Preparation of Mesoporous Nanosized KF/CaO–MgO Catalyst and its Application for Biodiesel Production by Transesterification

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Abstract A mesoporous nanosized KF/CaO–MgO catalyst was prepared by coprecipitation method, and was characterized by transmission electron microscopy, X-ray diffraction, nitrogen adsorption and laser confocal Raman microspectroscopy. The catalyst possessed a unique mesoporous structure with pore size of ca. 34 nm and the average particle size of ca. 35 nm. In comparison with CaO and KF/CaO catalyst, the as-prepared catalyst exhibited higher catalytic activity, higher resistance to saponification, and better acidoresistance (10 mg KOH/g oil). The factors affecting on transesterification were also investigated, and a desired biodiesel yield over 95% was obtained under an optimal preparation conditions.

Keywords Nanosized solid-base catalyst · Coprecipitation method · Transesterification reaction · Biodiesel production

1 Introduction

Biodiesel, defined as the monoalkyl esters of fatty acids, has been receiving great attention in recent years as one of renewable resources. The production of biodiesel is expected to increase significantly in the near future. It is well known that catalyst plays an important role in the production of biodiesel [1–3]. Up to now, the most common catalysts for biodiesel production were homogeneous catalysts, such as NaOH, KOH, $NaOCH_3$, $KOCH_3$, sulfuric acid, phosphoric acid and 4-toluene sulfonic acid [4, 5]. However, these catalysts need be neutralized and separated from methyl ester phase at the end of reaction, resulting in unavoidable generation of waste water [6, 7]. Heterogeneous catalysts utilized for biodiesel preparation comprised mainly of solid-acid and solid-base catalysts. For example, Gryglewicz et al. reported alkaline earth metal oxides for the catalysis of transesterification [8]. They found that MgO had lower activity than that of CaO in transesterificating rapeseed oil to biodiesel. Zhu et al. [9, 10] achieved high conversion of *jatropha curcas* oil by using CaO, being treated with CO_3^{2-} solution, as catalyst. A recent report further showed that such a kind of catalyst also exhibited well performances in water resistance and acid resistance [11]. The KF/CaO catalyst prepared by employing isochoric impregnation method, showed much higher catalytic activity than CaO [12]. Although heterogeneous catalysts have many advantages, the application of solid catalysts in transesterification reaction has been limited because of their low active site available for catalytic reaction [13–15]. Nano catalyst with mesoporous structure has large surface area and relatively big size. In comparison with nanosize catalyst, it is easer separate catalysts from products by using nano catalyst with mesoporous structure. Some research papers have reported that the reaction efficiency was improved with mesoporous complex supported nanosized catalyst [16, 17].

In this work, a mesoporous nanosized KF/CaO–MgO catalyst was prepared by coprecipitation method. The influence of the preparation conditions, such as calcination temperature and time, mass ratio of CaO/MgO and mass ratio of KF/CaO–MgO, on the activity of the as-prepared catalyst on biodiesel yield was investigated in detail. Transmission electron microscopy (TEM), powder X-ray diffraction (XRD), nitrogen adsorption and laser confocal

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Raman microspectroscopy were employed to characterize the micro- and molecular structure of the catalyst. The impact of the catalyst preparation conditions on catalytic activity was investigated. The as-prepared heterogeneous catalysts are very efficient in promoting the transesterification reaction even in the presence of free fatty acids, which allow the prompt separation of pure glycerol without requiring an expensive purification step.

2 Experimental

2.1 Preparation of Two-Component Complex Supported Catalyst

The two-component complex supporter was prepared via coprecipitation method. Aqueous solution of Na_2CO_3 and NaOH with molar ratio of 3:1 was prepared in a three-necked flask. The solution of $CaCl_2$ and $MgCl_2$ prepared in various Ca/Mg mass ratios was added dropwise to the flask. The system was aged at 333 K for 6 h, and then kept for an additional 1 h. After vacuum filtration, the solid was washed with distilled water, and dried at 343 K, and was calcined in a muffle furnace at 1,173 K for 4 h.

A series of KF/CaO–MgO catalysts with various mass ratio of KF to CaO–MgO (0.10, 0.15, 0.20, 0.25, 0.30, and 0.35) were obtained with isochoric impregnation of CaO–MgO and KF solution. The prepared catalysts were calcined in a muffle furnace at the respective predetermined temperatures (i.e., 673, 773, 873, 973 and 1073 K) for different time (1, 2, 3, 4 and 5 h). Other catalysts, such as KF/CaO (without $MgCl_2·6H_2O$) and CaO (without $MgCl_2·6H_2O$ and KF), were prepared using the same procedures as described above for comparison.

