyst has longer lifetime and maintained sustained activity after being used for five times, and were noncorrosive and environmentally benign. The separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and reaction time were investigated. The experimental results showed that a 14:1 M ratio of methanol to oil, addition of 6.0% catalyst, 60 °C reaction temperature and 1.5 h reaction time gave the best results and the biodiesel yield of 92.41% was achieved. The properties of obtained biodiesel are close to commercial diesel fuel and is rated as a realistic fuel as an alternative to diesel.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

As conventional fuels are diminishing and environmental pollution is aggravating, alternative fuels have gained significant attention [1]. Biodiesel fuel, as a promising alternative diesel fuel to conventional fossil diesel produced by a catalytic transesterification of vegetable oils, animal fats and waste cooking oils with short chain alcohol, is becoming a favorable biofuel in many regions of the world [2,3]. Compared to conventional diesel from petroleum, biodiesel is technically and economically more competitive because of its renewability, biodegradability, low emission profiles, high Flash point,

excellent lubricity and superior cetane number [4]. In addition, the use of biodiesel has the potential to reduce both the levels of pollutants and potential or probable carcinogens [5].

Biodiesel can be produced through transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst. In conventional homogeneous method of fatty acid methyl ester (FAME) synthesis, the removal of catalysts after reaction is unwanted step of biodiesel synthesis, where a large amount of wastewater is produced during neutralization the catalyst (NaOH or KOH) and FAME washing during separation from side products (glycerol, salt). Acid-catalyzed process often uses sulfonic acid and hydrochloric

* Corresponding author. Tel.: +86 51188791800.

E-mail address: fxqiu@163.com (F. Qiu).

0961-9534/\$ – see front matter © 2011 Elsevier Ltd. All rights reserved.

doi:10.1016/j.biombioe.2011.03.009

acid as catalysts, however, the reaction time is very long (48–96 h) even at reflux of methanol, and a high molar ratio of methanol to oil is needed (30–150:1) [6].

Compared with homogeneous catalysts, heterogeneous catalysts can provide green and recyclable catalytic systems [7,8]. The advantage of heterogeneous catalyst usage is its fast and easy separation from the reaction mixture without requiring the use of neutralization agent. There are many solid heterogeneous acid- and alkali-catalysts for biodiesel synthesis. Tungstated zirconia (WO_3/ZrO_2) was prepared by method of impregnation was a promising heterogeneous acid catalyst [9]. Various carbohydrate-derived and a carbon-based solid acid catalyst [10,11] have good catalytic activity to high free fatty acid-containing waste oils. Unfortunately, the performances of these acid catalysts are still inferior compared with the base catalysts. For this reason, a wide variety of solid bases have been examined for transesterification reactions for biodiesel synthesis. Example include CaO [12], SrO [13], KNO_3 loaded on flyash [14], $\text{ZnO-La}_2\text{O}_3$ [15] and zinc aluminate [16]. But, these heterogeneous catalysts require a high temperature to achieve the high conversion. Other heterogeneous base catalysts like CaMnO_3 [17], $\text{KNO}_3/\text{Al}_2\text{O}_3$ [18], and Mg–Al hydrotalcites [19] have also demonstrated some potential for activity in production of biodiesel. However, these catalysts need more time (more than 3 h) to reach the higher biodiesel yield. The result will increase the production cost due to the requirements for high temperatures and a long time operation.

Neodymium oxide (Nd_2O_3) or rare earth sesquioxides is widely used in various applications such as photonic, luminescent materials, catalyst for automotive industry, UV absorbent, glass-polishing materials, and protective coatings. However, in this work, a new type of catalyst for biodiesel synthesis with KOH as active component on neodymium oxide support was synthesized using the way of impregnation, and reported the activity and selectivity of the basic solids for the transesterification of soybean oil with methanol. A screening of the reaction conditions has been carried out by examining the effect of the concentration of catalyst, the initial methanol/oil, catalyst/oil molar ratio, reaction temperature and time.

2. Experimental

2.1. Materials

Soybean oil was purchased from Jinlongyu Company (Fujian, China). Methanol, zirconium dioxide (ZrO_2), titanium dioxide (TiO_2), alumina (Al_2O_3), neodymium oxide (Nd_2O_3), potassium hydroxide (KOH), potassium iodide (KI), potassium bromate (KBrO_3), potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{O}_4\text{K}$) and potassium nitrate (KNO_3) were obtained from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). All solvents were AR grade and were used without purification.

2.2. Preparation of catalyst

All the catalysts were prepared by incipient wetness impregnation of different porous medium supports with solution of potassium compounds. For this purpose, the required amount of aqueous KOH solution was slowly added to the support and

kept 24 h. The catalytic carrier was previously calcined in a muffle for 12 h at 600°C . After impregnation, the catalysts were dried for 12 h at 100°C and then the solid was calcined in a muffle furnace at designed temperature for 12 h before use for the reaction.

2.3. Characterization of the catalyst

FT-IR spectra of the samples were obtained between 4000 and 400 cm^{-1} on a KBr powder with an FTIR spectrometer (AVATAR 360, Nicolet, Madison, USA). A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the $4000\text{--}400\text{ cm}^{-1}$ range.

Scanning electron microscopy (SEM) images were obtained with 20-kV accelerating voltage with a field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan).

X-ray diffraction (XRD) patterns of selected samples were obtained were recorded by the reflection scan with nickel-filtered $\text{Cu K}\alpha$ radiation (D8, Bruker-AXS, Germany). The X-ray generator was run at 40 kV and 70 mA. All the XRD measurements were performed at 2θ values between 10 and 80° .

Thermogravimetric analysis (TGA) was performed on a Netzsch instrument (STA 449C, Netzsch, Seligenstadt, Germany). The programmed heating range was from room temperature to 1300°C , at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The measurement was taken using 6–10 mg samples.

The nitrogen adsorption and desorption isotherms were measured at -196°C using a NDVA2000e analytical system made by Quntachrome Corporation (USA). The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size distribution and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method.

Hammett indicator experiments were conducted to determine the basic strength of each catalyst. The Hammett indicators used were bromothymol blue ($\text{pK}_a = 7.2$), phenolphthalein ($\text{pK}_a = 9.8$), 2,4-dinitroaniline ($\text{pK}_a = 15$), and 4-nitroaniline ($\text{pK}_a = 18.4$). Typically, 300 mg of the catalyst was mixed with 1 mL of a solution of Hammett indicators diluted in 10 mL methanol and allowed to sit for at least 2 h. After the equilibration, the color of the catalyst was noted. The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change. To measure the basicity of solid bases, the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used.

2.4. Transesterification of soybean oil and chemical analyses

The transesterification reactions were performed at 60°C in a 125 ml three-neck reaction flask equipped with a condenser by refluxing 10 mL of methanol (247 mmol) with 15.82 g of soybean oil (commercial edible grade, acid value = 0.976 mg KOH/g, saponification index = 188.6 mg KOH/g, and average molecular weight = 896.88 g/mol) and 0.95 g of catalyst (6 wt.%). The catalyst was activating at 773 K for 12 h before use for the reaction. After the reaction completion, the samples were separated from catalyst and glycerol by centrifuge. The glycerol could be separated because it was insoluble in the esters

Download English Version:

<https://daneshyari.com/en/article/677864>

Download Persian Version:

<https://daneshyari.com/article/677864>

[Daneshyari.com](https://daneshyari.com)