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Transesterification of castor oil to biodiesel using NaY zeolite-supported La_2O_3 catalysts

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ABSTRACT

As the requirements for green and industrial production of biodiesel increase, recyclable mesoporous spherical catalysts need to be developed. To achieve this, La_2O_3/NaY spherical particle (3–5 mm) heterogeneous catalysts were prepared by a granulating machine for the production of castor oil biodiesel. The effects of calcination temperature on catalytic activity and crushing strength were investigated. The structure, composition and morphology of the La_2O_3/NaY were characterized by SEM-EDS, XRD and BET analyses. The effects of calcination temperature, catalyst concentration, ethanol/oil molar ratio, reaction temperature and time on the yield of fatty acid ethyl ester (FAEE) were optimized by single-factor analysis. The addition of surfactant has a positive effect on the La_2O_3 dispersion and pore size of zeolite NaY. The synthesized catalyst shows excellent reusability and crushing strength which are essential for industrial practices. Under the optimization conditions of catalyst concentration 10 wt%, molar ratio of ethanol to oil 15:1, reaction temperature 70 °C for 50 min, the FAEE yield of 84.6% was obtained.

1. Introduction

With the continuous development of science and technology, people's demand for energy is increasing and mineral energy shortage is becoming more and more serious. The energy crisis has gradually become a major challenge facing mankind. Meanwhile, the toxic gases and bituminous coal by refining and burning of traditional petrochemical fuels have caused serious environmental pollution. Therefore, it is urgent to find sustainable and alternative clean energy sources. Biodiesel, a non-toxic, biodegradable and renewable biomass energy, has attracted widespread attention. Meanwhile, biodiesel is regarded as an ideal substitute because of its physical and chemical properties similar to those of traditional petrochemical diesel fuel. Thus, it can be applied to compression-ignition diesel engines with little or no modification [1].

Typically, biodiesel, also known as a mixture of fatty acid methyl esters (FAME), is obtained from either vegetable oils or animal fats [2]. Currently used vegetable materials are sunflowers oil [3,4], rapeseed oil [5,6], soybean oil [7,8], palm oil [9,10], castor oil [11–14], papaya seed oil [15], jatropha seed oil [16,17] and so on. In China, a result of food security [10], the government explicitly prohibits the use of edible oils for the production of biodiesel. Castor oil is an important non-edible oil with unique properties in nature. Castor has the characteristics of drought, ridge and salt resistance which can be planted in most parts of China. In addition, the castor oil seed contains about 47–49% oil, which is mainly composed of ricinoleic acid [14]. The production capacity of castor oil in China is ranked the second in the world and it is an ideal raw material for biodiesel production [18].

The transesterification is carried out directly with the alkaline catalyst due to the low acid value of refined castor oil. Homogeneous catalysts such as NaOH [19], KOH [20], CH_3OK [21], CH_3ONa [22] have high catalytic activity for transesterification. However, the usage of homogeneous catalyst has a few disadvantages since it requires more complex processes to wash and purify products and produces large amounts of waste water [23]. In addition, homogeneous catalyst also causes equipment corrosion [24,25] and saponification of the raw materials. Recently, due to growing environmental and economic issues, the green approach of transesterification has stimulated the development of recyclable solid catalysts as a substitute for homogeneous catalysts [26]. The use of heterogeneous catalyst can reduce the problem associated with the homogeneous catalyst because heterogeneous catalyst can be easily separated from the liquid products and can be

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designed to have higher activity, higher selectivity and longer catalyst lifetimes [27].

Recently, new heterogeneous alkaline catalysts have been used for transesterification to produce biodiesel. Among them, MOFs [28,29], graphene [26,30], ion exchange resin [31,32], zeolite [4,33–36], hydrotalcite [5,37,38] and metal oxides [1,3,39–43] all have good activity in transesterification reaction. There are numerous lanthana supported catalysts that have been used due to their unique alkali catalytic activity. Lee et al. [1] reported that the conversion of biodiesel was 98.76% at 3 wt% CaO-La_2O_3 catalyst loading, methanol/oil molar ratio of 25:1 and reaction temperature of 160 °C for 3 h. Intensification of alkalinity of lanthana has been done by applying alkali promoters like calcium oxide [1,44], zirconia [45], aluminium oxide [46] and Ni metal [47]. Nizah et al. [48] used jatropha curcas oil with Bi_2O_3-La_2O_3 catalyst under reaction conditions of reaction time of 4 h, catalyst loading of 2 wt% (5% Bi_2O_3 doping amount), methanol/oil molar ratio of 15:1 at 150 °C and the conversion of biodiesel obtained was 93%. Maleki et al. [44] used lithium loaded on CaO-La_2O_3 mixed oxide for reaction with canola oil and obtained 96.3% FAME conversion using 15:1 methanol/oil molar ratio for 2.5 h with 5 wt% catalyst loading at 65 °C. In addition, the La_2O_3 as a catalyst for loading has also been reported. Sun et al. [45] reported La_2O_3/ZrO_2 catalysts for sunflower oil transesterification and reported that the FAME conversion was 90% with reaction conditions of 30:1 methanol to oil molar ratio, 21 wt% La_2O_3/ZrO_2 catalyst, at temperature of 200 °C for 5 h. Although they all have high FAME yields, a few people concerned the techniques of catalyst forming. Most of the heterogeneous catalysts reported are used directly in powder form, which caused inconvenience to subsequent processing. For example, powders and oils can easily stick to the reactor wall and are difficult to clean. At the same time, the catalyst powders are too small, difficult to recycle and easy to lose, which is not suitable for direct application to large-scale chemical equipment.

