

Nano-magnetic catalyst KF/CaO–Fe₃O₄ for biodiesel production

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ABSTRACT

A nano-magnetic catalyst KF/CaO–Fe₃O₄ was prepared by a facile impregnation method. The magnetic property of the catalyst was studied by vibrating sample magnetometer (VSM). The results demonstrated that the catalyst was ferromagnetic, and it could be recovered by magnetic separation. The nano-magnetic catalyst was also characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and BET surface area analyzer. It was found that the catalyst possessed a unique porous structure with an average particle diameter of ca. 50 nm. Besides, the factors affecting biodiesel yield were investigated, and a desired fatty acid methyl esters yield over 95% was obtained under the optimal conditions.

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1. Introduction

Due to the exhaustion of fossil resources and the increasing emissions of polluting, many studies are now being directed towards the exploitation of alternative renewable fuel [1–3]. Biodiesel, defined as the fatty acid methyl esters, has attracted great attentions in recent years as one of the most potential substituted energy resources [4].

Biodiesel is typically produced by reacting a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to form methyl or ethyl esters and glycerin [5–7]. Conventionally, the transesterification was carried out with homogeneous base catalysts as catalyst such as potassium methoxide and potassium hydroxide because of their high activity and conversion. The advantage of this process is production of methyl esters at very high yields under mild conditions and reaction generally takes about an hour for completion. Both edible and non-edible such as sunflower oil, palm oil and jatropha oil have been transesterified for biodiesel production. However, the separation of catalyst and the purification of products are time-consuming and expensive accompanied with a large volume of chemical wastewater [8,9].

In order to circumvent the difficulties with homogeneous catalysts, many researches have been conducted in search for ideal solid catalysts that have high stability, strong active sites, mesoporous and low cost [10–15]. Despite the solid catalysts are intensively investigated, there are still many difficulties for industrial applications [16]. One primary problem of solid catalyst is still the separation of the mixture related to the reuse of the catalyst

after filtration through the membrane [17,18]. Therefore, it is important to investigate easily recoverable and recyclable heterogeneous catalysts for transesterification.

To overcome these challenges, the nano-magnetic catalyst may be a better choice because the magnetic separation generally avoids loss of catalyst and increases its reusability in comparison to filtration or centrifugation [19,20]. Additionally, as nano-catalyst with large specific surface area and high catalytic activity, the nano-magnetic catalyst also exhibits good catalytic property. Magnetic or nano-magnetic catalyst has been applied widely in the fields of photocatalysis [21], biocatalysis [22], and phase-transfer catalysis [23]. There are, however, only a few reports on nano-magnetic catalysts used as transesterification catalysts. Ying and Chen [24] have stabilized the cells of lipase-producing *Bacillus subtilis* on the net of hydrophobic carrier with magnetic particles (Fe₃O₄) for the transesterification of waste cooking oils with methanol. Xie and Ma [25] have immobilized lipase on Fe₃O₄ nanoparticles as catalyst for biodiesel production. The both catalysts not only have high catalytic activity, but also show the advantages of easy separation and reuse. In previous work, we reported a nano-catalyst KF/CaO in the transesterification of Chinese tallow oil with methanol for biodiesel production [26]. The catalyst has high catalytic activity, high resistance to saponification, good rigidity and favorable acidoresistance. But we find that it is difficult to separate the catalyst rapidly and the recycle process of catalyst is complex.

In this paper, a nano-magnetic solid base catalyst KF/CaO–Fe₃O₄ was synthesized and used as catalyst for transesterification. The catalyst was characterized by TGA, TEM, XRD, Raman, AAS, BET surface area analyzer and VSM. The catalytic activity was evaluated using the transesterification of Stillingia oil, extracted from the seeds of Chinese tallow (*Sapium sebiferum*). The influence of various factors on the biodiesel yield was also investigated.

