

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 Fe₃O₄ with Na₂CO₃ and NaOH as precipitator, respectively. The optimum conditions for preparation of this catalyst were investigated. The influence of the proportion of Ca²⁺ to Fe₃O₄ on the catalytic performance has been studied. The catalyst with highest catalytic activity has been obtained when the proportion of Ca²⁺ to Fe₃O₄ is 7:1; the catalytic activity of the catalyst calcined from Ca(OH)₂ to Fe₃O₄ is better than that calcined from CaCO₃ to Fe₃O₄; 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. Ca₂Fe₂O₅, 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).

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1. Introduction

Biodiesel can be considered as an environmental friendly energy source. With regard to the emissions, it has been demonstrated that its net CO₂ 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 (NO₃)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/Al₂O₃ hydrotalcites and MgO (300 m²/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 hydroxaltes 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 Al₂O₃ supported K₂CO₃, 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 K₂CO₃ 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 Fe₃O₄ 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

FeSO₄·7H₂O and Fe₂(SO₄)₃·7H₂O 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 SO₄²⁻ was eliminated by washing many times.

2.3. Preparation of nanometer magnetic solid base catalyst

Some CaCl₂ was solved into distilled water, then a certain amount (the proportion of Ca²⁺ to Fe²⁺ + Fe³⁺ was controlled to be 10:1) of magnetic core was added into the CaCl₂ 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 Ca²⁺ to Fe₃O₄ were prepared with the same method. Meanwhile, the catalysts with different proportions of Ca²⁺ to Fe₃O₄, i.e. 5:1, 7:1 and 10:1, were made respectively with the precipitator being Na₂CO₃.

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 Na₂CO₃.

2.4. Methods of catalysts characterization and activity detection

SENSOR27 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-Tecna 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)₂7 (These catalysts are named with their precursors and the proportion of Ca²⁺ to Fe₃O₄ for short. For example, "Ca(OH)₂10" means that the precursor of the

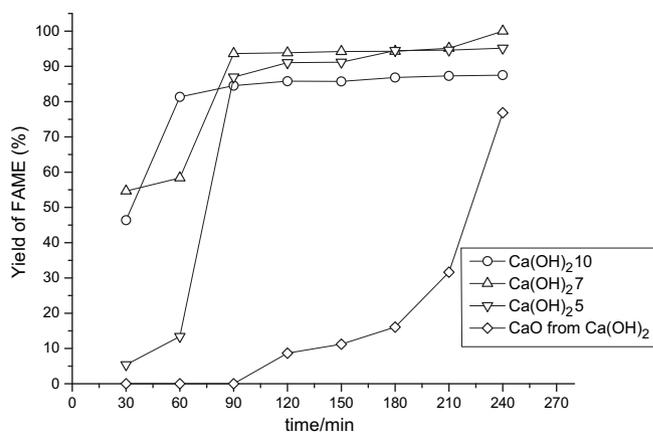


Fig. 1. Influence of different CaO load on catalytic performance for transesterification reaction.

catalyst is $\text{Ca}(\text{OH})_2\text{-Fe}_3\text{O}_4$ and the proportion of Ca^{2+} to Fe_3O_4 is 10:1) reaching 99% after 4 h reaction. It has been proved by other researchers that pure CaO catalyst shows a lower catalytic activity in normal surroundings. For instance, in Arzamendi et al.'s [18] study, catalyzed by CaO (Aldrich, 99.9%) for the transesterification of oil, the conversion is below 20% in 5 h and below 90% in 10 h. Masato Kouzu et al. [19] reported that the conversion of transesterification reaction can reach 93% when CaO catalyzed 1 h in the nitrogen atmosphere. However, the conversion cannot achieve 10% after 4 h reaction when the transesterification reaction was catalyzed by CaO calcined in air. Moreover, using nanocrystalline calcium oxides can enhance the catalytic activity of CaO . The nanocrystalline calcium oxides (crystal size = 20 nm; specific surface area = $90\text{ m}^2/\text{g}$) obtain 100% conversion of soybean oil at room temperature after 12 h while the conversion obtained by commercial CaO (crystal size = 43 nm; specific surface area = $1\text{ m}^2/\text{g}$) is only 2% [20]. Nevertheless, CaO loaded on Fe_3O_4 catalyzes the transesterification reaction very quickly and the conversion of the transesterification reaction is over 80% in 80 min. It is possibly because that a new kind of multiple oxide with higher catalytic activity for the transesterification reaction than CaO is formed during calcination. Meanwhile, for the transesterification reaction catalyzed by CaO loaded on MgO , the conversion can reach 92% under the conditions of methanol/oil molar ratio of 18:1, the catalyst dosage of 2 wt% of oil, and temperature of $64.5\text{ }^\circ\text{C}$ in 3.5 h [21]. $\text{Ca}(\text{OH})_2$ is outstanding probably due to the compatible proportion of Ca^{2+} to Fe_3O_4 . On one hand, if the proportion of Ca^{2+} is too big, redundant CaO may accumulate on the surface of $\text{CaO-Fe}_3\text{O}_4$ and prevents the contact between the activity sites and the reactant; on the other hand, if the proportion of Ca^{2+} is too small, less active multiple oxides, as well as basic active sites, are formed than that of $\text{Ca}(\text{OH})_2$. Therefore, there exists an optimum CaO proportion.

