Catal Lett (2012) 142:352–359
DOI 10.1007/s10562-012-0776-6

Biodiesel Preparation from Soybean Oil by Using a Heterogeneous $Ca_xMg_{2-x}O_2$ Catalyst

Wenlei Xie · Yawei Liu · Hong Chun

Received: 6 December 2011 / Accepted: 23 January 2012 / Published online: 10 February 2012

Abstract An effective heterogeneous catalyst, $Ca_xMg_{2-x}O_2$, was prepared and tested for soybean oil transesterification with methanol. The catalysts were characterized by using X-ray diffraction , Fourier transform infrared spectra, thermo gravimetric and differential thermal analysis , and Hammett indicator method. The catalyst with Ca/Mg ratio of 1.0 and calcined at 800 °C exhibited high catalytic activities. Under the suitable transesterification conditions (methanol/oil ratio 12:1, catalyst loading 6 wt%, reaction time 5 h, at reflux of methanol), the oil conversion of 91.3% could be achieved. The catalyst can be easily recovered and reused without significant deactivation.

Keywords Transesterification · Biodiesel · Heterogeneous catalyst · Vegetable oil

1 Introduction

Methyl esters of fatty acids, better known as biodiesel and produced by transesterification of vegetable oils with methanol, can be used as a viable alternative to replace fossil diesel oil. During the recent years, biodiesel has attracted much attention mainly due to the increase in the price of petroleum and environmental concerns. In addition to being renewable and biodegradable, the biodiesel fuel displays advantages such as lower emissions of CO, unburned hydrocarbons, particulate matter and SO_2 during the combustion process [1–3].

For industrial biodiesel production, homogeneous basic catalysts such as sodium or potassium hydroxides, carbonates or alkoxides, are commonly employed for the transesterification process to produce fatty acid methyl esters [4, 5]. However, the process catalyzed by homogeneous basic catalysts requires additional separation and purification process and results in a large amount of caustic wastewater. Besides, alkaline catalysts can react with free fatty acids present in vegetable oils, to form unwanted soap by-products, thereby leading to problems involving product separation and purification [4–6]. Therefore, vegetable oils with a low content of free fatty acids are required to allay soap formation and serious problems originating from emulsion formation [7]. To overcome such disadvantages associated with homogeneous base catalysts, the transesterification of vegetable oils over environmentally benign solid catalysts is a promising alternative method [8–10]. The utilization of heterogeneous catalyst requires less downstream process compared to that of homogeneous one, thus reducing the price of final biodiesel production. Moreover, a heterogeneous catalyst could be easily separated from the reaction mixture by filtration or centrifugation, and then could be reused [10–13]. For this reason, different heterogeneous catalysts for the transesterification reactions have been developed mainly based on basic alkaline and alkaline-earth compounds [14–19].

Since the transesterification of triglyceride is a reversible reaction, an increase in the amount of the reactants can result in higher yields. Stoichiometrically, three moles of methanol are needed for each mole of triglyceride in the transesterification reaction. However, in practice, a large excess of methanol is generally employed to shift the reaction equilibrium towards the

W. Xie (✉) · Y. Liu · H. Chun
School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, People's Republic of China
e-mail: xwenlei@163.com

direction of methyl ester formation, which therefore results in a quite polar reaction medium in which the reaction is carried out. As a result, the leached catalyst in the quite polar system for the solid catalyst can not be ignored because it could hinder its application as a heterogeneous catalyst. It is reported that potassium can be easily leached from the KOH/Al_2O_3 and KOH/NaY catalysts in the transesterification process, and this leached metals create some homogeneous catalytic activities and require removal from the final product [20]. Among solid base catalysts, calcium-based catalysts are shown to be a promising catalyst and have been widely investigated in the transesterification reaction due to their high activity and low cost [21–23]. However, the dissolution of the catalyst in the reaction media is concerned to hinder the benefits of its heterogeneous nature. It is found that CaO could be soluble in methanolic solution and a larger amount of leached species is observed especially when glycerol is present, which results from the formation of calcium diglyceroxide [24]. Thus, a fraction of bulk calcium oxide is dissolved in the reaction mixture solution, causing both homogeneous and heterogeneous pathway and eventually reducing the stability of the catalyst.

In order to reduce the leaching process, the mixed metal oxides are intended to improve the stability of calcium-based solid catalyst by the interaction of CaO with other metal oxides. Among the calcium-based catalysts, a solid base of CaO supported MgO exhibited good catalytic activities for the preparation of biodiesel; however the leaching of homogeneous catalytic species from the supported catalysts into the reaction media during the reaction, which was the major limitation of solid base catalysts, was observed, thus losing the advantages of a purely heterogeneous process for the production of biodiesel [25–27]. Therefore, it is extremely desirable to develop a calcium-based catalyst with a high catalytic activity and stability for a long-term transesterification reaction. For this purpose, in the present investigation, a solid base catalyst of $Ca_xMg_{2-x}O_2$, was prepared by three different methods, namely, impregnation, co-precipitation and modified co-precipitation method, and was then adopted for the preparation of biodiesel. The catalytic activity of the catalyst in the transesterification of soybean oil with methanol was evaluated regarding the conversion of soybean oil to methyl esters, and much attention was paid on the influence of calcination temperature and Ca/Mg ratio. Besides, the physicochemical properties of the as-prepared catalysts were investigated using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermo gravimetric and differential thermal analysis (TG–DTA) and Hammett indicator method.

