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Preparation and catalytic property investigation of a magnetic solid material - $CaO/NiFe_2O_4$

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A novel magnetic solid catalyst $CaO/NiFe_2O_4$ were prepared, which not only solved the separation problem of the small particle catalyst, but also improved the yield for synthesis of biodiesel and the recovery rate of catalyst. Compared with CaO and another magnetic solid catalyst CaO/Fe_3O_4, $CaO/NiFe_2O_4$ exhibited higher magnetic strength and catalytic property. Under the conditions of catalyst dosage of 1.0 wt. %, temperature of 70 °C, methanol/oil molar ratio of 15:1, the reaction yield reached to 95.5 % in 5 h. In the optimum reaction condition, the biodiesel yield can be maintained at 85 % after the catalyst was repeatedly used for 5 times, which is much better than those of CaO.

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1. Introduction

Biodiesel, also known as sunshine fuel, is made from plant and animal oils with alcohols by transesterification reaction. It has the key features of renewability, low emission, biodegradability, nontoxicity. Transesterification is a catalyzed process and, traditionally, homogeneous catalysts are empolyed, such as strong acid (H_2SO_4) or alkali (NaOH, KOH). The advantage of this process is production of methyl esters at very high yields [1]. However, the separation of catalyst and the purification of products are time-consuming and expensive accompanied with a large volume of chemical wastewater [2-3]. Hence, stimulating the conception of heterogeneous-catalyzed transesterification is imperative. Despite the success of various heterogeneous catalysts, many heterogeneous catalysts are not viable for wide industrial usage as most of the catalysts are expensive and need additional preparation effort. Among them, CaO seems to have a promising place and the increasing research on CaO is self-evidence of its capability in catalyzing the reaction [4]. Nevertheless, when CaO catalyzes the transesterification reaction directly, 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 [5]. In order to improve the efficience of separation of catalyst and product, the magnetic solid base catalyst may be a better choice because the magnetic separation generally avoids loss of catalyst and decreases its separation time in comparison to filtration or centrifugation [6-7]. Besides, nanoscale magnetic core can improve surface area of the catalyst, the magnetic catalyst also exhibits good catalytic property.

Liu has prepared the nano magnertic solid base catalyst by loading CaO onto the nanometer Fe_3O_4. 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 [8]. Xie and Ma have immobilized lipase on Fe_3O_4 nanoparticles as catalyst for biodiesel production [9]. Hu synthesized a nano-magnetic solid base catalyst KF-CaO/Fe_3O_4 and used as catalyst for transesterification [1]. But Fe_3O_4 is easily oxidated into Fe_2O_3 in air condition. There are still difficulties for industrial application.

In this paper, a novel magnetic solid base catalyst $CaO/NiFe_2O_4$ was synthesized. The catalyst was characterized by Hammett indicators, BET, TG, XRD and the magnetic property was also determined. The catalyst activity was evaluated by transesterification of soybean oil.

2. Experimental

2.1 Methods of magnetic core preparation

Magnetic core $NiFe_2O_4$ was prepared by hydrothermal method. Briefly, $NiSO_4 \cdot 6H_2O$ and $Fe_2(SO_4)_3 \cdot 6H_2O$ were dissolved in the ultrapure water with the proportion of 1:2, by magnetic stirring for 10 min. Appropriate amount of sodium hydroxide solution was dropped into the mixed solution with drastic stirring, and then stirred for 20 min to make them mixed. Put the mixed solution in reaction still, reacted 10 h at 180 ℃, separated in magnetic field, and SO_4^{2-} was eliminated by washing 3 times. Then dried in oven at 200 ℃ for 4 h. $NiFe_2O_4$ was obtained.

Magnetic core Fe_3O_4 was prepared by co-precipitation. Briefly, 0.01 mol $FeSO_4$ and 0.01 mol $Fe_2(SO_4)_3$ were dissolved in 25 mL deoxidized water. NaOH was then added dropwise to the solution in a water bath at 80 ℃ and with vigorous stirring for 30 min. The final pH value of the aqueous solution was washed to 7.0 by deoxidized water. And than dried for 12 h in a vacuum at 80 ℃, Fe_3O_4 was obtained.

