Nano-magnetic catalyst CaO/NaY–Fe_3O_4 for biodiesel production

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Abstract

Nano-magnetic catalyst CaO/NaY–Fe_3O_4 was prepared for biodiesel process. At the first, NaY nanozeolite was synthesized by a hydrothermal method and then, the amount of zeolite was adjusted in order to obtain the zeolite/iron oxide weight ratio of 3:1. The obtained zeolite was then impregnated with CaO nanoparticles. It was found that the activity of calcium oxide catalyst increased after being supported on nanozeolite. The results showed that the catalyst was ferromagnetic, and it could be recovered by magnetic separation. Catalyst characterization was carried out by X-ray diffraction and scanning electron microscopy. The effects of various parameters such as the catalyst loading, the molar ratio of methanol to oil and the reaction time on the activity of catalyst were determined by the transesterification of canola oil to biodiesel. The yield of methyl esters (ME) was 95.1 over a catalyst loading of 5 wt.% (30 wt.% of CaO on magnetic NaY), 8:1 methanol to oil molar ratio, and a reaction time of 5 h at the reaction temperature of 65 °C.

Keywords: Nano-magnetic catalyst, CaO/NaY, Transesterification, biodiesel production, canola oil

Introduction

Biodiesel is a renewable fuel consisting of fatty acid methyl esters (FAME) derived through transestrification of vegetable oils, animal fats and used oil with a short chain alcohol. Biodiesel is a green fuel for this reason; it is safe, non-toxic and decreases greatly diffusion of Co, SO_x, hydrocarbons, particle matter, polyaromatics and smoke compared to the diesel fuels. Homogeneous base catalysts such as KOH [1], NaOH [2], and sodium methoxide [3] are the most popular catalyst in production of biodiesel. They get yields of 97-99% in 0.5-1 h [3]. Theses homogeneous catalysts have some disadvantages such (1) they cannot be reused, (2) they produce large amounts waste water that increase the final production cost [4]. Many heterogeneous catalysts for refining biodiesel have been developed. Among metal oxides, calcium oxide is most convectional because it can be synthesized from cheap sources; it is non-toxic, have mild reaction condition, high activity, it possess basicity as high as alkali metal oxides while it showed less leaching of active sites into the product stream [5]. However, the specific surface area of CaO is usually small, also pure CaO is easy to form gels in methanol, so the activity of CaO is affected. For example, Granados et al [6] found that pure CaO was partially soluble in methanol and a larger amount of leached Ca^{2+} ions was observed in the glycerol phase. In order to address these problems, some composite catalysts have been synthesized to enhance the stability of CaO, including MgO-CaO mixed oxides [7]. Different alkali metal compounds supported on alumina or zeolit were demonstrated as effective solid base catalysts for the transestrification of vegetable oils [8,9]. Zeolit exhibits no activity, but when loaded with NaOH, KNO_3, KF, KI or K_2CO_3 and activated at high temperatures, the supported solid catalysts show high catalytic activities. Also it is found that the support has an effect on the activity of the heterogeneous catalyst [10]. In this study, CaO as active component on zeolit support was synthesized. Scattering of CaO on the big surface of NaY zeolite raise the basicity and base strength of CaO, thus improve the activity of CaO catalyst in the transestrification process.

The basic reaction could be represented in Fig. 1.

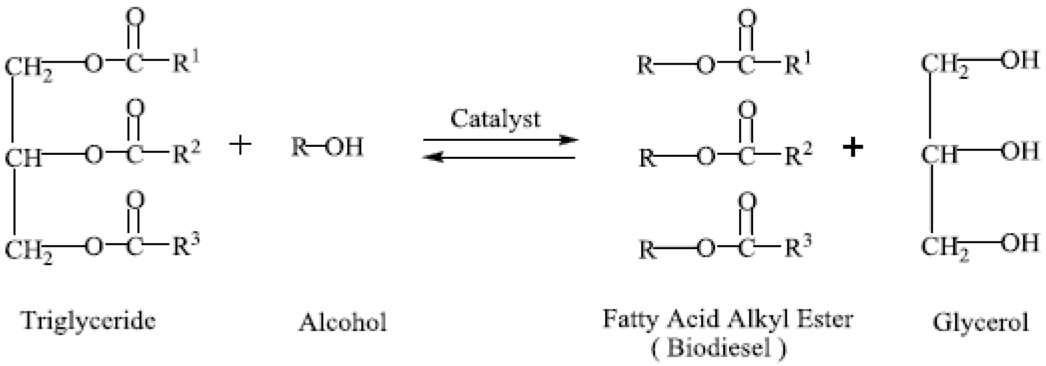

Fig. 1. Reaction scheme for oil transestrification.

