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Biodiesel from palm oil via loading KF/Ca–Al hydrotalcite catalyst

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ABSTRACT

The solid base catalyst KF/Ca–Al hydrotalcite was obtained from Ca–Al layered double hydroxides and successfully used in the transesterification of methanol with palm oil to produce biodiesel. With the load of KF, the activity of Ca–Al mixed-oxides had been improved much. For the mass ratio 80 wt.%($KF \cdot 6H_2O$ to Ca–Al mixed-oxides) catalyst, under the optimal condition: 338 K, catalyst amount 5%(wt./wt. oil) and methanol/oil molar ratio 12:1, after 5 h reaction, the fatty acid methyl esters yield could reach 97.98%; for the mass ratio 100 wt.%($KF \cdot 6H_2O$ to Ca–Al mixed-oxides) ones, under the same reaction condition, only needed 3 h to get the FAME yield of 99.74%, and even only reacted 1 h, the FAME yield could obtain 97.14%.

1. Introduction

The un-reproducibility of petroleum and the increasing needs for it, as well as the environmental problems called the birth of new energy substitute. Being one of the best among them, biodiesel, which main content is fatty acid methanol esters (FAME), is one of the most potential substituted energy resources [1], is considered a renewable and practically inexhaustible source of energy. Their physic-chemical properties such as energy content, cetane number, and viscosity are similar to those of petroleum-based diesel fuels. Thus, biodiesel can be used in compression–combustion (diesel) engines with little or no modifications.

The most widely method to produce biodiesel is transesterification of animal fat or vegetable oil with methanol or ethanol [2], which can be catalyzed by bases, acids and enzymes [3], or directly acted with supercritical alcohols [4,5]. The supercritical alcohol method has no industrial application value because of its large energy consumption and critical demands on reactors. Therefore, the most widely used method is still catalytic transesterification. Among all catalysts, bases are more widely used in industrial production for their faster reacting rate than acid [6] and lower price than enzymes. However, homogenous strong alkyls, the catalyst most widely used in industry, have many disadvantages such as separating problems of catalyst and product, huge amount of water, sensitive to water and acid, which directly limits the raw materials of biodiesel.

In order to solve these problems, the use of heterogeneous catalysts has been explored. Based on their advantages: non-corrosive, environmentally friendly, much more easily being separated from the liquid products, and designed to give higher activity, selectivity and longer catalyst lifespan [7,8], solid base catalysts have attracted much more attention than other kinds. This type of catalysts, used in biodiesel synthesis, includes simple metal oxide such as MgO or CaO

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[9,10], ion exchange resin [11], and supported ones such as Na/NaOH/γ-Al_2O_3 [12], KF/γ-Al_2O_3 [13,14], montmorillonite KSF [15], cesium(or potassium)-exchanged zeolite X [16].

Additionally, layered double hydroxides (LDHs) with general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, which is also called as hydrotalcite (HT) or hydrotalcite-like compound, and the mixed metal-oxides from them can catalyze the transesterification reaction, too. The structure of hydrotalcites is based upon layered double hydroxides with brucite like ($Mg(OH)_2$) hydroxide layers containing octahedrally coordinated M^{2+} and M^{3+} cations [17,18]. Calcination at appropriate temperature decomposes the hydrotalcite into interactive, high surface area and well-dispersed mixed metal-oxides, which completely destroyed the layered structure. The most interesting property of HT is that its acid/base property could be easily controlled by varying their compositions [17]. Many researches have been done on transesterification catalyzed by LDHs. Corma et al. [19,20] have reported that calcined Li–Al and Mg–Al LDHs are able to catalyze the glycerolysis of fatty acid methyl esters to monoglycerides (the reverse of biodiesel synthesis), Shumaker et al. [21,22] used calcined Li–Al LDHs to catalyzed soybean oil with methanol, and Liu et al. [23] used calcined Mg–Al hydrotalcite to catalyzed poultry fat with methanol. All of these studies showed that LDHs, except the Li–Al LDHs, performed low activities at the lower temperature, but when the reaction was performed in autoclave at high temperature, the conversion of soybean oil or acidic cottonseed oil could reach 90% [24,25]. While based on the hydrotalcite properties, loading active substance can improve the activity of the HT. Sun et al. [26] have reported that KNO_3/HT showed stronger alkalescency and more active in methylation of cyclopentadiene than KNO_3/Al_2O_3. And Trakarnpruk et al. [27] loaded CH_3COOK on calcined hydrotalcite and synthesized biodiesel at the condition of a 30:1 methanol to oil molar ratio at 373 K for 6 h and 7 wt.% catalyst, the fatty acid methyl esters(FAME) content could get to 96.9%.