2.2 Preparation of magnetic calcium-base solid base catalysts

Some $CaCl_2$ was solved into distilled water, then a certain amount (the proportion of CaO to M was controlled to be 1:1、3:1、5:1、6:1、7:1、10:1) of magnetic core M ($NiFe_2O_4$、Fe_3O_4) 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 ℃, and then the magnetic material was washed over and over again by saturation calcium hyroixde and then dried for 12 h in a vacuum at 80 ℃. Finally, the sample was calcined for 3 h at 500 ℃ to transform to multiple oxides to achieve nanometer magnetic solid base catalyst.

2.3 Catalytic activity tests and biodiesel analytical Methods

Dehydrated soybean oil 8.71 g and methanol 3.84 g were mixed in 100 mL roundflask and heated at 70 ℃ for 5 h. After the reaction, the reaction mixture was then cooled to room temperature and three phases were formed. The upper phase mainly containing the desired biodiesel could be isolated simply by liquid/liquid separation using decantation. The product was directly measured by gas chromatography.

The biodiesel products were analyzed by FULI GC9790 using a flame ionization detector (FID) and small caliber capillary column of PEG-2M. The oven program was set to an initial temperature of 150 ℃ (held for 1 min), increasing to 215 ℃ at a rate of 5 ℃/min, where the temperature was held for 6 min. The temperatures of injector and interface were both held constant at 280 ℃. The internal standard method for determinating the yield of biodiesel was used, with methyl salicylate as internal standard. In our work, the composition of biodiesel was 56.5 % methyl linoleate, 23.2 % methyl oleate, 10.6 % methyl palmitate, 6.6 % methyl linolenate and 3.1 %methyl stearate from the gas chromatogram.

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 soybean oil; n is the diluted multiple of biodiesel; C_{esters} (g/mL) is the mass concentration of biodiesel; ρ_{oil} (g/mL) is the density of soybean oil; V_{esters} (mL) and V_{oil} (mL) are the volumes of biodiesel and soybean oil, respectively.

2.4 Methods of catalysts characterization and activity detection

Basic strength of the magnetic solid bases ($H\_$) was determined by using Hammett indicators. The specific surface area was obtained by Coulter (SA3100) at 200℃ deaeration temperature for 2h deaeration time. Thermal decomposition of the $CaO/NiFe_2O_4$ sample was evaluated by thermogravimetric analysis (TG), the temperature rate was 15 ℃/min. X-ray powder diffraction (XRD) was carried out with a Bruker D8-Advance diffractometer with Cu-Ka radiation at a scanning rate of 4 °/min from 2 theta=10° to 2 theta=90°. The catalytic activity was determined by GC9790 gas chromatograph.

3. Results and discussion

3.1 Catalysts characterization

3.1.1 Base strength

Basic strength of the solid bases ($H\_$) was determined by using Hammett indicator. After 50 mg catalyst was dispersed in an ethanol solution of the hammett indicator, color change of the hammett indicator was observed. In these experiments, the following Hammett indicators were used: neutral red ($H\_= 6.8$), phenol ($H\_= 8.2$), nile blue ($H\_= 10.1$), 2,4-dinitroaniline ($H\_= 15.0$) [10]. Through the color change, it was concluded that the basic strength of the three catalysts is all in the range of 10.1-15.0, and summarized in Table 1. The results showed that the three calcium-based catalysts exhibited strong basicity.

Table 1. Basic strength.

Catalysts	Neutral red (H_-=6.8)	Phenol (H_-=8.2)	Nile blue (H_-=10.1)	2,4-dinitroaniline (H_-=15.0)
CaO	√	√	√	×
CaO/Fe_3O_4	√	√	√	×
CaO/$NiFe_2O_4$	√	√	√	×

3.1.2 Specific surface area

The specific surface area of CaO/Fe_3O_4 and CaO/$NiFe_2O_4$ were given in Table 2. The specific surface area of CaO/$NiFe_2O_4$ is more than that of CaO/Fe_3O_4, which is possibly because CaO distributes evenly on the magnetic core $NiFe_2O_4$ to form a larger surface area. Besides, the magnetic core $NiFe_2O_4$ is more stable than Fe_3O_4, Fe_3O_4 changes into Fe_2O_3 easily in air condition, so the physical properties such as particle size may also be changed. The newly produced $CaFe_2O_5$ may distribute unevenly on the magnetic core which also decreases the specific surface area.