2. Experimental

2.1. Materials

All of the reagents used, were supplied from Merck company. The refined canola oil was purchased from sabus mazand oil factory. The properties of canola oil used in the transestrification reaction are given in Table 1.

Starting materials were colloidal silica (Ludox, 30 wt.%), sodium aluminate ($NaAlO_2$, Al_2O_3 wt.% =55), sodium hydroxide (NaOH, 97 wt.%), the organic additive TMAOH (25% TMA solutions), Calcium oxide, methanol (>99wt%), FeSO4.7 H2O, FeCl3 6 H2O, and Canola oil.

Table 1.Fatty acid composition of canola oil

Fatty acids	Composition %
Palmitic acid (C16:0)	6.69
Steraric acid (C18:0)	2.99
Oleic acid (C18:1)	57.15
Linoleic acid (C18:2)	21.8
Linolenic acid(C20:0)	0.79
Arachidic acid(C22:1)	0.23
Orcat acid (C18:3)	7.69
Others	2.66

2.2. Synthesis of NaY

The molar composition of the gel used for NaY zeolites nanoparticles synthesis was 4Na2O:1.0Al2O3:6SiO2:200H2O:5TMAOH [11]. First, a mixture of NaOH, sodium aluminate and template and distilled water was prepared. Then, ludox was added dropwise to the reaction mixture. The initial gel system was subjected to a three-stage crystallization to form NaY aggregate particles. In the first stage (initial aging), the content of the bottle was aged at room temperature for 48–120 h without any stirring. In the second stage, the aged precursor was moved into a preheated oven set at 50 °C and further aged for another 24–48 h. In the third and final stage, the precursor gel was hydrothermally treated at 100 °C for 30 h. All the products were readily recovered by centrifugation, followed by washing with DI water until pH became natural. Then dried at 110 °C , then calcined at 550 °C for 8 h.

2.3. Catalyst preparation (magnetic zeolite NaY)

The composites were prepared from a suspension of NaY zeolite in 400 mL solution of $FeCl_3$ (7.8 g, 28 mmol) and $FeSO_4$ (3.9 g, 14 mmol) at 70 °C. A solution of NaOH (100 mL, 5 $molL^{-1}$) was added dropwise to precipitate the iron oxides [12]. The amount of zeolite was adjusted in order to obtain the zeolite/iron oxide weight ratio of 3:1.

2.4. Preparation of magnetic CaO/NaY-Fe_3O_4

The magnetic NaY zeolite was calcined at 550 °C for 8 h, using a 3.5 °C/min ramp, to eliminate any adsorbed water. Zeolite was then impregnated with a mixure of CaO nanoparticles/ethanol for 60 min in an ultrasonic bath, following the method proposed by Agranovski et al [13]. The solvent was removed by evaporation under vacuum. The catalysts were then dried overnight at 120 °C and calcined at 600 °C for 4 h. CaO nanoparticles concentration onto the zeolite surface was varied in 30 wt % of CaO per zeolite weight.

2.6. Transestrification reaction

The canola oil transestrification process was carried out in a 100 ml continuously stirred spherical reactor coupled to a condensation with oil bath. The mechaninal stirring rate was 800 rpm. The reaction procedure was as follows:

First, the catalyst was dispersed in methanol under stirring in an oil bath at room temperature for an hour, then, the canola oil was added into the mixture and heated to reaction temperature (65 °C). After the reaction, the mixture was collected, the catalyst was isolated by a permanent magnet and the residual methanol was separated from the upper liquid phase (the lower phase is glycerin) via evaporation. The upper layer was collected for further purification. It was washed with DI water at 40-50 °C in decanter. The water is denser than biodiesel and it was collected from the bottom of decanter, the water was added until the pH of inlet water and outlet water became the same. After the evaporation of excess water at 110 °C , the methyl esters were quantified using a GC.

The yield of biodiesel was calculated according to [14]:

$$Yield\ (\%) = \frac{M_1 \times f}{M_2} \times 100 \qquad (1)$$

where M1 is the mass of the top phase obtained after phase separation, f is the percentage of ME content in the top phase obtained by the GC analysis, and M2 is the mass of canola oil used.