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2. Experimental

2.1. Preparation of nano-magnetic solid catalyst

Magnetic core was prepared by a convenient co-precipitation method based on literature with some modifications [27]. Briefly, 27.8 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 79.6 g of $\text{Fe}_2(\text{SO}_4)_3$ were dissolved in 1000 mL of deionized water, $\text{NH}_3 \cdot \text{H}_2\text{O}$ was then added dropwise to the solution in a water bath of 65 °C and with vigorous stirring for 30 min. The final pH value of the aqueous solution was maintained at about 12.0. Then the mixture was aged for 60 min. The black solid was separated by a permanent magnet and washed with distilled water until the pH value of filtrate decreased to 7.0. After dried at 60 °C for 24 h, the precipitate was pulverized.

Nano-magnetic solid base catalyst was prepared by an impregnation method. Briefly, 5.0 g of Fe_3O_4 and 100.0 g of MOs (MgO, CaO and SrO) was fully mixed. Then the mixture was completely dipped in aqueous solution of KF with different mass in range of 5.0–45.0 g (ca. 5–45 wt.% of KF loading) and subsequently dried at 105 °C for 24 h. Finally, the dried material was calcined in temperatures range of 300–800 °C in muffle furnace. The final catalyst was stored in a desiccator.

2.2. Characterization of nano-magnetic solid catalyst

The thermal stability of catalyst was examined using NETZSH TG 209C (Germany) from room-temperature to 900 °C under an inert nitrogen atmosphere and a heating rate of 10 °C min^{-1} . Transmission electron microscopy (TEM) was recorded on a JEM-100CXII electron microscope (Hitachi, Japan). The samples were dispersed in ethanol and then treated ultrasonically in order to disperse individual particles over a copper grid. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-RB diffractometer (Rigaku, Japan) under the following conditions: $\text{FeK } \alpha$ radiation ($\lambda = 1.9373 \text{ \AA}$), tube voltage of 36 kV, a tube current of 20 mA and the count time of 0.2 s per 0.02° in the range of 10–90°. Laser Raman spectroscopic measurements were performed on a Renishaw inVia Raman spectrometer (Renishaw, UK) equipped with an integral microscope (Olympus). The excitation source was Ar laser (633 nm), focused with a 50× long-local-length objective microscope and providing a power of 20 mW on the sample. BET surface area was measured with a Quantachrome Autosorb-1-C chemisorption–physisorption analyzer (America). A weighed sample of the catalyst was prepared by outgassing for 6 h at 180 °C on the degas port. The surface area was calculated using the BET equation over the pressure range $P/P_0 = 0.05\text{--}0.30$. The KBr pellet technique was applied for determining FT-IR spectra of the samples. Spectra were recorded on a Nicolet AVATAR-330 spectrometer (America) with 4 cm^{-1} resolution. Magnetization curve were measured on a vibrating sample magnetometer (VSM, Nanjing, China) with a magnetic field of 15,000 Oe.

2.3. Reaction procedure

Stillingia oil was purchased from Dawu County, Hubei Province, PR China. The average molecular weight of Stillingia oil is 896 g mol^{-1} . The fatty acid composition consists of 0.21% myristic acid, 7.51% palmitic acid, 2.60% stearic acid, 16.50% oleic acid, 32.75% linoleic acid, 39.36% linolenic acid and traces of other acids. All experiments were performed in a 100 mL glass reactor equipped with a condenser and a mechanical stirrer. In a typical reaction, 25.0 g of Stillingia oil was added into a mixture of 1.0 g of nano-magnetic solid base catalyst and 13.4 mL of anhydrous methanol (methanol/oil molar ratio 12:1). The mixture was refluxed at 65 °C, with mechanical stirring for 3 h. After the reaction,

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 rotary evaporation.