In order to reveal the effect of the precipitator on the catalytic activity, the catalysts precipitated by NaOH and Na_2CO_3 were compared. Fig. 2A–D illustrate that the catalysts that calcined from $\text{Ca}(\text{OH})_2$ to Fe_3O_4 are better than that calcined from CaCO_3 to Fe_3O_4 , though CaO calcined from CaCO_3 is better than that calcined from $\text{Ca}(\text{OH})_2$.

3.1.2. Determination of recovery rate of catalysts

Transesterification reactions were catalyzed by CaO and $\text{Ca}(\text{OH})_2$ respectively for 4 h under the conditions of methanol/oil molar ratio of 15:1 and the catalyst dosage of 2% to oil at $70\text{ }^\circ\text{C}$. After 0.5 h quiescence in the 2200 G magnetic field, the upper layer liquid was poured out and the remaining mixture was washed with isopropanol three times and then dried. According to the experiment results, the recovery rate of CaO is 55.95% while that of $\text{Ca}(\text{OH})_2$ is 91.45%.

3.1.3. Lifetime tests of catalysts

Catalyzed by $\text{Ca}(\text{OH})_2$ and CaO , respectively, transesterification reactions of *Jatropha curcas* oil were conducted under the same conditions. For every test, the experiment continued for 4 h. For every catalyst, the tests repeated 10-times using fresh oil. The comparison results are shown in Fig. 3.

It can be observed in Fig. 3 that, after 5-times use, FAME yield is more than 90% for $\text{Ca}(\text{OH})_2$, and after 10-times use, the FAME conversion still can reach more than 70%. However, for CaO , under the same conditions, the FAME conversion decreases to 22% after 5-times use, and after 8-times use, its catalytic activity is totally lost. Actually, after reaction, the CaO catalyst almost cannot be seen in the reactor since a large amount of CaO has been dissolved into the methanol or formed colloidal suspensions with methanol in the upper liquid and poured out with the reaction products.