Reults and discussion

Powder X-ray diffraction measurements were conducted on a XPERT-PRO diffractometer using a radiation source of Cu Kα. Data were collected over a 2θ range of 5-80° with a step size of 0.02. The X-ray diffraction (XRD) phases and the nanosize of the catalysts were identified using the powder diffraction file. Fig. 2 shows the XRD patterns of two catalysts. The peaks at 2θ = 6.23, 10.23, 12, 15.56, 23.48, 27.558, 32.19 confirmed NaY zeolite. Fig. 2 also shows the XRD patterns of CaO/NaY-Fe_3O_4. Note that the peaks of zeolite without CaO nanoparticles appear at the same angle than zeolite with CaO. This suggests that the introduction of the oxide into the zeolite does not substantially affect the crystalline structure of the faujasite, even after calcination. Characteristic CaO peaks were obtained at 36°, 39.5°, 29.5°, 32°, and 53.5°. The some of peaks are superimposed with NaY zeolite typical peaks.

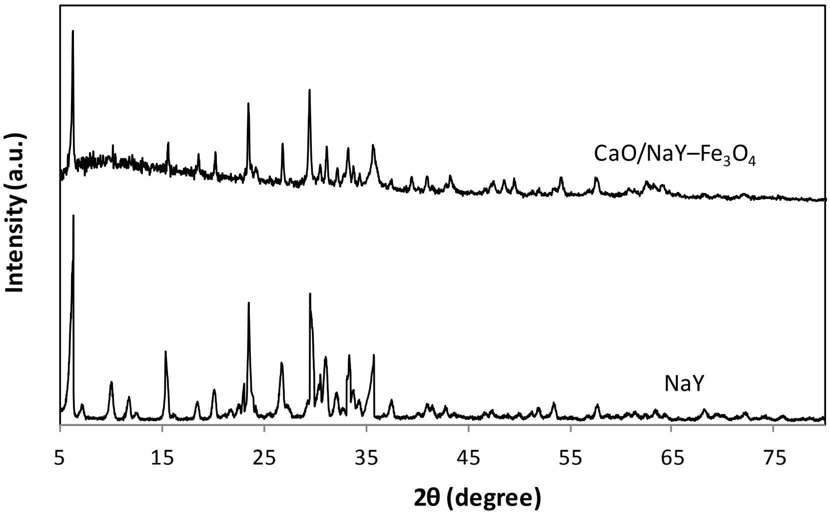

Fig. 2. XRD pattern of NaY and CaO/NaY-Fe3O4.

The surface morphology of the catalyst particle characterized using scanning electron microscopy (SEM) (Zeiss) operating at 15 kV accelerating voltage is shown in Fig. 3.