The biodiesel was quantitative analyzed in the presence of methyl salicylate as internal standard by GC using HITACHI163 gas chromatography instrument. The oven temperature was programmed from 190 °C to 280 °C at an increasing rate of 10 °C min^{-1} and held at 280 °C for 6 min. The injector and detector temperatures were 300 °C. The flow rate of N_2 , H_2 and air were 25, 40 and 400 mL min^{-1} , respectively. The split ratio was 30:1. The mass concentration of biodiesel was obtained by the GC and the yield of biodiesel was calculated by the following equation:

$$\text{Yield} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\% \\ \approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100\% \approx \frac{C_{\text{esters}} \times n}{\rho_{\text{oil}}} \times 100\%$$

where both m_{actual} (g) and $m_{\text{theoretical}}$ (g) are the actual mass and theoretical mass of biodiesel; m_{oil} (g) is the mass of Stillingia oil; n is the diluted multiple of biodiesel; C_{esters} (g mL^{-1}) is the mass concentration of biodiesel; ρ_{oil} (g mL^{-1}) is the density of Stillingia oil; V_{esters} (mL) and V_{oil} (mL) are the volumes of biodiesel and Stillingia oil, respectively [28].

3. Results and discussion

3.1. Influence of preparation conditions on catalytic activity

The catalytic activity of a series of catalysts was evaluated in the transesterification of Stillingia oil with methanol as model reaction. Various parameters such as KF loading and calcination temperature have been investigated to achieve the maximum catalytic activity.

To investigate the influence of the KF loading on catalytic activity, a series of catalysts were prepared at different KF loading (all samples were calcined at 600 °C for 3 h). Fig. 1a shows the results regarding the effect of KF loading on the catalytic activity. For KF/CaO- Fe_3O_4 , the biodiesel yield is improved from 78% to 95% when the KF loading increases from 15 wt.% to 25 wt.%. It can be assumed from this results that the active sites of catalyst surface increase with increasing the loading of KF. When the KF loading is beyond 25 wt.%, however, the activity of catalyst is decreased with the increase of loading of KF, and the biodiesel yield is only 81.1% at 45 wt.% KF loading. This is probably due to the fact that the excessive KF covers the active sites of catalyst surface, resulting in the decrease of catalytic activity [26]. Similar trends are also observed with other both KF/MgO- Fe_3O_4 and KF/SrO- Fe_3O_4 nano-magnetic catalysts. The biodiesel yield increases with the increase of KF loading, and then the highest yield is obtained when the loading of KF to MgO and SrO are 10 wt.% and 35 wt.%. Subsequently, the yield is obviously decreased with the increase of loading of KF. It is possible that the excessive KF covers the active sites of catalyst surface, which in turn leads to the decrease of catalytic activity. Therefore, the optimum loading of KF to CaO, MgO and SrO are 25 wt.%, 10 wt.% and 35 wt.% in this study, respectively.

Another important parameter to be optimized is the calcination temperature. In the preparation process of catalyst, calcination treatment of catalyst at high temperature is favorable for the interaction between support and active ingredient, which generates new active sites for the catalyst. Therefore, calcination temperature is crucial for increasing the catalytic activity. Fig. 1b demonstrates the results concerning influence of calcination temperature on the catalytic activity of three catalysts. Obviously, the biodiesel yield initially increases with the increase of the calcination temperature. Then, the yield reaches the maximum value at 600 °C, 600 °C, and

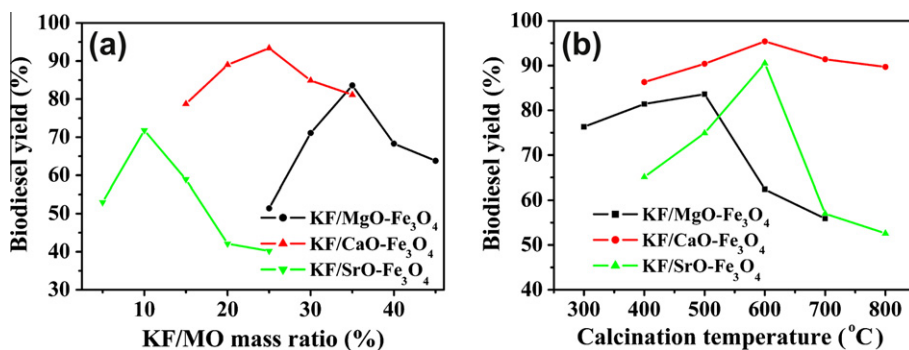


Fig. 1. Effects of (a) loading KF; (b) calcination temperature on activity of KF/CaO-Fe₃O₄ nano-magnetic solid base catalyst. Transesterification conditions: 25.0 g of *Stillingia* oil, 13.4 mL of anhydrous methanol, 1.0 g of catalyst, 65 °C of reaction temperature, 3 h of reaction time.