The purpose of this work was to synthesize a new type of La_2O_3/NaY catalyst for transesterification of castor oil. The catalysts were synthesized via a physical mixing method. The uniform spherical catalyst particles of 3–5 mm in diameter were made by the rotation of the granulation machine (LW-83 dB, Zibo Shunyuan Machinery Factory, Zibo, China). The La_2O_3/NaY catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), N_2 adsorption (BET). The optimum reaction parameters such as catalyst concentration, ethanol/oil molar ratio, reaction time and reaction temperature for transesterification were analyzed to determine the stability of catalyst La_2O_3/NaY. The reusability of the catalyst was also studied.

2. Experimental

2.1. Materials

The zeolite NaY was supplied from Sinopec Catalyst Co., Ltd Qilu Division, Zibo, China. Lanthanum oxide, sodium carboxymethyl cellulose (CMC) and kaolin were purchased from Jining Tianyi New Material Co. Ltd. Refined castor oil was friendly supplied from Zibo Jinxuan Resources and Environmental Technology Development Co., Ltd, Zibo, China and used without additional processing. The fatty acid composition of the castor oil was determined by chromatography (GC) analysis as follows: ricinoleic acid 88.7%, oleic acid 4.7%, palmitic acid 2.8%, stearic acid 2.1%, gaidic acid 0.8%. Ethyl heptadecanoate and a standard FAEE C_{16}-C_{20} for GC calibration were purchased from Shanghai Klamar (China). Other chemicals that have been applied in this work such as ethanol, *n*-hexane, nitric acid, and potassium hydroxide were of analytical grade.

2.2. Catalyst preparation

The La_2O_3/NaY catalyst was obtained by physical mixing. The zeolite NaY, sodium carboxymethyl cellulose, lanthanum oxide and kaolin were grinded and mixed evenly in the ball grinding mill at a certain proportion (the mass ratio of NaY:Kaolin:La_2O_3:CMC = 70:20:10:2.5). A small amount of the mixture was placed in a turntable granulator and sprayed in the binder solution to form seed crystals. Then, the mixture was slowly added and continued to spray in the binder solution to form uniform spherical particles (3–5 mm). The obtained spherical particles were dried at 80 °C for 12 h, then placed in a crucible and calcined in a muffle furnace (SX-G04123, Shanghai Liangyi Scientific Instruments Co., Ltd., Shanghai, China). The calcination temperature was programmed from room temperature to 600, 800, 1000 °C at the rate of 2 °C·min^{-1} and then kept constant for 3 h, which were labeled as La_2O_3/NaY-600, La_2O_3/NaY-800 and La_2O_3/NaY-1000, respectively. Target catalyst was obtained by naturally cooling to room temperature. In addition, a certain amount of surfactants (4 wt%) was added to the mixture and calcined at 800 °C, labeled as S-La_2O_3/NaY-800.

2.3. Characterization of the catalysts

The La_2O_3/NaY catalysts were characterized by X-ray diffraction (XRD) on a Bruker AXS (D8 ADVANCE) with a Cu Kα radiation (wavelength, λ = 0.154 nm, 35 kV, 30 mA) [49]. The La_2O_3/NaY samples were examined from 10° to 60° (2θ) with a scan rate of 0.048°/s at 40.0 kV.

The total surface area of the La_2O_3/NaY catalysts were obtained using a Brunauer-Emmett-Teller (BET) method with nitrogen adsorption by ASAP 2020 system (Micrometitics USA) at −196.0 °C. In addition, the pore size and pore volume were also analyzed. The surface morphology analysis of the catalysts was studied by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). The NaY and La_2O_3/NaY were photographed using FEI (SIRION 200) at 10 kV and a magnification of 5000×. The surface elements of the catalysts were analyzed and obtained by EDS (Oxford-instruments INCA Energy). The mechanical strength of the La_2O_3/NaY catalyst was measured by the particle strength meter (HB-KQD 1705146, Jinan Haibo Laboratory Instrument Co., Ltd. Jinan, China). Each set of catalyst was measured fifty times, and the average value was obtained.

The basic strength and basic strength distribution of the catalyst were determined by direct titration with a Hammett indicator. Hammett indicator H_0 was used to quantitatively represent the basic strength, which was calculated by Eq. (1) [50].

$$H_0 = PK_a + \log[B]/[BH^+] \quad (1)$$

[B] and $[BH^+]$ represent the concentrations of the indicator and the conjugate acid, and *pKa* is the logarithm of the dissociation constant of the indicator.

2.4. Alkaline transesterification

The transesterification reaction was carried out in a 250 ml three-necked flask equipped with a condenser at atmospheric pressure. The reactants were stirred in a magnetic whisk and heated in a warmer jacket (SZCL-A, Zhengzhou Great Wall Branch Industry & Trade Co., Ltd. Zhengzhou, China). 30.0 g of castor oil and the required amount of catalyst and ethanol were added in each experiment. The four different reaction parameters were optimized including catalyst concentration (2–12 wt%), molar ratio of ethanol to oil (3:1–18:1), reaction time (20–60 min) and reaction temperature (50–75 °C). After the reaction, the mixture was filtered to remove the catalysts and its volume was measured. The crude biodiesel was refined that excess ethanol was removed under reduced pressure using a rotary evaporator, glycerol and other impurities were removed by washing with water, and finally the product was dried over anhydrous sodium sulfate.

The FAEE concentration was measured by an internal standard curve method using ethyl heptadecanoate as the internal standard