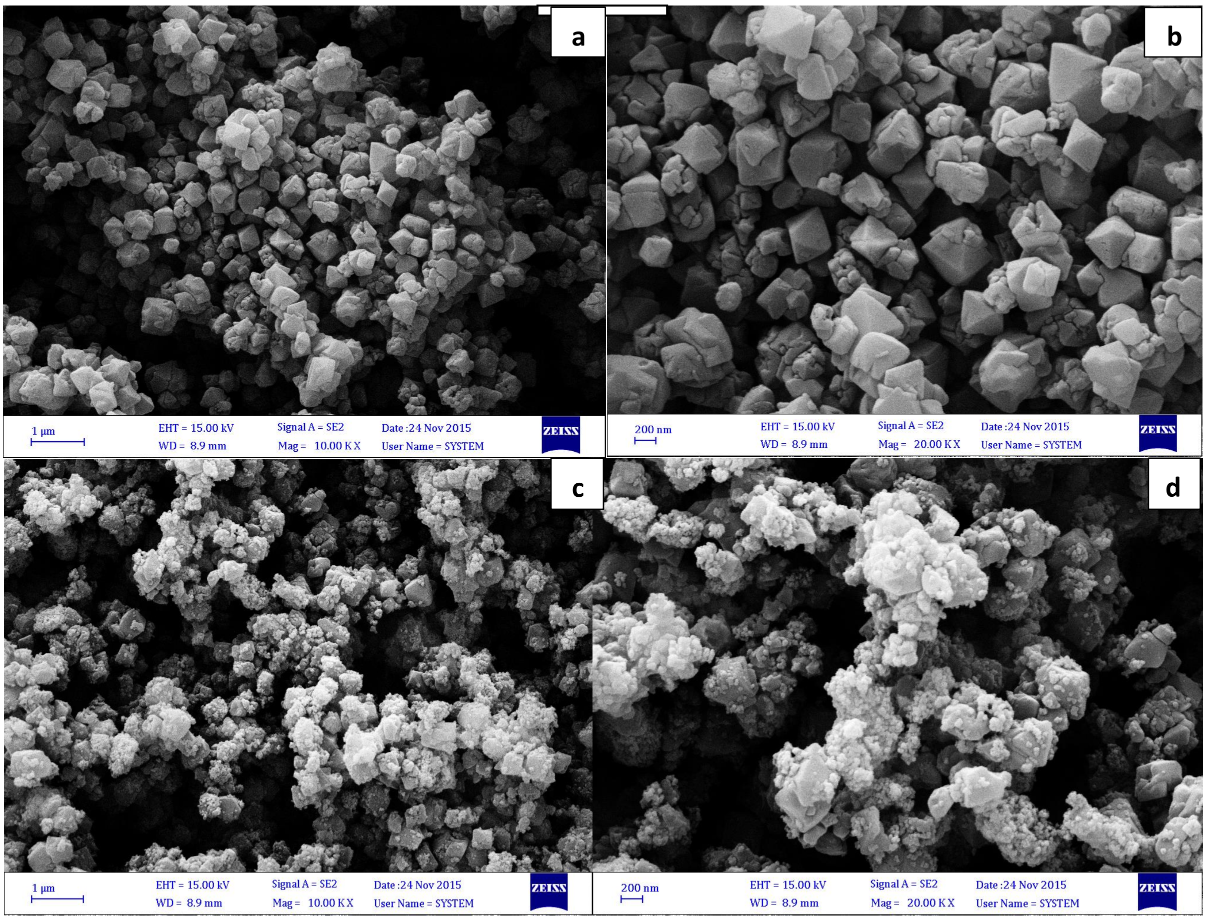

Fig. 3. (a, b) SEM image of NaY, (c, d) SEM image of CaO/NaY-Fe_3O_4.

3.2. Optimization of reaction conditions on the transesterification of canola oil

3.2.1. Effect of catalyst loading

Catalyst amount is an important parameter which affects the conversion of triglycerides to methyl esters. The effect of the catalyst loading on the biodiesel yield was also investigated by varying the catalyst mass ratio from 3 to 10 wt.% (based on the weight of oil). The results are shown in Fig. 4. From this figure, it can be noted that an increase in the mass of catalyst loading from 3 wt% to 5 wt% causes a marked increase of yield of triglyceride from 71.37% to 95.1%. Further increase in the mass of catalyst loading from 5 wt% to 10 wt% causes a decrease of yield of triglyceride.

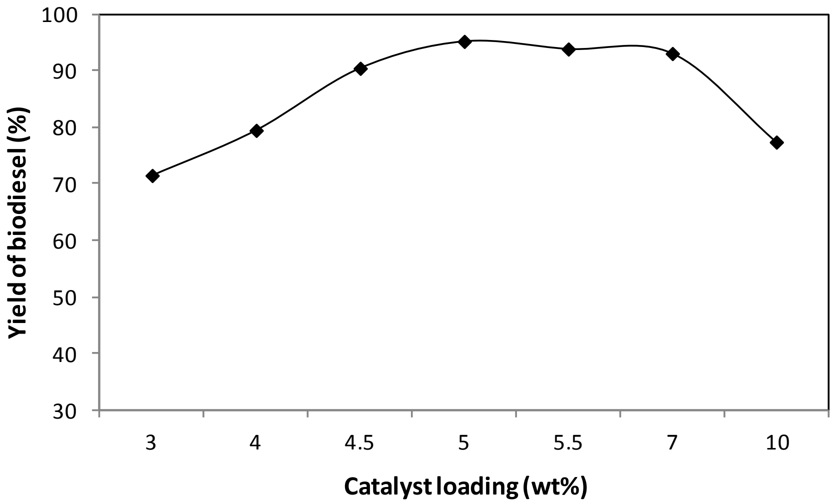

Fig. 4. Effect of catalyst loading on the biodiesel yield. Conditions for CaO/NaY-Fe_3O_4 catalyst: temperature: 65 °C; methanol-to-oil molar ratio: 8; reaction time: 7 h.

3.2.2. Effect of molar ratio of methanol/canola oil

Since the transesterification is a reversible reaction, in the reaction mixture, the mole of methanol must be excess enough to force the reaction towards the formation of the FAME. The effect of the molar ratio of methanol to triglyceride on the yields of FAME was examined by varying the amount of methanol with a fixed amount of soybean oil and catalyst and time of reaction .The initial amount of methanol was set at 6, 8, and 10 mol ratio, respectively. The results are shown in Fig. 5. The yield of triglyceride increased with increasing methanol addition. When the molar ratio of methanol/soybean oil was 8, the yield of triglyceride reached in 93.75%. The excess of methanol is favorable to the yield of triglycerides into monoglycerides, but there is also a slight recombination of FAME and glycerol to form monoglycerides. The FAME and the byproduct glycerol are nearly immiscible, but monoglyceride can significantly effect on glycerol solubility in FAME, so the glycerolysis of FAME will occur, and then decreased the triglycerides conversion. From above analysis, the molar ratio of methanol to triglyceride cannot be too high.