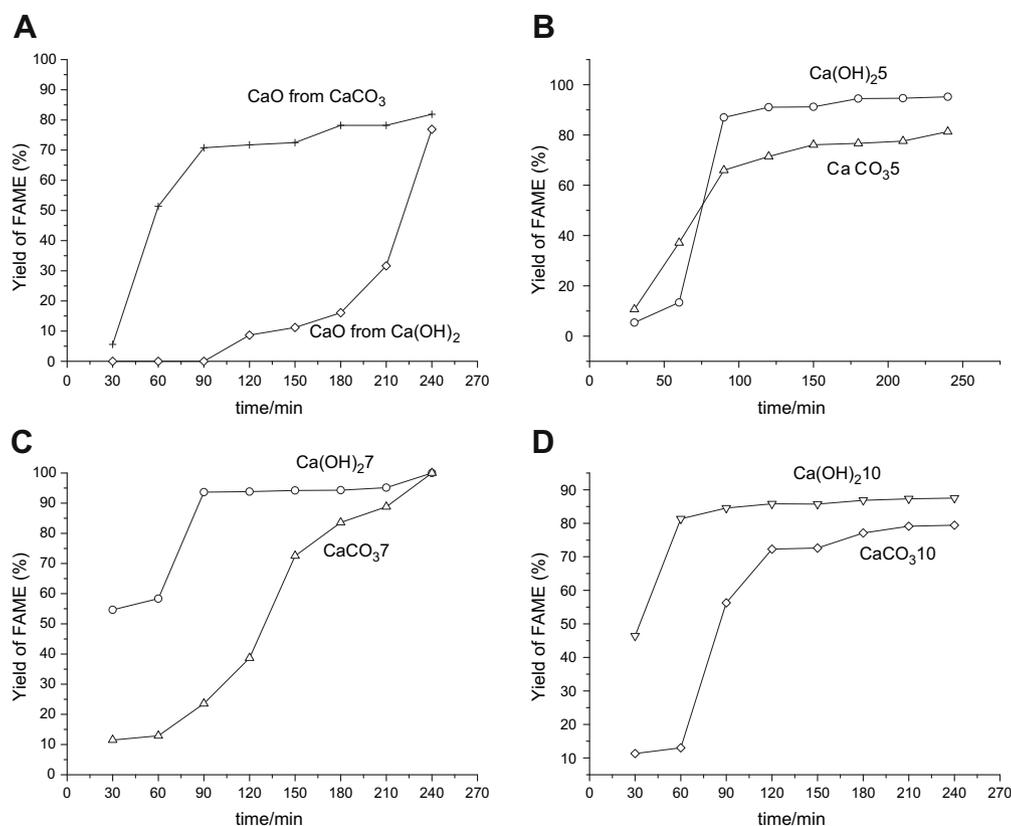


Fig. 2. (A) Effect of different precipitator on the catalytic activity of catalysts. (B) Effect of different precursor on the catalytic activity of catalysts. (C) Effect of different precursor on the catalytic activity of catalysts. (D) Effect of different precursor on the catalytic activity of catalysts.

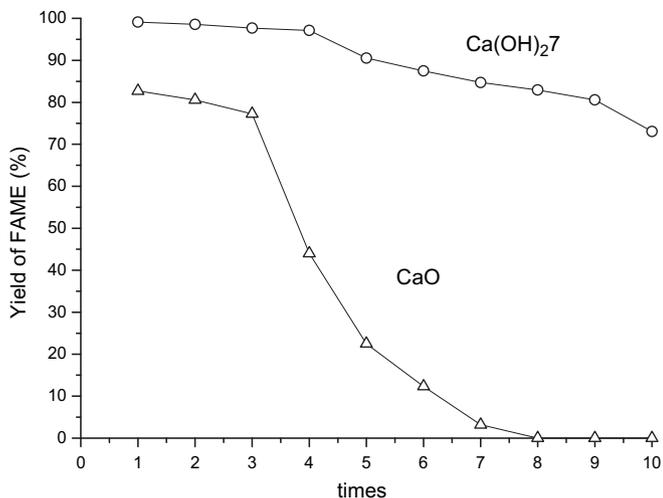


Fig. 3. Lifetime comparison of Ca(OH)₂7 and CaO.

3.2. Catalysts characterization

3.2.1. Differential thermogravimetric analysis of catalysts precursor

Ca(OH)₂ and CaCO₃ can decompose to CaO by calcination. The catalysts prepared with 6 precursors: Ca(OH)₂10, CaCO₃10, Ca(OH)₂7, CaCO₃7, Ca(OH)₂5 and CaCO₃5 were investigated by the method of thermogravimetric analysis and Fig. 4 shows the result.

Based on Fig. 4, the mass of Ca(OH)₂ supported catalyst reaches a plateau at 700 °C, while the mass of CaCO₃ supported catalyst comes steady at 780 °C. The ratio of decomposition of samples can be figured out by analyzing the loss of mass and the results are listed on Table 1. Thereby, the calcination temperature was determined to be 800 °C.

3.2.2. Specific surface area

Table 2 lists the specific surface areas of catalysts. The specific surface area of CaO is larger than that of any other kind of magnetic catalysts. This can be explained by that: during catalyst calcination, abundant pores will be formed when the generated gas escapes from the inner side of the catalyst; however, for magnetic core supported Ca(OH)₂ or CaCO₃ catalyst, the proportion of CaO is smaller, as well as the molecular weight of Fe₃O₄ being larger than

Table 1
Ratio of decomposition of catalysts at 800 °C.

