Production of biodiesel from soybean oil catalyzed by attapulgite loaded with C$_{6}$H$_{5}$O$_{6}$KNa catalyst

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Abstract—Biodiesel is a green, safe, renewable alternative fuel, which is of great significance to solving the problem of energy shortage and environmental pollution. A series of solid base catalysts were prepared with the support of attapulgite (ATP), the load of C$_{6}$H$_{5}$O$_{6}$KNa by impregnation method, and were used to catalyze transesterification of soybean oil with methanol to biodiesel. The activities of prepared catalysts were investigated compared to pure ATP. The optimal conditions for the catalyst preparation were investigated: molar ratio of Na : ATP was 1.7 : 1 and calcination temperature was 400 °C. The prepared catalysts were characterized by several techniques such as Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, N$_{2}$ adsorption-desorption measurements, X-ray diffraction and the Hammett indicator method. The prepared solid base catalyst can be separated from reaction system effectively and easily. The effects of the molar ratio of methanol to oil, reaction temperature and amount of catalyst on the biodiesel yield were investigated. The experimental results showed that a 22 : 1 molar ratio of methanol to oil, 10.0% of catalyst amount, 65 °C of reaction temperature and 3.0 h of reaction time gave the best results. The catalyst has longer lifetime and maintained sustained activity after being used for five cycles.

Key words: Transesterification, Biodiesel, Attapulgite, Solid Base Catalyst

INTRODUCTION

Traditional fossil resources, which will be exhausted shortly, are supplying the majority of the energy needs of the world nowadays. Therefore, finding alternative fuels has attracted considerable attention in recent years. Among these alternative fuels, biodiesel is a promising nontoxic and biodegradable fuel arising from biomass. Fatty acid methyl esters (FAME) show great potential as diesel substitute, and they are known as the sources of biodiesel, which are synthesized by direct transesterification of vegetable oils with a short-chain alcohol in the presence of a catalyst [1-3]. Currently, most commercial processes used for biodiesel synthesis employ a homogeneous catalyst such as NaOH [4,5] and KOH [6]. Georgiann et al. reported the production of biodiesel from the soybean frying oil using 2% NaOH as catalyst [5]. It can give a high yield of methyl esters (95%) after a short reaction time (20 min) because the homogeneous base catalyst can significantly accelerate the transesterification reaction. However, it is considerably costly to separate homogeneous catalysts from the reaction mixture [7-10], and purification steps are time consuming and not environmentally benign because a large amount of waste water is produced during these steps [11]. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts, mainly because of environmental constraints and simplifications in the existing processes.

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [12-14]. As a result, research on chemical reaction using heterogeneous catalysts had increased over the past decade. Researchers found many solid heterogeneous acid- and alkali-catalysts for biodiesel synthesis. Various carbonyl- and a carbon-based solid acid catalyst have good catalytic activity to high free fatty acid-containing waste oils. However, as the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, base catalysis is preferred to acid catalyzed routes, and is thus most often used commercially [15].

Attapulgite [Mg$_{8}$Si$_{4}$O$_{20}$(OH)$_{4}$(OH)$_{2}$, 4H$_{2}$O, ATP] or Palygorskite is a hydrated magnesium aluminum silicate that exists in nature as a fibrous mineral [16]. It is widely used in petroleum, chemical, building materials, paper, medicine and agriculture due to its special chemical and physical properties and processing properties. In addition, it is a natural, cheap and its rough surface results in a relatively high surface area which can be a good carrier. In this work, a new type of catalyst for biodiesel preparation with C$_{6}$H$_{5}$O$_{6}$KNa as active component on ATP support was prepared using the impregnation method, and a screening of the reaction conditions was carried out by examining the effect of the concentration of catalyst, the initial methanol/oil, catalyst/oil molar ratio, reaction temperature and time. To the best of our knowledge, this is the first time that the preparation and application of a catalyst C$_{6}$H$_{5}$O$_{6}$KNa/attapulgite are reported.
EXPERIMENTAL

1. Materials

Methanol, sodium chloride (NaCl), sodium thiourea (Na_{3}SO_{4}), sodium nitrate (NaNO_{3}), sodium biphosphate (NaH_{2}PO_{4}), sodium bicarbonate (NaHCO_{3}), sodium tartrate (C_{4}H_{4}O_{7}Na), and sodium potassium tetrahydroxide (C_{2}H_{4}O_{2}KNaNa4H_{2}O) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Soybean oil was obtained from Jinlongyu Company (Fujian, China). ATP was obtained from a Clay Factory. All solvents were AR grade and were used without purification.