2.2 Characterization of the As-Prepared Catalyst

TEM (H-7650, HITACH, Japan), XRD (JDX-10P3A, Japan), and laser confocal Raman microspectroscopy (Invia Raman Microscope, Renishaw, UK) were used to characterize the microstructural features of the catalysts in our protocol. XRD patterns were measured under the following conditions: Cu K_α radiation ($\lambda = 0.154$ nm), tube voltage of 40 kV, tube current of 40 mA, scanning speed 10°/min and scanning range 10–70°. Raman spectra were recorded in the spectral range of 300–2,000/cm^{-1} on an inVia micro-Raman spectroscopy system (Renishaw, UK), equipped with an He–Ne laser excitation source at an emitting wavelength of 633 nm. A nitrogen adsorption apparatus (Quantachrome, Autosorb 1) was employed to measure the specific surface area and the pore size of samples.

2.3 Transesterification Reaction

Rapeseed oil (Grade one, acid value < 1 mg KOH/g, water content < 0.1%) from Xinyang Wanfu Oils & Fats Co. Ltd. was used as the vegetable oil. The acid value was determined following the National Standards of PRC: GB/T 5530-1998. Transesterification reaction was carried out in a 100 mL glass reactor equipped with a condenser and a magnetic stirrer. Anhydrous methanol was used in the transesterification reaction. Reaction conditions were as follows: molar ratio of methanol to oil was 12:1, catalyst content 3% of the total reactants, reaction temperature 343 K, and reaction time 3 h. The yields of biodiesel samples were measured by GC [18].

3 Results and Discussion

3.1 Influence of Mass Ratio of CaO/MgO on Biodiesel Yield

Figure 1 shows the effect of CaO–MgO mass on the yield of biodiesel, where the mass ratio of CaO to MgO was varied with 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0. As shown in Fig. 1, the biodiesel yield increased with the increase of CaO–MgO mass ratio. The highest yield was achieved at a mass ratio of 8:2. This yield was higher than that of transesterification catalyzed by CaO. It seems that the addition of MgO increases the catalytic activity [19]. However, biodiesel yield decreased when CaO–MgO mass ratio was over 8:2.
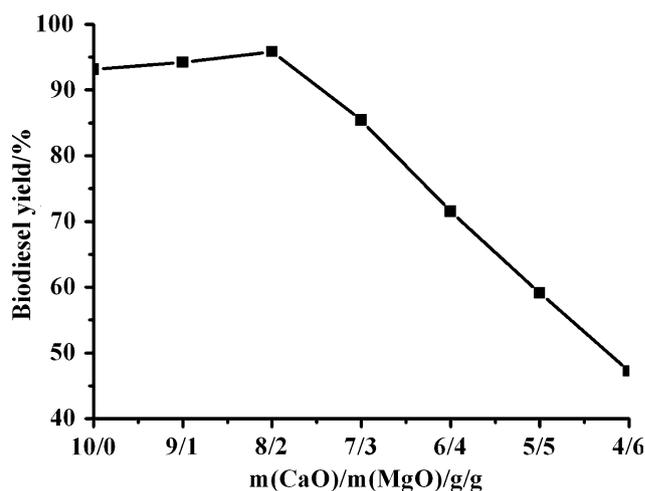

Fig. 1 Effect of CaO–MgO mass ratio on biodiesel yield. Preparation conditions: KF/support mass ratio 25%, calcination temperature 873 K, calcination duration 3 h

3.2 Influence of Mass Ratio of KF/CaO–MgO on Biodiesel Yield

The effect of KF/CaO–MgO mass ratio on biodiesel yield was investigated in detail. As shown in Fig. 2, the biodiesel yield increased as the mass ratio increased from 0.10 to 0.25, and the highest yield was obtained at mass ratio of 0.25. However, biodiesel yield decreased at the mass ratio over 0.25. It seems that the covering of the basic sites caused by excess KF occurred at the mass ratio over 0.25, and hence lowered the surface area effective for catalysis, thus resulting in decrease of the catalyst activity.