Samples	TG% at 800 °C	Decomposition ratio %
Ca(OH) ₂ 10	85.40	78.80
CaCO ₃ 10	66.56	93.62
Ca(OH) ₂ 7	83.08	100.00
CaCO ₃ 7	69.68	91.74
Ca(OH) ₂ 5	82.93	100.00
CaCO ₃ 5	68.75	100.00

that of CaO. Among all of the magnetic catalysts, the specific surface area of Ca(OH)₂7 is the largest, which is possibly because that for an optimum proportion of Ca(OH)₂ to Fe₃O₄, CaO distributes evenly on the magnetic core to form a larger surface area. When the proportion of Ca²⁺ to Fe₃O₄ is not great enough, such as 5:1, CaO cannot form such a lot of micro-pores; when the proportion is too great, such as 10:1, CaO may cluster together to cover some micro-pores. Hence, those are the reasons why the specific surface area of Ca(OH)₂7 is larger than that of any other magnetic catalysts.

3.2.3. X-ray diffraction

Fig. 5 shows the XRD pattern of the catalyst Ca(OH)₂7. There are two kinds of crystal in this catalyst, Ca₂Fe₂O₅ and CaO. After calcining the precursor of Ca(OH)₂-Fe₃O₄ at 800 °C for 8 h, Ca₂Fe₂O₅, a kind of combined metal oxide crystalloid, is generated. This crystalloid maybe promotes the catalytic activity of magnetic catalyst.

In the pattern of XRD, the smaller the micro-crystalloid is, the larger the main peak area of interference function is, and the wider interference peak is. According to Scherer formula $D = 0.89\lambda/\beta\cos\theta$, the average particle size can be figured out. In this formula, λ is the wavelength of X-ray; β is FWHM of pure interference peak; θ is the half diffraction angle. Therefore, average particle size of main phase of crystalloid sample can be obtained with the calculation of the parameters of the three tallest peaks in the pattern. The average particle diameter is calculated to be 49.76 nm.

3.2.4. Magnetic strength analysis

The magnetic strength of Ca(OH)₂7 was measured by VSM, and the result is exhibited in Fig. 6.

Fig. 6 suggests that, in the first place, it is proved that whether magnetic core Fe₃O₄, or the precursors of catalysts and the catalysts, they all display superparamagnetism because all the curves go through the original point. Secondly, the magnetic strength of precursor is smaller than that of pure Fe₃O₄, furthermore, the decreased proportion of magnetic strength is equal to the amount of CaO loaded on Fe₃O₄. The magnetic strength of magnetic catalysts is smaller than 1 eum/g possibly because some Fe₃O₄ is oxidized to α -Fe₂O₃ during the calcination process.

Because of the magnet, catalyst Ca(OH)₂7 can be separated from reaction system rapidly by forcing magnetic field and absorbed to the bottom of lower layer of glycerin. That is the reason why the recovery rate of magnetic catalysts can reach up as high as 91.45%.

Table 2
The specific surface area of catalysts.

Catalysts	The specific surface area (m ² /g)
Ca(OH) ₂ 10	1.74
CaCO ₃ 10	1.18
Ca(OH) ₂ 7	3.72
CaCO ₃ 7	1.96
Ca(OH) ₂ 5	1.96
CaCO ₃ 5	1.36
CaO (from Ca(OH) ₂)	5.90
CaO (from CaCO ₃)	3.94

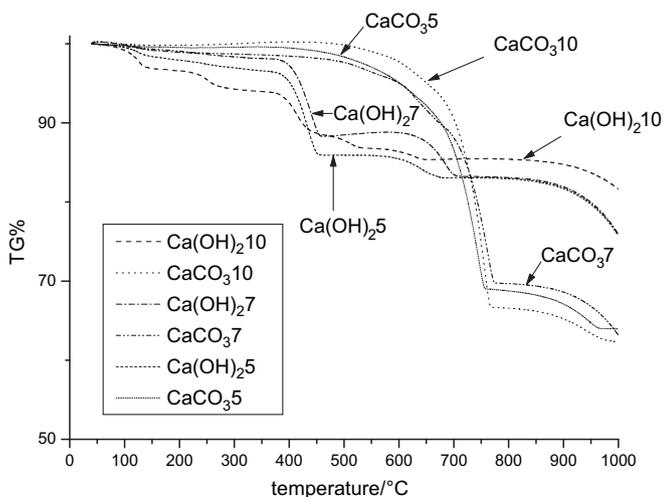


Fig. 4. The TG curves of catalysts prepared from different precursors.