500 °C for KF/CaO-Fe₃O₄, KF/SrO-Fe₃O₄ and KF/MgO-Fe₃O₄, respectively. However, the biodiesel yield decreases gradually with further increasing the calcination temperature. This is probably due to the fact that overheating result in the surface sintering and the reduction of specific surface area, which in turn leads to the decrease of catalytic activity [16]. The current results indicate that the optimal calcination temperature is 600 °C, 600 °C, and 500 °C for KF/CaO-Fe₃O₄, KF/SrO-Fe₃O₄ and KF/MgO-Fe₃O₄, respectively.

3.2. Reaction procedure

KF/CaO-Fe₃O₄ was utilized to catalyze transesterification of *Stillingia* oil with methanol for biodiesel production. The reactions were carried out at 65 °C for 3 h, with 25.0 g of *Stillingia* oil, 13.4 mL of anhydrous methanol (methanol/oil molar ratio of 12:1) and 1.0 g of catalyst. For comparison purpose, CaO, KF/CaO, KF/MgO-Fe₃O₄ and KF/SrO-Fe₃O₄ were also used to catalyze transesterification of *Stillingia* oil with methanol. The results are illustrated in Table 1. It is found that KF/CaO-Fe₃O₄ shows higher catalytic activity as compared to KF/MgO-Fe₃O₄ and KF/SrO-Fe₃O₄. The catalytic activity is in accordance with the surface area of the catalysts. Whilst, it is also found that the Fe₃O₄ magnetic core almost no impact on the catalytic activity of KF/CaO-Fe₃O₄ against that of KF/CaO.

3.3. Structural characterization

Fig. 2 illustrates the thermo-gravimetric analysis (TGA) curves of CaO-Fe₃O₄ and KF/CaO-Fe₃O₄ obtained in nitrogen. TGA curve of CaO-Fe₃O₄ presents two events, one at 350–451 °C, associated with the crystal water loss, and another at 509–674 °C which is attributed to the decomposition of Ca(OH)₂. The loss weight of two events is 19.5% and 8.4%, respectively. TGA curve of KF/CaO-Fe₃O₄ also displays two loss weight peaks, at 350–451 °C and 688–749 °C, corresponding to the crystal water loss (16.3%) and sintering of the preformed compound (2.9%) respectively. The results of the thermal analysis suggest that the best calcination tem-

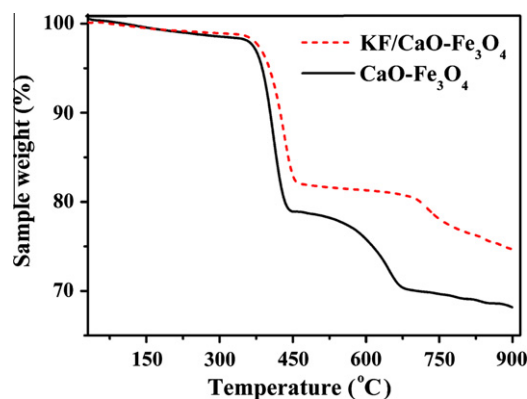


Fig. 2. TGA of CaO-Fe₃O₄ and KF/CaO-Fe₃O₄.

perature of nano-magnetic solid base catalyst is in the range of 509–688 °C.