Table 2. BET parameter of catalysts.

Catalysts	The specific surface area (m^2/g)
CaO/Fe_3O_4	0.3130
CaO/$NiFe_2O_4$	4.3233

3.1.3 TG

Fig. 1 illustrated the thermogravimetric analysis curves of $Ca(OH)_2$ obtained in nitrogen. The curve displayed one loss weight platform at 360-470 ℃, $Ca(OH)_2$ decomposes into CaO. The one loss weight platform indicates that the decomposition product is purified. The result also suggests that the calcination temperature must be more than 500 ℃.

Fig. 2 illustrated the thermogravimetric analysis curves of CaO/$NiFe_2O_4$ (calcinated at 800 ℃ for 3 h) obtained in nitrogen. The curve displayed two loss weight platform, one at 360-420 ℃, associated with the crystal water loss, and another at 420-590 ℃ which is attributed to the decomposition of $Ca(OH)_2$. The loss weight of the two events is 1.97 % and 1.00 %. The results suggest that the stability of CaO/$NiFe_2O_4$ is relatively good.

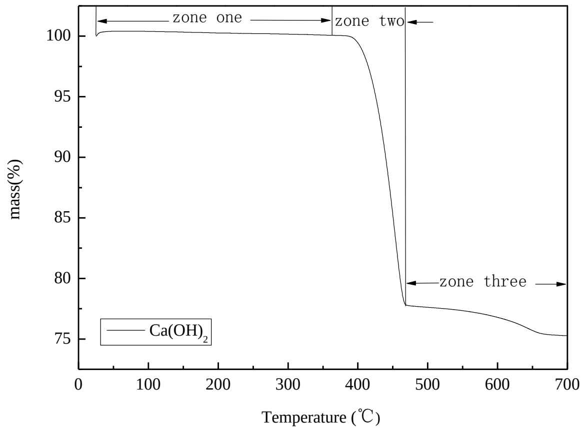

Fig. 1. TG of $Ca(OH)_2$.

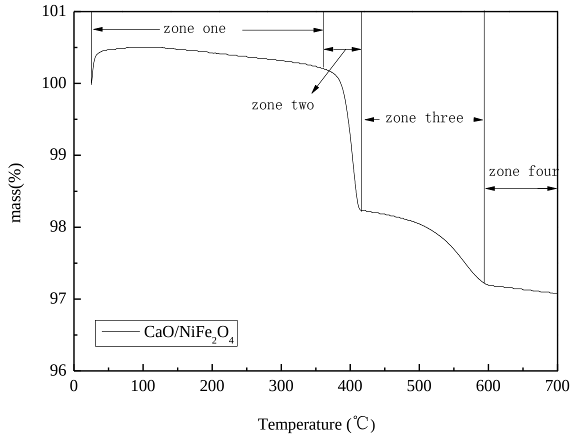

Fig. 2. TG of CaO/$NiFe_2O_4$.

3.1.4 XRD

The magnetic solid base catalysts were further characterized by XRD. Fig. 3 shows the XRD of CaO/$NiFe_2O_4$ and $NiFe_2O_4$. Through comparison, the diffraction peaks of $NiFe_2O_4$ (18.4°, 30.2°, 35.5°, 35.7°, 37.3°, 43.2°, 54.0°, 57.3°, 63.0°) decreased in CaO/$NiFe_2O_4$, whereas the diffraction peaks of CaO (32.3°, 37.4°, 53.9°, 64.2°, 67.4°, 79.7°, 88.6°) appeared completely which indicated the crystallinity of CaO is very good. Besides, the diffraction peaks of $NiFe_2O_4$ migrated to the low angle which made the d-spacing increased. Though the strength of diffraction peaks of $NiFe_2O_4$ decreased, the newly formed crystal phase of CaO was favorable for enhancing the catalytic activity and stability of the catalyst.

