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Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst

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ABSTRACT

In this work, hydrotalcite-derived particles with Mg/Al molar ratio of 3/1 were synthesized by a coprecipitation method using urea as precipitating agent, subsequently with (MHT) microwave-hydrothermal treatment, and followed by calcination at 773 K for 6 h. These particles were micro-sized mixed Mg/Al oxides as characterized by SEM and AFM. But actually they were nanosized according to the calculations from XRD data. Because of their strong basicity, the nanoparticles were further used as catalyst for biodiesel production from *Jatropha* oil after pretreatment. Experiments were conducted with the solid basic catalyst in an ultrasonic reactor under different conditions. At the optimized condition, biodiesel yield of 95.2% was achieved, and the biodiesel properties were close to those of the German standard. The catalyst can be reused for 8 times.

1. Introduction

Biodiesel has drawn more and more attention in recent years because it is renewable and has less detrimental effects on environment as compared with conventional diesel derived from petroleum [1]. Biodiesel obtained from renewable biomass feedstocks can be used in diesel engines or blended at various proportions with petroleum diesel as fuel [2]. It consists of monoalkyl esters that are usually produced by transesterification of plant oil with methanol or ethanol. It has similar and sometimes better physical and chemical properties than petroleum diesel, such as higher flash point, ultra-lower sulphur concentration, better lubricating efficiency and few pollutants produced [3–6]. However, biodiesel is expensive due to the high price of plant oil and some processing technological issues, such as catalyst and equipment. Therefore, little commercial biodiesel is used in China. The raw materials exploited commercially by some developed countries are edible oils such as, rapeseed, soybean, palm, sunflower, coconut and linseed oils [3,7]. The fraction of raw materials for world commercial biodiesel production is rapeseed oil 84%, sunflower oil 13%, palm oil 1%, soybean oil and others 2% [7]. Using edible oils to produce biodiesel in developing countries such as China with limited arable land per capita is not feasible and is banned. Therefore, only non-edible plants are considered as favorable resources for biodiesel production, such as Chinese tallow [8] and *Jatropha curcas L.* trees [9,10], which are producing non-edible oil in appreciable quantity and can be grown in a large-scale on non-cropped marginal lands and wastelands. *Jatropha curcas L.*, a drought-resistant shrub or tree, is widely distributed in the wild in semi-cultivated tropical or subtropical areas in Central and South America, Africa, India, and South China. It has a productive lifespan in excess of 30 years. The fatty acid composition of *Jatropha* oil is similar to other edible oils, but the presence of some toxic materials in kernel (e.g., curcin) renders the oil unsuitable for cooking purposes [11,12]. The oil content in *Jatropha* seed ranges from 25% to 40% by weight and in the kernel itself ranges from 45% to 60% [10]. Nowadays, *Jatropha* trees, as a potential alternative biodiesel crop, are widely cultivated in Southwest of China such as Yunnan, Sichuan, and Guangxi provinces [9]. In the near future, it will supply part of crude oil for commercial biodiesel production in China.

The conventional industrial production of biodiesel is through transesterification of crude oil with a homogeneous strong base catalyst such as NaOH and KOH [1,3,13]. After reaction, recovery of glycerol, removal of base catalyst from products, and treatment of alkaline wastewater are costly and non-environmental. Furthermore, a homogeneous base catalyst is ineffective for production biodiesel from high acid-value crude oils due to the formation of soap. Tan et al. [14] reported a catalyst-free biodiesel production method, using waste palm cooking oil as raw material and

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supercritical methanol. But the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1). Therefore, heterogeneous solid catalysts were used for the transesterification process, where a better separation and reuse of the catalysts without saponification were achieved [15].

Preparation and application of solid superbase catalysts are an emerging area that is attracting more and more attention, because the catalysts are easily separated for reuse and possess a high activity for various reactions under mild conditions. They can replace homogeneous base catalysts in order to minimize the production of pollutants. LDHs (Layered double hydroxides) are important inorganic materials with layered structure and anion exchanged capacity. As classical solid base materials, calcined LDHs are widely used as catalyst in the production of biodiesel [16–18]. In previous work [17], transesterification process was carried out with reflux of methanol, methanol/soybean-oil molar ratio of 15/1, reaction time of 9 h and catalyst amount of 7.5%, and oil conversion rate was only 67%. In the work of Brito et al. [18], waste oil as feedstock, biodiesel production was performed at high temperatures ranging from 353 to 433 K, methanol/oil molar ratio from 12/1 to 48/1 and catalyst concentration from 3 to 12%, respectively, and 90% biodiesel yield was achieved. Ultrasonic radiation is a relative new technique that results in the formation and collapse of micro-scale bubbles in liquid to generate local high temperature and high pressure. So, it can be used as an alternative energy source to promote reactions. It enormously reduces reaction time, methanol/oil molar ratio and catalyst concentration. Therefore, biodiesel production with calcined hydrotalcite catalyst coupled with ultrasonic radiation is likely to become a new effective method.

