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The nanometer magnetic solid base catalyst for production of biodiesel

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ABSTRACT

Nanometer magnetic solid base catalysts were prepared by loading CaO on Fe_3O_4 with Na_2CO_3 and NaOH as precipitator, respectively. The optimum conditions for preparation of this catalyst were investigated. The influence of the proportion of Ca^{2+} to Fe_3O_4 on the catalytic performance has been studied. The catalyst with highest catalytic activity has been obtained when the proportion of Ca^{2+} to Fe_3O_4 is 7:1; the catalytic activity of the catalyst calcined from $Ca(OH)_2$ to Fe_3O_4 is better than that calcined from $CaCO_3$ to Fe_3O_4; under the conditions of methanol/oil molar ratio of 15:1, catalyst dosage of 2 wt% and temperature of 70 °C, the biodiesel yield reaches to 95% in 80 min, even to 99% finally. The catalytic activity and recovery rate of the nanometer magnetic solid base catalysts are much better than those of CaO. Calcination temperature was determined by differential thermogravimetric analysis. $Ca_2Fe_2O_5$, a kind of new metal multiple oxide, was found in the catalyst through X-ray diffraction. At the end, these catalysts were characterized by scanning electronic microscope (SEM), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM).

1. Introduction

Biodiesel can be considered as an environmental friendly energy source. With regard to the emissions, it has been demonstrated that its net CO_2 emission is rather low taking into account its renewable origin. Other toxic emissions like CO, SO_x, unburned hydrocarbons and soot particles are also considerably reduced when burnt in the Diesel engine (the results concerning the NO_x emission indicates slightly higher values than conventional diesel).[1] Meanwhile, its lubricant property can prolong the engine's life. Other advantages of the biodiesel are high cetane number, high flash point and acceptable cold filter plugging point (CFPP), which makes it very attractive as an alternative fuel.[2] Therefore, biodiesel seems like one of the best successor of fossil fuel.

Basic homogeneous catalysts are applied in the transesterification reaction for traditional biodiesel production. And they have high catalytic activity because of the multiple contact between reagents and catalysts. Freedman et al. [3] reported that NaOH can transform vegetable oil to biodiesel completely in an hour. But their disadvantages are the complicated process of post treatments and pollution. The advantages of basic solid catalysts are easy separation and simple post treatments. Nevertheless, the specific surface area of these kinds of catalysts is too small to contact reagents abundantly and reduce biodiesel conversion. Nanometer magnetic basic solid catalyst combines the merit of basic homogeneous catalysts – the huge specific surface area, and the merit of basic solid catalysts – separated easily from the reagents. Therefore, Nanometer magnetic basic solid catalyst can reduce the costs and protect the environment.

Nowadays, solid base catalysts for transesterification become a focus of research. Mazzochia et al. [4] found that though Ba $(OH)_2$ had a high catalytic activity, there were 0.06% and 0.25% Ba $(OH)_2$ remaining in the resulting fatty acid methyl esters (FAME) and glycerin, respectively. Thereby, Ba $(OH)_2$ is not a completely heterogeneous catalyst. Yang and Xie [5] catalyzed transesterification reaction using ZnO loaded Sr $(NO_3)_2$ at 873 K for 5 h. The rate of FAME yield is 94.5% at reflux of methanol (65 °C), with a 12:1 molar ratio of methanol to soybean oil and a catalyst amount of 5 wt%. However, the used catalyst is significantly deactivated and cannot be directly reused for transesterification. Leclercq et al. [6] tested the catalytic activity of commercial MgO/Al_2O_3 hydrotalcites and MgO (300 m^2/g) in the transesterification of rapeseed oil. The result shows that MgO is more active than hydrotalcites. Some other research illustrates that MgO and hydrotalcites still has high activity even the water content is 10 000 ppm at 180 °C, which is of great significance for decreasing pretreatment costs [7]. Nevertheless, Oku et al. [8] confirmed that MgO and calcined hydrotalcites were soluble in the resulting FAME, and the relict mass

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concentration of Mg and Al was 17 800 ppm and 6900 ppm, respectively. Hence, it cannot be the catalyst for industrial biodiesel production. Corma et al. [9] reported that calcined Li/Al hydrotalcites was more active for the transesterification than the Mg/Al material (or MgO) due to their higher Lewis basicity. Based on the result of Corma, Shumaker et al. [10] studied calcined Li/Al layered double hydroxide as a catalyst for the conversion of soybean oil to FAME. High FAME yield was achieved at the evaporation temperature of methanol and low catalyst load (2–3 wt%) and short reaction time (~2 h). Furthermore, the catalyst still has high catalytic activity after 3-times using, yet a little Li element filters out from the catalyst. Some literatures have also reported that the sodium [11] or potassium [12–14], as well as MgO or Al_2O_3 supported K_2CO_3, exhibited high catalytic activities for the transesterification reaction at the temperature of 60–63 °C, when they were prepared by loading on a support(normally alumina) using several precursors and calcined at 500–600 °C. But K_2CO_3 was found dissolved into the solution [15].