Palm oil (PO) is one of the four leading vegetable oils traded on the world market. As cheaper than canola oil, rapeseed oil, or soybean oil, the use of PO would reduce the overhead cost of biodiesel production, and generate a supply of diesel fuel substitute, which now plays a very important role in biodiesel production [28]. In our early work, KF/Mg–Al HT [29] had been obtained and successfully used in the transesterification of PO, and the catalyst showed its activity in this reaction with a FAME yield of 85% at optimal condition. Considered that Ca–Al HT had same structure with the Mg–Al HT, while higher alkalescence, in this work, the heterogeneous catalysts KF/Ca–Al HT were prepared and their catalytic activities were investigated in the transesterification of palm oil with methanol, and at atmospheric pressure the yield of FAME could get over 99%.

2. Experiment

2.1. Materials

Palm oil of unknown provenance was obtained from Nanjing Runtai market. On analysis reported below (Table 3), it appeared to be close to a crude palm oil (CPO) rather than a food grade refined and bleached material.

CH_3OH were purchased from Nanjing Chemical Reagent Co., Ltd., and $KF\cdot 6H_2O$, $CaCl_2$, $Al(NO_3)_3\cdot 9H_2O$, NaOH and Na_2CO_3 were purchased from Guangdong Guanghua Chemical Factory Co., Ltd..

2.2. Catalyst preparation and characterization

2.2.1. Catalyst preparation

The Ca–Al hydrotalcites were prepared by co-precipitation method. Solution A (80 ml) contained $CaCl_2$ (0.06 mol) and Al $(NO_3)_3\cdot 9H_2O$ (0.02 mol), while solution B (80 ml) contained NaOH (0.16 mol) and Na_2CO_3 (0.04 mol). Both two solutions were synchronously dropped into 50 ml 338 K water slowly accompanied with vigorous mechanical stirring, maintaining the pH between 10 and 11. The mixture was held at 338 K while keeping stirred vigorously for 48 h and then filtered and washed with water until the pH value of filtrate was near 7. The precipitate was dried at 373–398 K over night and calcined at 823 K for 5 h, and then it conversed into Ca–Al mixed-oxides.

The Ca–Al mixed-oxides was grinded with $KF\cdot 6H_2O$ by the mass ratio of 20, 40, 60, 80, 100 wt.%, while dropping some water. Then the paste was dried at 338 K over night to obtain the catalyst.

2.2.2. Catalyst characterization

The catalyst was characterized by powder X-ray diffraction (XRD) and scanning electro microscope (SEM). XRD measurements were performed on a Rigaku D/max-A instrument with a Cu Kα radiation at 50 kV and 30 mA and a scan speed of 0.02 min^{-1}.

2.3. Transesterification

Transesterification experiments were carried out in a 100 ml four-necked flask, provided with thermostat, mechanical stirring systems. 30 g PO and different amount of methanol and catalyst were added and heated to a given temperature accompanied with stirring. The reaction were taken under the refluxing temperature, other condition were as following: 20%–100% of the mass ratio of KF/Ca–Al mixed-oxides, 6:1–18:1(molar ratio) of methanol/oil, 1–5 wt.% of the catalyst amount and 1–5 h of the transesterification time. After reaction, the reactor was cooled to room temperature, and the catalyst was removed from the product mixture by filtration. The excess methanol was recovered by rotary evaporation under reduced pressure. Phase separation of the filtrate resulted in the isolation of the methyl esters and glycerol. The top layer was the biodiesel phase of the methyl esters.

The product mixture was analyzed by the gas chromatograph (Ouhua GC 9160) equipped with a DB-5Ht capillary column (15 m × 0.25 mm × 0.25 mm) by FID. Nitrogen was as a carrier gas with a flow rate of 2 ml min^{-1}. The injector and detector temperatures were 523 K and 633 K. The oven temperature program consisted of: start at 323 K (keep 1 min), ramp at 15 K min^{-1} to 453 K, then continue ramp at 7 K min^{-1} to 503 K, and then at 20 K min^{-1} to 653 K(keep 10 min^{-1}).

The FAME yield in each experiment was calculated from its content in the composition as analyzed by GC. The yield was