The purpose of this work is to synthesize hydrotalcite particles and subsequently to calcine them as catalyst for biodiesel production. Hydrotalcite particles were prepared in an ultrasonic reactor by coprecipitation of aqueous nitrate solutions of Mg and Al using urea as precipitating agent, and subsequently with MHT (microwave-hydrothermal treatment). The synthesized particles, after calcination, were used as solid basic catalyst in the transesterification of *Jatropha* oil to test their activities in the ultrasonic reactor. Experiments under different reaction conditions, such as methanol/*Jatropha*-oil molar ratio, catalyst concentration, reaction temperature and ultrasonic power, were performed in order to optimize biodiesel yield. The reasons for catalyst deactivation were also studied.

2. Experimental

2.1. Materials

Nitrates of Mg and Al (99.8% purity) used in the synthesis were obtained from Chengdou Fine Chemical Co. Ltd. Urea (99.0% purity) and methanol (99.0% purity) were purchased from Shanghai Fine Chemical Co. Ltd. *Jatropha* oil with high FFAs (free-fatty-acids) was obtained from our institute in Xishuangbanna, Yunnan province, Southwest of China [9]. According to the Chinese National standards GB 9014.2-88 and GB 164-64, *AV* (acid value) and *SV* (saponification value) of the *Jatropha* oil were measured as 10.5 mg KOH/g and 191.0 mg KOH/g, respectively. So its molecular weight was calculated as 932 g/mol by the formula: $M = (56.1 \times 1000 \times 3)/(SV - AV)$ [19].

2.2. Catalyst preparation

Hydrotalcite particles with Mg/Al molar ratio of 3/1 were synthesized by a coprecipitation method using urea as precipitating agent, and with MHT. In this method, a solution (0.15 M Mg nitrate and 0.05 M Al nitrate) was made in a three-neck flask by dissolving the two solid nitrates in deionized water. Urea {[urea]/[NO_3^-] molar ratio of 4/1} was then added into the flask. The flask was submerged in an oil bath at 373 K with stirring about 500 rpm in the ultrasonic reactor for 2 h. The slurry obtained was subsequently submitted to MHT in the mother liquor for 2 h at 393 K. After filtered, washed thoroughly with deionized water and dried at 373 K for 10 h at a vacuum condition, solid hydrotalcite particles were obtained. They were characterized by powder XRD (X-Ray Diffraction). Catalytic activity of hydrotalcite was studied by the transesterification of *Jatropha* oil with methanol to biodiesel. Without calcination, hydrotalcite displayed no particular catalytic activity in the reaction. But, after calcined, hydrotalcite was in the form of OH contained mixed Al-Mg oxides which had heterogeneous surface basicity with basic sites of low (OH-groups), medium (Mg-O pairs), and strong (O^{2-} anions) basicity and exhibited a significant activity [20]. So, hydrotalcite particles were calcined at 773 K for 6 h in a muffle furnace and used as catalyst for the following biodiesel production.

2.3. Biodiesel production

Biodiesel production process is strongly influenced by the fatty acid composition and FFAs content of crude oil. The *AV* of fresh *Jatropha* oil in Xishuangbanna, Yunnan province, is from 5 to 12 mg KOH/g. Owing to its high FFAs, the transesterification of *Jatropha* oil to biodiesel catalyzed directly by solid catalyst had a low conversion rate. Even using longer reaction time, only 80.4% biodiesel yield was achieved. In order to increase biodiesel yield, FFAs in *Jatropha* oil need to remove. A two-step process of *Jatropha* oil to biodiesel was used to resolve the problem [10].

First, an acid-esterification pretreatment was performed with concentrated sulfuric acid as catalyst. The three-neck flask with a water-cooled condenser was filled with 200-mL *Jatropha* oil, 40-mL anhydrous methanol and 4-mL sulfuric acid. The mixture was vigorously stirred and refluxed at 318 K in an ultrasonic reactor for 1.5 h. After reaction, the mixture was filtered, and the unreacted methanol was separated from the liquid phase via rotary evaporation. The oil was washed three times with sodium chloride solution then dried using anhydrous sodium sulfate. After the pretreatment, the *AV* of the pretreated oil was reduced to only 0.7 mg KOH/g with 93.3% esterification rate. The reaction equation was described as below:

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \quad (1)$$

The second step, a base-catalyzed transesterification reaction (Eq. (2)) was carried out in the same ultrasonic reactor with the calcined hydrotalcite catalyst:

$$\begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_2 \\ | \\ CH_2OOCR_3 \end{array} + 3CH_3OH \overset{\text{Catalyst}}{\rightleftharpoons} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R_1COOCH_3 \\ | \\ R_2COOCH_3 \\ | \\ R_3COOCH_3 \end{array} \quad (2)$$

Biodiesel yield was calculated as:

$$\text{Biodiesel yield}(\%) = (\text{total actual weight of methyl esters} \times 100)/(\text{total theoretical weight of methyl esters}) \quad (3)$$

where, total weight of methyl esters were produced from both steps, total theoretical weight was obtained assuming 100% conversion of fatty acids in *Jatropha* oil according to Eqs. 1 and 2.

The reaction procedure was as follows: first, the catalyst was dispersed in methanol with mechanical stirring (about 600 rpm).