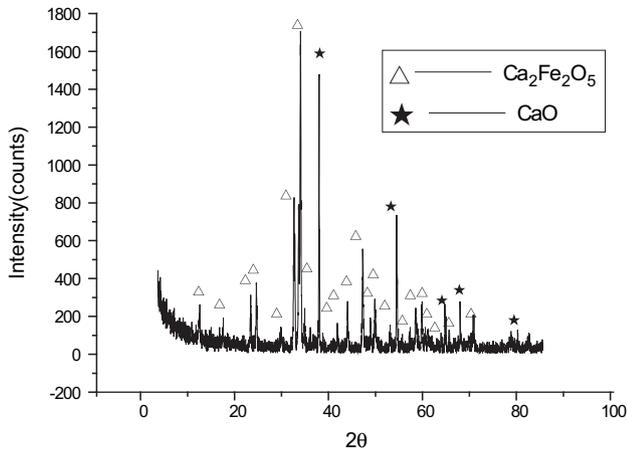


Fig. 5. XRD pattern of Ca(OH)_{2.7}.

3.2.5. Scanning electronic microscope and transmission electron microscopy

Fig. 7A, the transmission electron microscopy photograph, reveals that the Fe₃O₄ appears as tiny balls whose diameter is 10 nm. Nanometer Fe₃O₄ have superparamagnetism which means that the matter with this nature displays magnet in magnetic field,

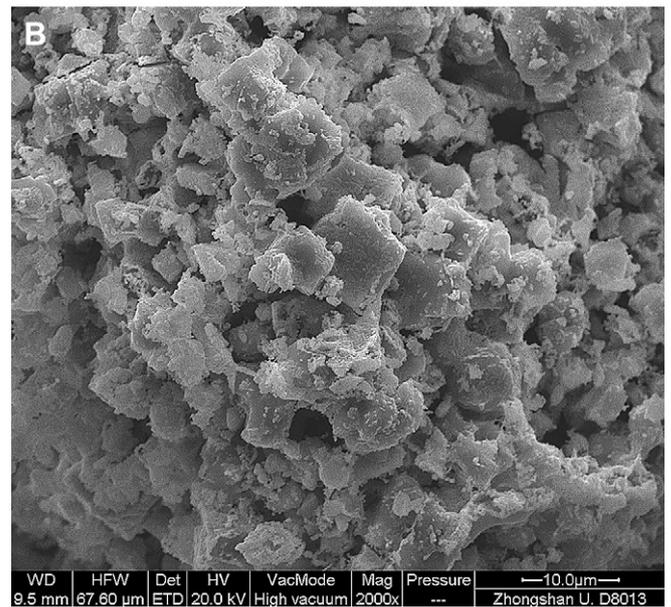
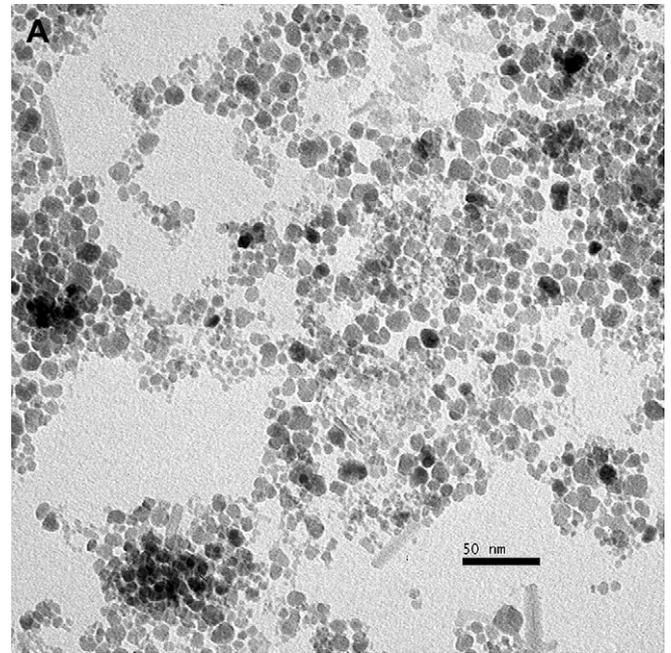


Fig. 7. (A) TEM photo of Fe₃O₄. (B) SEM photo of CaO-Fe₃O₄.