The nano-magnetic solid catalysts are further probed by powder XRD (Fig. 3). Before calcined (curve a in Fig. 3b), the catalyst is composed of CaO (32.3°, 37.4°, 53.9°, 64.2°), Ca(OH)₂ (18°, 29°, 47.2°, 63°) and KF (34.1°, 71.8°). After calcined (curve b in Fig. 3b) at 600 °C, the diffraction peaks of Ca(OH)₂ and KF disappear, and a new diffraction peak of KCaF₃ (20°, 28.4°, 35°, 40.5°, 79.7°) emerges. The newly formed crystal phase is favorable for enhancing the catalytic activity and stability of catalyst [26]. Other both nano-magnetic catalysts, KF/MgO-Fe₃O₄ and KF/SrO-Fe₃O₄, are characterized by powder XRD (Fig. 3a and c). As can be seen, when the both catalysts are calcined at high temperature, laden KF also react with MgO or SrO to form stable crystal phase. In order to explain the effect of calcination temperature, we further investigated the calcination process of nano-magnetic catalyst with Raman (unshown). The results obtained with Raman are well consistent with that of XRD.

Fig. 4 depicts the TEM image of KF/CaO-Fe₃O₄. The catalyst has a unique porous structure with an average particle diameter of ca. 50 nm (Fig. 4A and C). The presence of microstructures explains its high catalytic activity. The catalytic activity is further confirmed by the large BET surface area of 20.8 m² g⁻¹ for KF/CaO-Fe₃O₄ versus only 4.6 m² g⁻¹ for CaO. The magnetic cores are well encapsulated in the catalyst (Fig. 4B), which are beneficial to the separation of the catalyst (Fig. 5b and c). The same results have also been got in the FT-IR spectra of nano-magnetic catalyst KF/CaO-Fe₃O₄ (unshown). The IR absorption peaks observed at 576 cm⁻¹ is characteristic peak of Fe₃O₄. The magnetization curve demonstrates that the catalyst has the ferromagnetic behavior characteristic with little remanence and coercive force (Fig. 5a).

Table 1
BET surface area, pore diameter and catalytic activity of catalysts.

Catalysts	S _{BET} (m ² g ⁻¹)	d _{pore} (nm)	Yield (%)
CaO (600 °C calcined)	4.6	8.6	85.9
KF/CaO (600 °C calcined)	19.2	39.4	96.8
KF/CaO-Fe ₃ O ₄ (600 °C calcined)	20.8	42.0	95.0
KF/MgO-Fe ₃ O ₄ (500 °C calcined)	4.1	13.7	83.6
KF/SrO-Fe ₃ O ₄ (600 °C calcined)	5.9	21.3	87.6

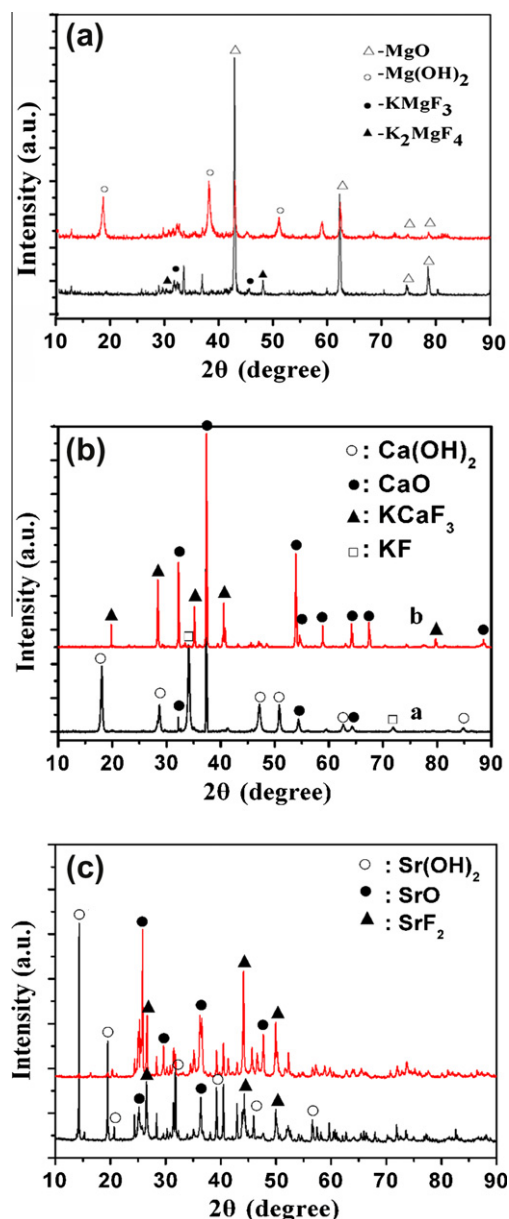


Fig. 3. XRD patterns of nano-magnetic catalysts before and after calcination. (a) KF/MgO-Fe₃O₄; (b) KF/CaO-Fe₃O₄; (c) KF/SrO-Fe₃O₄.