3.3 Influence of Calcination Temperature and Time on Biodiesel Yield

It was reported that new activated center for the catalyst can be developed during calcination process, and calcination conditions have a significant impact on the catalytic activity [20]. As shown in Fig. 3, the catalyst calcined at 673 K showed lower activity, owing to the formation of less active center. The biodiesel yield achieved the maximum value by utilizing the catalyst calcined at the temperature of 873 K. It seems that the active center was well developed at this temperature, and the catalyst showed favorable efficiency for catalysis. However, the biodiesel yield decreased when calcination temperature was higher than 873 K. The surface area values and pore diameter of catalysts calcined at 873, 973 and 1073 K are given in Table 1. As shown in Table 1, the average pore size of catalyst calcined at 873 K was ca. 34 nm, which was increased when the calcination temperature was higher than 873 K. This maybe caused by the aggregations of the preformed active compounds at high temperature, and
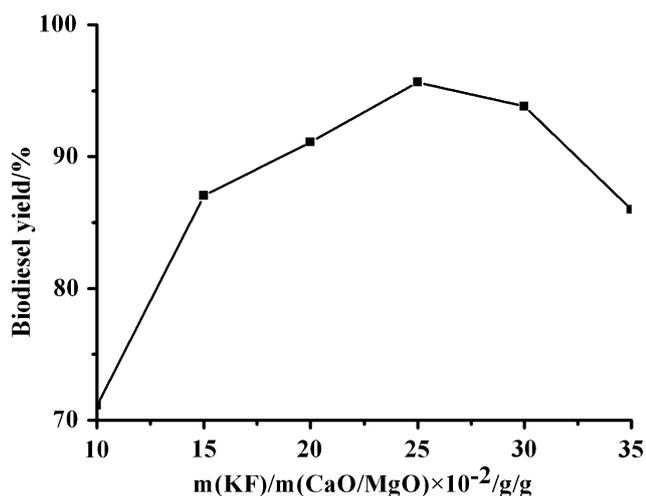

Fig. 2 Effect of the KF/CaO–MgO ratio on biodiesel yield. Preparation conditions: CaO–MgO mass ratio 4 (8:2), calcination temperature 873 K, calcination duration 3 h
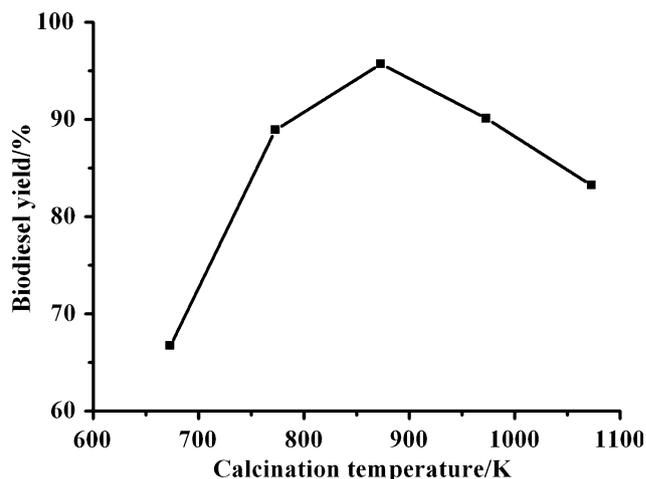

Fig. 3 Effect of calcinations temperature on biodiesel yield: Preparation conditions: mass ratio of CaO to MgO 4 (8:2), mass ratio of KF to CaO–MgO 25%, calcination duration 3 h

Table 1 The surface area values and average pore diameter of catalysts calcined at different temperature

Calcination temperature (K)	Surface area (m^2/g)	Average pore diameter (nm)
873	113.8	34
973	102.3	36
1,073	87.6	38

hence decreased the specific surface area, resulting in a decrease in catalytic efficiency.

The effect of calcination time on the biodiesel yield was also investigated. With the prolongation of calcination time, the yield gradually increased and reached the maximum value at the calcination time of 3 h. The biodiesel yield increased with the increase of catalytic active center. However, the number of active centers might decrease with a longer calcination time due to the sintering effect, thus leading to a decrease in biodiesel yield.