Fig. 4 shows the XRD of CaO/Fe_3O_4 and Fe_3O_4. Two new diffraction peaks of Fe_2O_3 and $CaFe_2O_5$ were formed in CaO/Fe_3O_4, the diffraction peak of CaO as the catalytic center was disappeared, which could be explained in detail by the catalytic activity in the following Fig. 6.

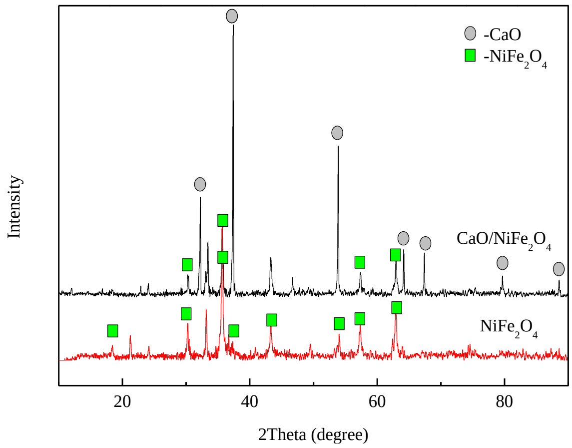

Fig. 3. XRD of $CaO/NiFe_2O_4$ and $NiFe_2O_4$.

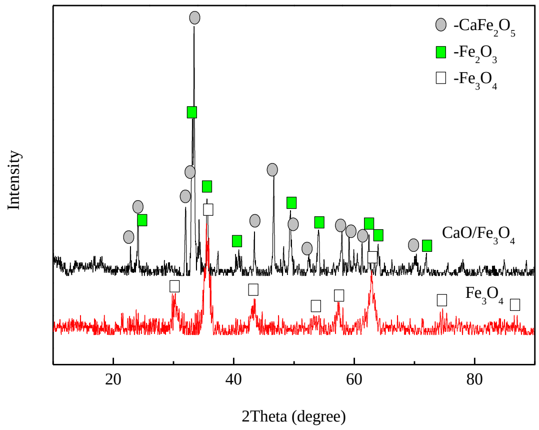

Fig. 4. XRD of CaO/Fe_3O_4 and Fe_3O_4.

3.1.5 Magnetic strength analysis

The magnetic strength of the catalyst was investigated by magnet. 0.5 g catalyst was put into soybean oil and dispersed for 5min by using ultrasonic. The catalyst was placed in the bottle for 12h with the magnet put on one side of the bottle. The phenomenon was shown on Fig. 5. It can be concluded that $CaO/NiFe_2O_4$ provides high magnetic property. $CaO/NiFe_2O_4$ can be separated easily by exerting magnetic field after transesterification reaction. That can simplify the process and decrease catalyst costs.

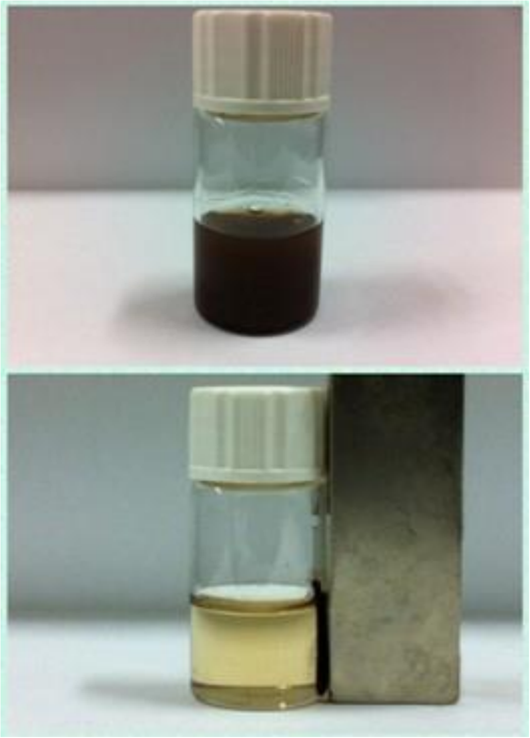

Fig. 5. Magnetic strength.