3.4. Stability of nano-magnetic catalyst

The stability test of nano-magnetic catalysts was carried out by dissolving catalyst in methanol. After removal of the catalysts, free M²⁺ (Ca, Mg and Sr) concentration in the biodiesel was analyzed with atomic absorption spectrometry. The results display that free M²⁺ (Ca, Mg and Sr) concentration in methanol is 30 ppm, 24 ppm and 83 ppm for KF/CaO-Fe₃O₄, KF/MgO-Fe₃O₄ and KF/SrO-Fe₃O₄, respectively. For pure KCaF₃, however, the Ca²⁺ has hardly been observed (free Ca²⁺ concentration in methanol is less than 1 ppm), indicating the KCaF₃ has excellent stability in methanol. Compared with CaO (167 ppm Ca²⁺), KF/CaO-Fe₃O₄ catalyst is more stable in methanol. The result demonstrates that KCaF₃ converted into KF and CaO at high temperature can inhibit obviously the leaching of CaO from catalyst. Similar results are also obtained for other both KF/MgO-Fe₃O₄ and KF/SrO-Fe₃O₄ nano-magnetic catalysts. Mg²⁺ and Sr²⁺ concentration in methanol is 133 ppm and 347 ppm for MgO and SrO. By loading KF, the stability of both catalysts is improved notably, which is attributed to the new crystal phase converted into KF and MO at high temperature. These results consist with the previous XRD characterization.

3.5. Water-tolerant of the nano-magnetic catalyst

In the base-catalyzed transesterification of *Stillingia* oil to biodiesel, water has important effects on biodiesel yield. As shown in Fig. 6, the yield of biodiesel is increased from 82% to 95% when water content increases from 0.5 wt.% to 2.7 wt.%. This is probably due to the fact that water molecules are adsorbed firstly on the catalyst surface to form OH⁻. Then, the surface OH⁻ abstracts proton from methanol to generate CH₃O⁻. Certainly, the catalyst can also abstract H⁺ from methanol to form CH₃O⁻. But the OH⁻ is more easily adsorbed on the surface of catalyst than CH₃O⁻ [29]. Therefore, by adding a little water (no more than 2.7 wt.%), the reaction rate can be accelerated and the yield of biodiesel is improved in a short time. When the water content is beyond 2.7 wt.%, the biodiesel yield decreases with the increase of water content, and the biodiesel yield is only 80% at 3.1 wt.% water content. Therefore, the water content in oil should be kept under 2.7 wt.% to prevent catalyst deterioration and biodiesel hydrolysis.

3.6. Reusability and recovery of the nano-magnetic solid base catalyst

The reusability of KF/CaO-Fe₃O₄ was examined by carrying out reaction cycles. The catalyst, after 3 h transesterification, was separated by a permanent magnet. Then it was washed with anhy-