3.4 Comparison of Acidoresistance of Difference Solid-Base Catalysts

In the production of biodiesel, if the free fatty acid level is too high, it may cause problems with soap formation (saponification). Saponification will result in deactivation of solid base catalyst due to solid base reacting by acid or active sites of catalyst coating by soap. Acidoresistance indicates the ability of anti-poisoning of as-prepared catalyst. Figure 4 shows the acidoresistance of CaO, KF/CaO and KF/CaO–MgO catalysts. Rapeseed oils with different acid value were achieved by mixing with oleic acid. It was found that biodiesel yields exceed 80% when acid value was less than 10 mg KOH/g oil by using KF/CaO–MgO
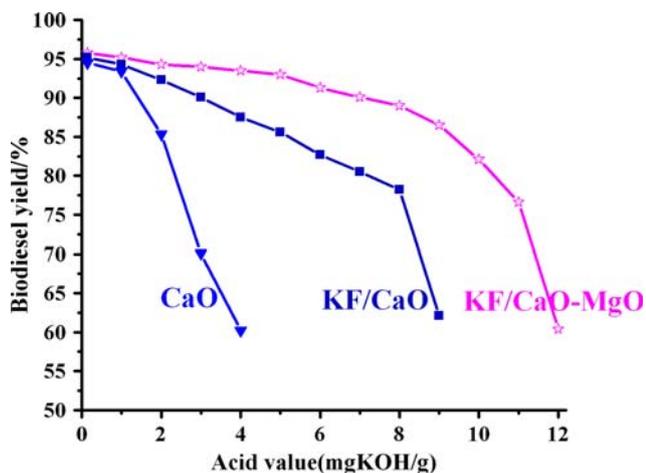
Fig. 4 Comparison of acidoresistance of CaO, KF/CaO and KF/CaO–MgO catalysts: Reaction conditions: molar ratio of methanol to oil 12:1, catalyst amount 3%, reaction temperature 343 K, reaction time 3 h

catalyst, while biodiesel yields were less than 80% when acid value was less than 7 mg KOH/g oil and 2 mg KOH/g oil for KF/CaO and CaO catalysts, respectively. These results indicated that KF/CaO–MgO catalyst resisted higher acidity compared with KF/CaO and CaO catalysts.

3.5 Characterization of the Catalyst by TEM, Raman Spectra, and XRD

In order to establish the correlation between the structure and the catalytic activity of KF/CaO–MgO catalyst, TEM was used to characterize its microstructures. Figure 5 describes TEM image of the as-prepared KF/CaO–MgO catalyst. As shown in Fig. 5, the solid catalyst displayed a mesoporous structure. The grains with size in the range of 100–300 nm were well distributed in the bulk catalyst. These results indicated that the as-prepared catalyst was a kind of mesoporous nanosized solid-base catalyst.
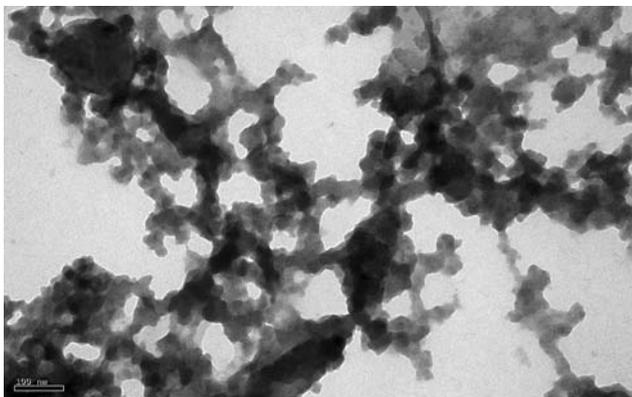

Fig. 5 TEM image of as-prepared KF/CaO–MgO catalyst, the *scale bar* corresponds to 100 nm
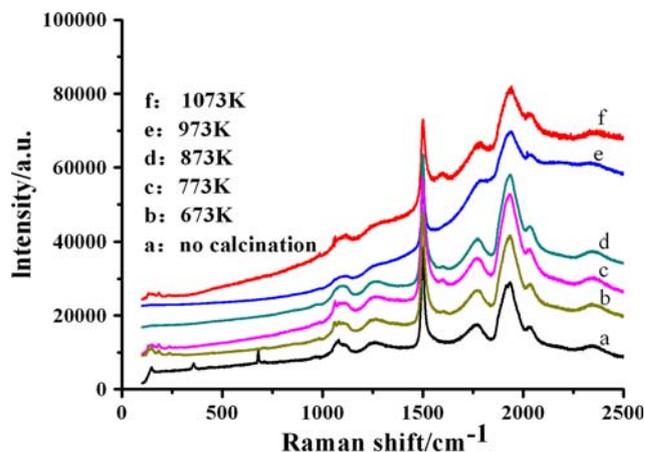

Fig. 6 Raman spectra of KF/CaO–MgO catalyst before calcination and after calcination at different temperatures

Figure 6 displays Raman spectra of the as-prepared catalyst before (a) and after (b–f) calcinations. In Fig. 6a, the vibration band of KF (678.2 cm^{-1}), MgO (1087.72, 778.07, 651.4, 528.6 cm^{-1}) and CaO (1931.95, 1763.34, 1497.63, 1257.04, 1092.78 cm^{-1}) were clearly observed, which is in agreement well with the standard Raman spectra of the respective KF, MgO and CaO (unshown). The background fluorescence of $KCaF_3$ was also clearly observed, indicating the formation of $KCaF_3$ before calcination. Figures. 6b–f represent Raman spectra of the catalysts calcined from 673 to 1073 K. It can be seen that the respective vibration band assigned to MgO and CaO did not change after calcination at different temperatures. However, the vibration band of KF (678.2 cm^{-1}) seems to disappear completely upon calcination of the sample, suggesting that the KF has reacted with the support. The intensity of background fluorescence was increased with the increase of temperature, due to the generation of more $KCaF_3$.