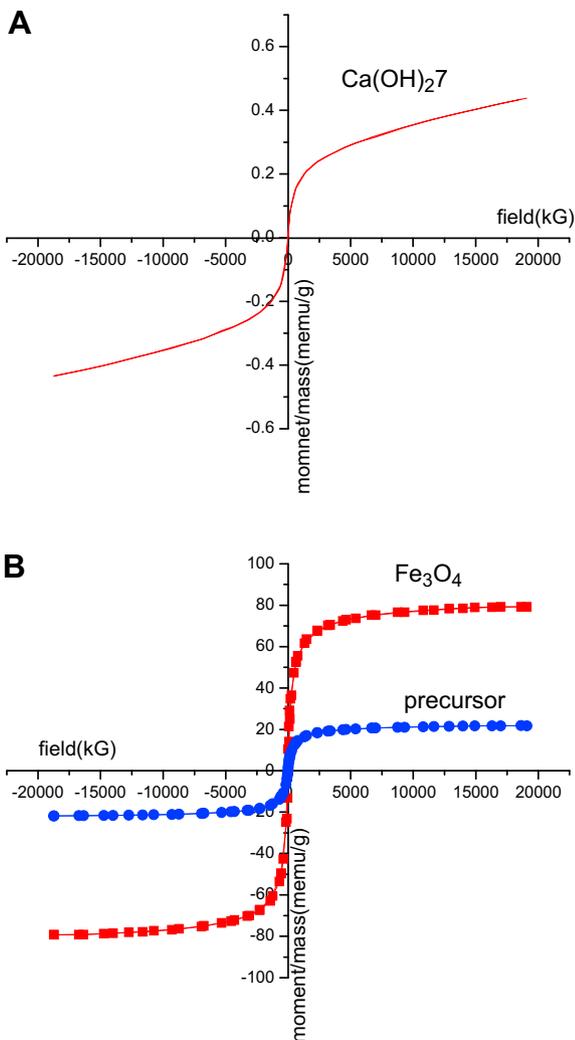


Fig. 6. (A) M-H curves of super paramagnet of catalysts. (B) M-H curves of super paramagnet of catalysts.

but non-magnetic in the non-magnetic surrounding. When CaO is loaded on the magnetic core, it still has this feature. This nature makes catalysts disperse well in the reactant system and be separated easily by the external magnetic field.

Fig. 7B, the Scanning electronic microscope photograph of Ca(OH)_{2.7}, demonstrates that the main substance Ca₂Fe₂O₅ is cuboid and some of pure CaO attaches on the surface of the cuboid. It suggests that when Ca²⁺:Fe₃O₄ = 10, there is more pure CaO on the surface which prevents the connection between the catalysts and reagents; when Ca²⁺:Fe₃O₄ = 5, there are less active crystalloids formed. Maybe this is another reason why Ca(OH)_{2.7} is most active for transesterification reaction.

4. Conclusions

Nanometer magnetic solid base catalysts can be prepared by loading CaO on Fe₃O₄ with Na₂CO₃ or NaOH as precipitator.

$\text{Ca}_2\text{Fe}_2\text{O}_5$, a new kind of crystalloid with high catalytic activity, is formed by calcining the precursors. This achieves assembly of magnet and catalytic activity.

The catalytic activity of catalysts which are obtained by calcining $\text{Ca}(\text{OH})_2\text{-Fe}_3\text{O}_4$ is better than that by calcining $\text{CaCO}_3\text{-Fe}_3\text{O}_4$. Furthermore, $\text{Ca}^{2+}:\text{Fe}_3\text{O}_4 = 7$ is the optimum proportion for catalytic activity. The conversion rate of transesterification reaction catalyzed by $\text{Ca}(\text{OH})_2$ can reach 95% in 80 min, and to 99% in 4 h.

The recovery rate of $\text{Ca}(\text{OH})_2$ after reaction can reach up to 91.45%, which is much higher than 55.95%, the recovery rate of CaO . Moreover, the conversion rate of transesterification reaction is more than 90% when the reaction is catalyzed by 5-times used $\text{Ca}(\text{OH})_2$, and after 10-times use, it is still more than 70%.

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