3.2 Catalytic activities of magnetic solid base catalyst

3.2.1 Performance of various catalysts

The biodiesel yields for the various catalysts are shown in Fig. 6. Fig. 6 indicated that the catalyst activity of CaO/ Fe_3O_4 was less than that of other catalysts. That may be that Fe_3O_4 is not stable in air condition, it can be easily transformed into Fe_2O_3, the XRD patterns indicated the presence of $CaFe_2O_5$, and the new substance may reduce the catalyst activity. The catalyst $CaO/NiFe_2O_4$ provided highest activity and was selected for further studies.

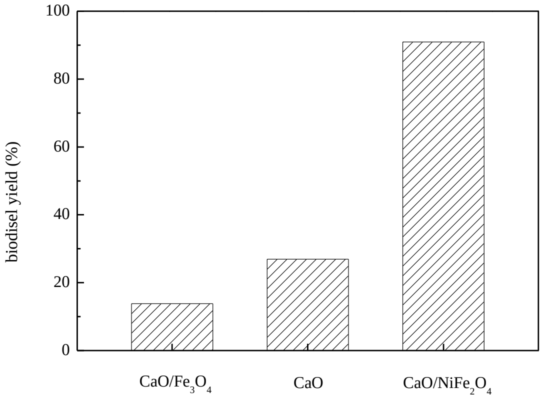

Fig. 6. Biodiesel yields achieved with various catalysts.

3.2.2 The effect of molar ratio of CaO and $NiFe_2O_4$ on biodiesel yield

Fig. 7 gives the effect of molar ratio of CaO and $NiFe_2O_4$ on biodiesel yield. The biodiesel yield steeply increased with the molar ratio when the range is 1:1 to 5:1, then the biodiesel yield gradually declined with increasing molar ratio. A ratio of 5:1 provided the highest biodiesel yield.

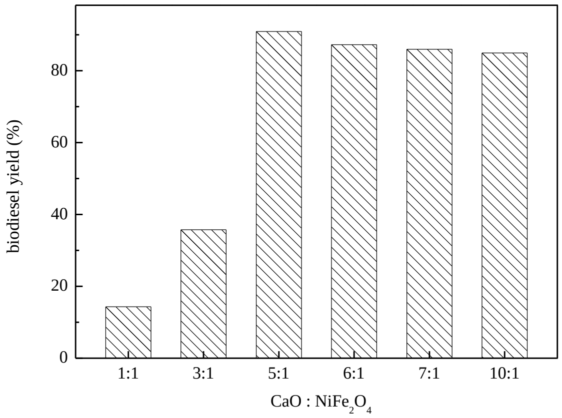

Fig. 7. Effect of molar ratio of CaO and $NiFe_2O_4$ on biodiesel yield.

3.2.3 The optimization of catalyst preparation and reaction conditions

Calcination temperature and time have a very important influence on catalyst activity. Through investigation, the optimum calcination temperature is 800 ℃ and the optimum calcination time is 3 h.

The optimum reaction conditions were also investigated. Under the conditions of catalyst dosage of 1.0 wt. %, temperature of 70 °C, methanol/oil molar ratio of 15:1, the biodiesel yield reached to 95.5 % in 5 h.

In the optimum reaction condition, the biodiesel yield could be maintained at 85 % after the catalyst was repeatedly used for 5 times. Therefore, it can be concluded that CaO/$NiFe_2O_4$ catalyst not only exhibits a favorable catalytic performance but also has perfect reusability.

4. Conclusion

The magnetic solid base catalysts were developed by co-precipitation. The specific surface area of CaO/$NiFe_2O_4$ was 4.32 m^2/g whereas CaO/Fe_3O_4 just reached to 0.31 m^2/g. CaO/$NiFe_2O_4$ exhibited higher magnetic strength, so it can be separated from reaction system rapidly by forcing magnetic field. What’s more, the catalytic activity of CaO/$NiFe_2O_4$ was better than that of CaO/Fe_3O_4. The biodiesel yield could reach 95.5 % in 5 h under the condition of catalyst dosage of 1.0 %, temperature of 70 ℃, methanol/oil molar ratio of 15:1. Moreover, the biodiesel yield was more than 85 % when the catalyst CaO/$NiFe_2O_4$ was used for 5 times, which is much better than those of CaO. Because of its high catalytic activity and stability, CaO/$NiFe_2O_4$ is a promising functional catalyst to be applied into industrial field.

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