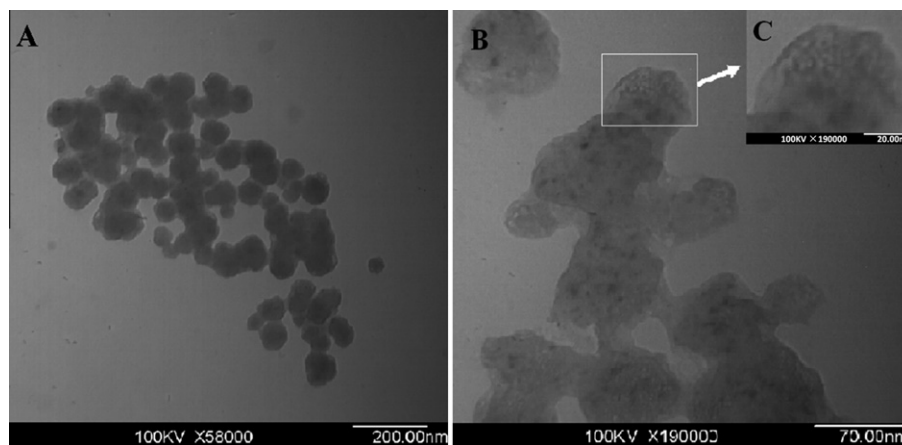


Fig. 4. TEM image of the catalyst; B magnified images from A; C magnified images from B.

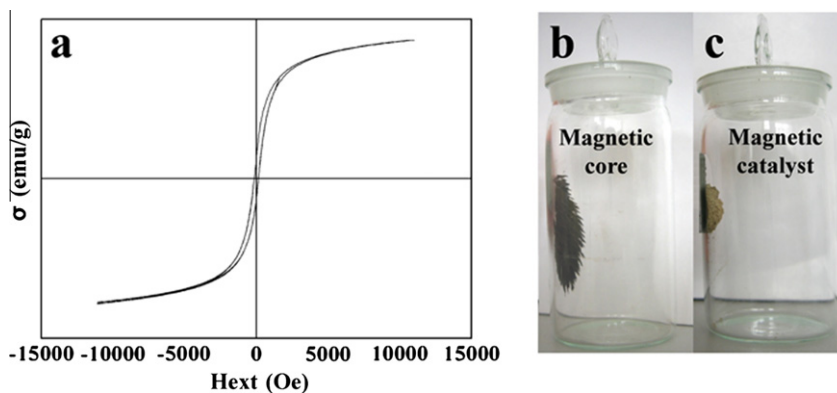


Fig. 5. Magnetization curve of KF/CaO-Fe₃O₄ (a); photographs of magnetic core (b) and KF/CaO-Fe₃O₄ (c).

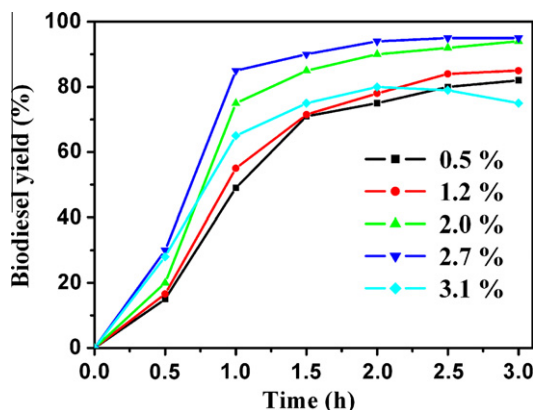


Fig. 6. Effects of water on biodiesel yield. Transesterification conditions: 25.0 g of Stillingia oil, 13.4 mL of anhydrous methanol, 1.0 g of catalyst, 65 °C of reaction temperature, 3 h of reaction time.

drous methanol and dried at 105 °C for calculating the catalyst recovery (catalyst recovery is defined as the percent of the mass of collected catalyst relative to that of fresh catalyst). The dried catalyst was used subsequently in a second reaction cycle under the same reaction conditions as before. Results for all consecutive reaction cycles are given in Fig. 7. It is found that the catalyst maintains sustained catalytic activity even after being reused for 14 times and the catalyst is reduced about 10 wt.%. After 16 times of reuse, however, the catalyst loses activity seriously. Although the catalyst