CaO as a transesterification catalyst has been proved to be effective. Nevertheless, when CaO catalyzes the transesterification reaction directly, the lattice oxygen species on the surface would form hydrogen bonds with methanol or glycerin easily, which increases the viscosity of glycerin and forms suspensoid with CaO. As a result, CaO catalyst, as well as glycerin, is difficult to be separated. It complicates the post treatments, even pollutes the environment and increases the costs. [16] However, CaO anchored on supporters can solve the issue. Furthermore, the importance of supporters of catalysts and the percentage of CaO can be observed from the results of Monica C.G. Albuquerque et al.'s [17] research. The catalysts of CaO loaded on different supports with different weight percentage have been tested about their catalytic activity.

The nanometer magnetic catalyst which is prepared by loading CaO onto the nanometer Fe_3O_4 could improve the catalytic performance. This catalyst can connect reagents sufficiently and be separated easily by exerting magnetic field after transesterification reaction. That can simplify the process and decrease costs. A series of experiments were conducted to improve this kind of catalyst by changing the molar percentage of CaO.

2. Materials and methods

2.1. Materials

The materials include Jatropha curcas oil, analytically pure agents of anhydrous calcium chloride, sodium hydroxide, sodium carbonate, ferric sulfate, ferrous sulfate, ammonia et al.

2.2. Methods of magnetic core preparation

$FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 7H_2O$ were dissolved in the distilled water with the proportion of 1:2, and 20% ammonia was dropped into the solution with drastic stirring. After aging for 1 h, black precipitates were formed, and SO_4^{2-} was eliminated by washing many times.

2.3. Preparation of nanometer magnetic solid base catalyst

Some $CaCl_2$ was solved into distilled water, then a certain amount (the proportion of Ca^{2+} to $Fe^{2+} + Fe^{3+}$ was controlled to be 10:1) of magnetic core was added into the $CaCl_2$ solution. The solution of NaOH was titrated into the solution under vigorous stirring and aged for 18 h at 65 °C, then the magnetic material was precipitated by placing at 2200 Gauss magnetic field from permanent magnet NeFeB. The magnetic material was washed over and over again until its pH value came to 7 and then dried for 12 h in a vacuum at 80 °C. Finally, the sample was calcined for 8 h at 800 °C to transform to multiple oxides to achieve nanometer magnetic solid base catalyst.

The catalysts with different proportions (5:1 and 7:1) of Ca^{2+} to Fe_3O_4 were prepared with the same method. Meanwhile, the catalysts with different proportions of Ca^{2+} to Fe_3O_4, i.e. 5:1, 7:1 and 10:1, were made respectively with the precipitator being Na_2CO_3.

In order to compare the catalytic activity of the nanometer magnetic solid base catalyst with that of pure CaO, the CaO catalyst was prepared in the same way with the precipitators being NaOH and Na_2CO_3.

2.4. Methods of catalysts characterization and activity detection

TENSOR27 from BRUKER (Germany) Company was used for TG-DTA analysis in a nitrogen atmosphere at 5 °C/min heating rate; The specific surface area was obtained by Coulter (SA3100) at 150 °C deaeration temperature for 3 h deaeration time; Xportpro from Panalytical Company was used for X-ray diffraction; SEM photograph was taken by Quanta 400 thermal field from Philips FEI company and TEM picture was attained by FEI-Tecnai 12; Magnetic strengths of samples were detected by Lakeshore7410 VSM; The rates of transesterification were monitored by SHIMAZU GC2100, and the condition was as below: in a nitrogen atmosphere, the split ratio was 30, the inject temperature was 210 °C, and the detector temperature was 195 °C.

3. Results and discussion

3.1. Catalytic activities of magnetic solid base catalysts

3.1.1. The optimization of catalyst preparation

To explore the effect between the activity of catalyst and the load amount of CaO, all of the catalysts activities were tested under the same conditions of methanol/oil molar ratio of 15:1, catalyst dosage of 2 wt% and temperature of 70 °C. 120 ml Jatropha curcas oil and 73.5 ml methanol were put into three-necked flask and reacted for 4 h and were sampled every half an hour. The results are shown in Fig. 1.

Fig. 1 indicates that the catalytic activity of pure CaO is less than that of other catalysts. Catalyzed by CaO, the conversion of oil to esters cannot reach 80%, while for magnetic catalyst, the conversion rate reaches more than 80%, especially the $Ca(OH)_2 7$ (These catalysts are named with their precursors and the proportion of Ca^{2+} to Fe_3O_4 for short. For example, "$Ca(OH)_2 10$"means that the precursor of the

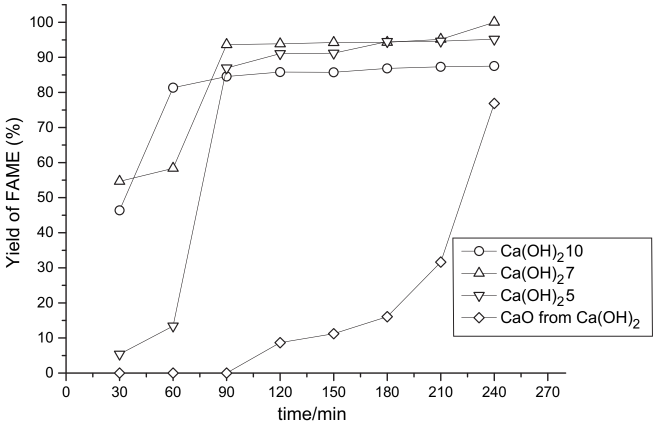

Fig. 1. Influence of different CaO load on catalytic performance for transesterification reaction.