Figure 7 indicates XRD patterns of the as-prepared catalyst before (a) and after (b) calcinations. The Scherrer equation was applied to peak at 37.36, which presents maximum of intensity. The average particle size of KF/CaO–MgO catalyst was obtained to be ca. 35 nm. As shown in Fig. 7a, the components of the catalysts mainly include: $Ca(OH)_2$ ($2\theta = 18.02°$, $28.66°$, $34.08°$, $47.10°$, $50.80°$, $54.36°$, $62.58°$, $64.24°$), CaO ($2\theta = 32.64°$, $37.36°$, $53.92°$, $55.64°$, $67.40°$), MgO ($2\theta = 42.92°$, $61.88°$), $CaKF_3$ ($2\theta = 28.28°$, $35.10°$, $40.48°$, $59.32°$) and $MgKF_3$ ($38.58°$, $45.74°$), according to JCPDS cards. This suggests that $KCaF_3$ and $KMgF_3$ were generated before calcination. However, XRD patterns of $CaKF_3$ and $KMgF_3$ became stronger after calcination (Fig. 7b), indicating production of more $CaKF_3$ and $KMgF_3$. This result is in agreement well with that of Raman spectra. The newly formed $KCaF_3$ and $KMgF_3$ improved the activity of the catalyst, and increased the ability of resistance to saponification reaction [21].
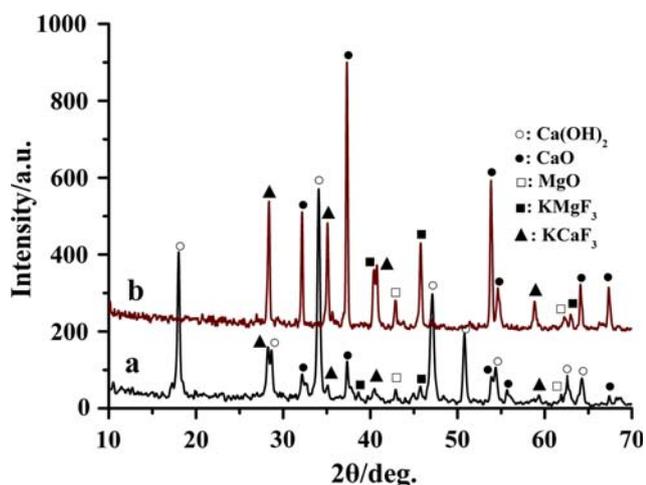
Fig. 7 XRD patterns of KF/CaO–MgO catalyst before *a* and after *b* calcination

Several studies have indicated that Ca ions are leached from CaO in the process of transesterification and that the contribution of homogenous catalysis is significant [22, 23]. However, the addition of MgO can block the leach of Ca ions in the transesterification, which will increases the catalytic activity of CaO [24]. To further prove it, the degree of leach of KF/CaO–MgO catalyst was evaluated by contacting the catalyst with methanol under the same experimental conditions as used in the transesterification process, except for the presence of rapeseed oil. After 2 h of reaction, the catalyst was quickly removed by filtration, and methanol was mixed with rapeseed oil, which was maintained at 343 K for 2 h. No conversion was observed, indicating the catalysis process was not homogeneous catalysis caused by leaching of K, Ca or Mg ions. We also investigated effect of recycling experiments on biodiesel yield. The results showed that biodiesel yield was in excess of 90% after six times recycle.

4 Conclusions

Mesoporous nanosized solid-base catalyst loaded on a two-component complex supporter was prepared by utilizing CaO and MgO as complex carrier via coprecipitation method. When mass ratio of calcium oxide and magnesia oxide was 8:2, mass ratio of KF to CaO–MgO 0.25, calcination temperature 873 K and calcination time 3 h, the prepared catalyst performed the highest activity of 95%. Characterization of TEM and XRD indicated that the grain size and particle size of the catalyst was in nanoscale. The current catalyst solved the problems such as saponification of calcium oxide, low resistance to acid of KF/CaO, which improved adaptability of solid base to feedstocks. Raw materials for preparation of the current catalyst were cheap,

easily gained, and environmentally benign. The catalyst used in the preparation of biodiesel illustrated a good prospect of development and application.

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