2. Preparation of Catalyst

The ATP was carried out by acid treatment and the process was as follows. The attapulgite was deposited in a hydrochloric acid solution (100 mL, 2 mol/L) in a flask, and stirred magnetically for 100 min at 60°C. Then, the solution was vibrated with the aid of an ultrasonic instrument for 10 min at room temperature. After the supernatant was removed, the residue was centrifuged and washed with distilled water several times until pH=7 and dried under vacuum at 100°C for 12 h. After grinding, the pretreated attapulgite solid was obtained and stored in desiccator.

The catalyst was prepared by incipient wetness impregnation with different concentration of aqueous tartaric acid potassium sodium solution. For this purpose, the required amount of aqueous tartaric acid potassium sodium solution was slowly added to the carrier and kept 24 h. After impregnation, the catalyst was 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. The solid base catalyst was obtained.

3. Catalyst Characterizations

The Hammett indicator method was used to determine the basic strength of the catalyst [17,18]. Basic strength was expressed by an acidity function (H\_\-) defined by Eq. (1):

\[ H\_\- = pK_{BH} + \log \frac{[BH]}{[BH]^\-} \]  \hspace{1cm} (1)

where \([BH]\) and \([BH]^\-\) are the concentrations of the indicator and its conjugate base, respectively, and pK_{BH} is the logarithm of the dissociation constant of the indicator used.

The indicators used were as follows: bromothymol blue (pK_{BH}=\-\ 7.2), phenolphthalein (pK_{BH}=\-\ 9.8), and 2,4-dinitroaniline (pK_{BH}=\-\ 15.0) [19,20]. 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 equilibration, the color of the catalyst was noted. The basic strength of the catalyst was taken as the amount of aqueous tartaric acid potassium sodium solution that was required to change the color of the catalyst and its conjugate base.

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 [21].

FT-IR spectra of the samples were obtained between 4,000 and 4,000 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 4,000-4,000 cm\(^{-1}\) range. Scanning electron microscopy (SEM) images were obtained with a 20-kV accelerating voltage with a field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan). The morphology of the particles was observed by transmission electron microscopy (TEM) (TECNAI-12, Philips Company, Eindhoven, Netherlands) with an acceleration voltage of 120 kV.

The component on the surface of samples was measured by energy dispersive X-ray spectrometer (EDX) (S-4800, Hitachi High-Tech, Japan). X-ray diffraction (XRD) patterns of selected samples were recorded by reflection scan with nickel-filtered Cu K\alpha radiation (D8, Brucker-AXS, Germany). The X-ray generator was run at 40 kV and 70 mA. All the XRD measurements were performed at 2\theta values between 5 and 80°.

The nitrogen adsorption and desorption isotherms were measured at –196°C using a NDV2000e analytical system made by Quantachrome Corporation (USA). The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method.

4. Transesterification Reaction

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 10.0 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 1.0 g of catalyst. 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 and had a much higher density. Then methanol was removed using rotary evaporation, and the obtained product was analyzed by gas chromatography (GC) to determine the biodiesel yield.

5. Analysis Methods

Reference materials and samples were analyzed by a 7890A gas chromatograph (Agilent Technology Inc. USA), equipped with a flame-ionization detector (FID) and an HP-5 capillary column (30 m × 0.32 mm × 0.25 µm). The carrier gas was nitrogen. The oven temperature ramp program was 135°C for 10 min, 170°C at 10°C/min, and held for 10 min. 250°C at 25°C/min, and held 2 min. The flow rate of hydrogen was 30 mL/min and the flow rate of air was about 400 mL/min. Temperatures of the injector and detector were 280 and 300°C. The injection was performed in split mode with a split ratio of 10:1. Biodiesel yield was quantified in the presence of tricaprylin as an internal standard. The biodiesel for each sample was analyzed by dissolving 10 µl of biodiesel sample and 8 µl tetradecane as the internal standard into 1 ml of n-hexane and injecting 1 µl of this solution in GC, in the same condition described as above. The biodiesel yield was calculated from the content of methyl esters analyzed by GC with the following Eq. (2):

\[ \text{Biodiesel yield} = \frac{m_{\text{tricaprylin}}A_{f_{\text{tricaprylin}}}f_{\text{tricaprylin}}}{A_{\text{tricaprylin}}m_{f}} \]  \hspace{1cm} (2)

where \(m_{\text{tricaprylin}}\) is weight of the internal standard, \(A_{r}\) is peak area of FAME, \(f_{\text{tricaprylin}}\) is response factor, \(A_{\text{tricaprylin}}\) is peak area of the internal standard, and \(m_{f}\) is weight of the sample [22].

Sulfur content of biodiesel was determined by inductively coupled plasma emission spectrometer (ICP) using Intrepid XP Radial ICP-OES (VISTA-MPX, Varian, USA) with a concentric nebulizer and CCD detectors technology.

Flash point was determined by a closed-cup tester (BF-02, Dalian North Analytical Instruments Co., Ltd.), by the standard ASTM D 93. The acid number, which is expressed as mg KOH/g, was deter-