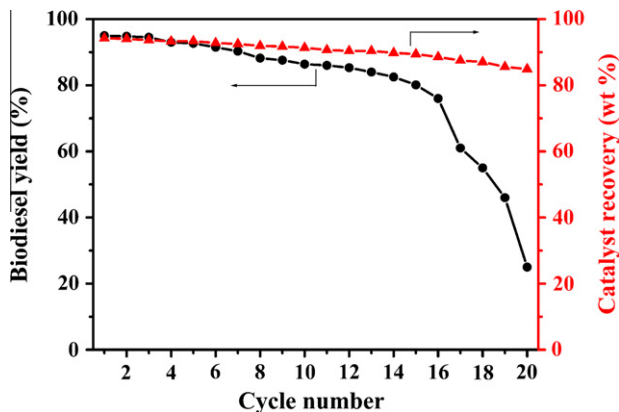


Fig. 7. Reusability and recovery of KF/CaO-Fe₃O₄. Transesterification conditions: 25.0 g of Stillingia oil, 13.4 mL of anhydrous methanol, 1.0 g of catalyst, 70 °C of reaction temperature, 3 h of reaction time.

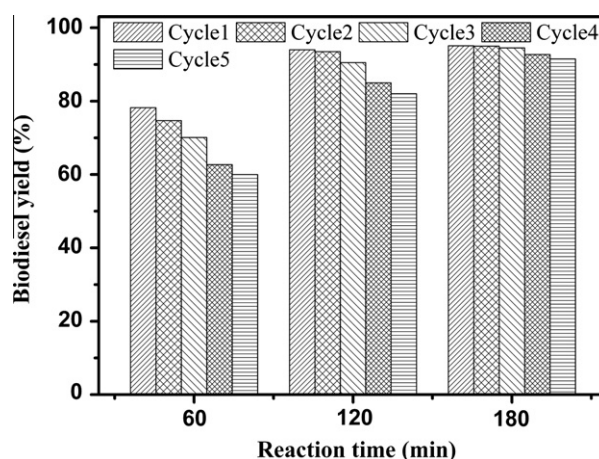


Fig. 8. Change of reaction rate with reaction time. Transesterification conditions: 25.0 g of Stillingia oil, 13.4 mL of anhydrous methanol, 1.0 g of catalyst, 70 °C of reaction temperature, 3 h of reaction time.

is reduced again from 90.2 wt.% to 84.4 wt.%, catalyst deterioration was probably due to its failure to maintain the formation of CaO [30].

The change of reaction rate with reaction time at the first five recycling is given in Fig. 8. As can be seen, the initial rate of transesterification of Stillingia oil with methanol decreases gradually with each reaction cycle. This is probably due to the loss of active components in the process of reaction and separation. With the continuation of reaction, the yield of biodiesel nearly reached the fresh catalyst level finally.

In contrast to the catalytic behavior, the catalyst maintains a high recovery. It can be observed in Fig. 7 that, after 14 times of reuse, catalyst recovery is more than 90%. And after 20 times, the recovery still can reach more than 84%, indicating the current nano-magnetic catalyst can be separated by magnetic separation technology. The decrease in recovery is probably related to both facts: the dissolution of catalyst and the loss of catalyst in the middle of the collecting operation. According to our experimental results, nano-magnetic catalyst KF/CaO-Fe₃O₄ exhibits good durability and high recovery.

4. Conclusions

A nano-magnetic solid base catalyst KF/CaO-Fe₃O₄ based on Fe₃O₄ magnetic core was developed by impregnation method and characterized by various techniques. The results indicate that the nano-magnetic solid base catalyst has a unique porous structure

with an average particle diameter of ca. 50 nm and a ferromagnetic property with little remanence and coercive force. The nano-magnetic solid base catalyst with 25 wt.% KF loading and 5 wt.% Fe₃O₄, calcined at 600 °C for 3 h, shows the best activity. The Fe₃O₄ magnetic core has little effect on the catalytic activity of KF/CaO–Fe₃O₄ compared with that of KF/CaO catalyst. The current nano-magnetic catalyst is able to be reused up to 14 times without much deterioration in its activity. Furthermore, the catalyst recovery is more than 90%. When the reaction is carried out at 65 °C with a methanol/oil molar ratio of 12:1 and a catalyst concentration of 4 wt.%, the biodiesel yield exceeds 95% at 3 h of reaction time. The nano-magnetic solid base catalyst, KF/CaO–Fe₃O₄, used in the preparation of biodiesel illustrates a good prospect of development and application.

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