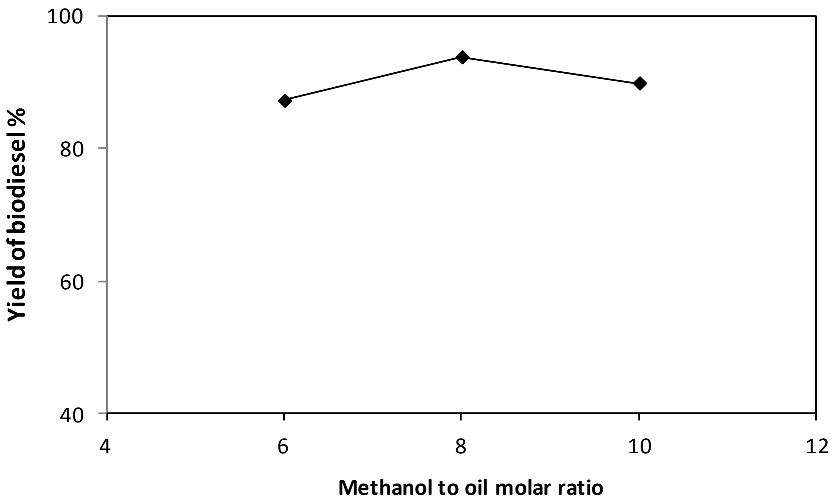

Fig. 5. Effect of molar ratio of methanol to oil on the biodiesel yield. Conditions for CaO/NaY-Fe_3O_4 catalyst: temperature: 65 °C; catalyst loading of 5.5 wt%; reaction time: 5 h.

3.2.3. Effect of reaction time

Under the given conditions (65 °C, methanol/oil molar ratio of 8, 5.5 wt% catalyst), biodiesel yield was almost unchanged (89-93.75%) by changing the time from 4-7 hours. The results are shown in Fig. 6. From this figure, it can be noticed that an increase in the reaction time from 4 until 5 hours causes a marked increase of yield (5 hour is the optimum time for the reaction). Further increase in the reaction time from 4 to 7 hours, causes a less effect on the conversion of triglyceride.

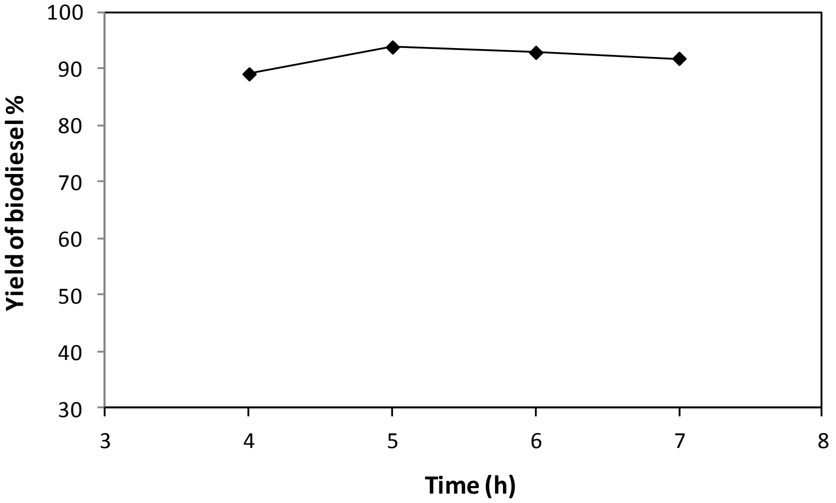

Fig. 5. Effect of molar reaction time on the biodiesel yield. Conditions for CaO/NaY-Fe_3O_4 catalyst: temperature: 65 °C; catalyst loading of 5.5 wt%; m/o: 8.

Conclusions

A new heterogeneous catalyst (CaO/NaY-Fe_3O_4) has been successfully prepared and characterized for the transesterification of canola oil. It has been confirmed that high methyl esters content is strongly correlated with the basicity of the employed catalyst. A high methyl esters content (87-95%) can be obtained by the prepared catalyst under mild conditions (reaction temperature 65 °C and atmospheric pressure). The catalyst with 30 wt.% CaO loading on magnetic NaY was found to be the optimum catalyst, which gave the best catalytic activity. Under the optimal conditions 8:1 molar ratio of methanol to oil, a catalyst amount of 5 wt.% and 65 °C, the biodiesel yield exceeded 95.1 after 5 h of reaction. This catalyst seems promising for biodiesel production.

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