2 Experimental

2.1 Materials

Commercial edible grade soybean oil was obtained from market. According to GC (Shimadzu DC-9A) analysis, the fatty acid in the used soybean oil consists of palmitic acid, 12.3%; stearic acid, 5.8%; oleic acid, 26.5%; linoleic acid, 49.4%; and linolenic acid, 5.9%. The acid value of the soybean oil was less than 0.1 mg KOH/g, and the average molecule weight was 874 g/mol, calculated from the saponification index (S.V. = 192.6 mg KOH/g). Alkaline-earth metal salts, such as $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were purchased from Luoyang Chemical Regent Factory (Luoyang, China). All other employed materials were of analytical grade and were used as received without further purification.

2.2 Catalyst Preparation

The $Ca_xMg_{2-x}O_2$ catalysts were prepared by different methods, including the impregnation, the conventional co-precipitation, and the modified co-precipitation method. Details of the preparation of these catalysts were described as follows.

The impregnated $Ca_xMg_{2-x}O_2$ (denoted as $Ca_xMg_{2-x}O_2$ (IP)) catalyst with Ca/Mg molar ratio of 1:1 was prepared by the wetness impregnation method using MgO as support. The MgO carrier was first pretreated at 500 °C to stabilize the crystalline structure. Afterward, calcium nitrate was loaded onto magnesium oxide by an impregnation method from aqueous solutions containing different amounts of $Ca(NO_3)_2$. At the end of the impregnation, the sample was dried overnight at 100 °C, and then calcined at a set temperature (typically at 800 °C) in air for 5 h. Upon calcination, the $Ca(NO_3)_2$ impregnated in the support was decomposed to calcium oxide.

The conventional co-precipitated $Ca_xMg_{2-x}O_2$ (denoted as $Ca_xMg_{2-x}O_2$ (CP)) catalyst with Ca/Mg molar ratio of 1:1, was prepared by co-precipitation of $Mg(NO_3)_2$ and $Ca(NO_3)_2$ aqueous solution. Typically, 10.2 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 9.4 g $Ca(NO_3)_2 \cdot 4H_2O$ were firstly dissolved in 200 mL of deionized water. A NaOH aqueous solution in a separation funnel was dropped into the mixed solution with vigorous stirring until the pH reached 12. The resulting slurry solution was further aged in the mother solution at room temperature for 24 h and was then separated by vacuum filtration, following which the precipitate was thoroughly washed with deionized water at least four times and dried in an oven at 120 °C overnight. The $Ca_xMg_{2-x}O_2$ (CP) catalyst was obtained by calcination of the precipitate at 800 °C for 5 h. After calcination, the corresponding metal oxides were formed.

The catalyst prepared by a modified co-precipitated method was designated as $Ca_xMg_{2-x}O_2$ (MP) and the preparation procedure was briefly described below. This method was also employed for the preparation of CaO–CeO_2 catalyst in the literature [28]. Initially, appropriate quantities of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ for different compositions in the final composites, in terms of Ca/Mg molar ratio, were dissolved in deionized water and the resulting precursor solutions were homogeneously mixed. To this solution, an ammonia aqueous solution in a separation funnel was subsequently added dropwise with continuous stirring until the pH value of 10 was achieved. At this pH value, the calcium ions could not be precipitated since the $Ca(OH)_2$ precipitate was not produced in an ammonia aqueous solution, whereas the $Mg(OH)_2$ precipitates were mainly formed in this conditions. After that, the resulting slurry mixture was continuously stirred for 24 h in the mother solution at room temperature, leading to the formation of gel solution. Finally, the water was removed from the gel solution and, the gels obtained hereby were oven-dried overnight at 120 °C and subsequently calcined under air atmosphere at temperatures of 500–1,000 °C for 5 h in a muffle furnace to decompose the precursor into its corresponding metal oxides. After calcination, the catalyst was immediately kept in the vacuum oven before used for the catalyst characterization and catalytic study. The concentration of the precursor solution was adjusted so as to yield the desired Ca/Mg molar ratio in the final catalysts. The Ca/Mg molar ratio was calculated based on the amounts of the initial materials.

Since the obtained catalyst is prone to be contaminated by the CO_2 contained in air, a higher temperature pretreatment is necessary before the solid base catalyst is used. In the in situ activation prior to reaction, strong basic sites are formed on the composites resulting from the decomposition of precursor compounds and retained high efficiency in the catalytic processes.

2.3 Catalyst Characterization

Powder XRD measurements were performed on a Rigaku D/max-3B diffractometer with the Cu Kα radiation ($\lambda = 0.154$ nm). An accelerating voltage of 40 kV and a current of 50 mA were used. The XRD phases present in the sample were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standards) database files.

The FT-IR spectra of the sample were recorded using KBr pellet technique on a Shimadzu IR-Prestige-21 spectrometer in the wavenumber region of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1}. The thermal behavior of the catalyst was evaluated by a STA409PC DT and TG analyzer operating under a flow of air at a 20 °C/min heating rate up to 1,000 °C.

Basic strengths of the catalyst (H_-) were determined with various Hammett indicators and the base amount (described as basicity) was assessed by the Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) titration [29]. The Hammett indicators were bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$) and 2,4-dinitroaniline ($H_- = 15.0$). Approximately 25 mg of the solid base was shaken with 5 mL of indicator methanol solution and left to equilibrate until further color changes were not observed. If the indicator exhibited a color change, the catalyst was considered to be stronger than the indicator; and if not, the catalyst was labeled as weaker than the indicator. The method of titration was used to determine the basicity of the catalyst. The solid base catalyst was mixed with a known concentration of benzene carboxylic acid. The basic catalyst will neutralize acids by an equivalent amount to its basicity. The resultant concentration of benzene carboxylic acid was determined by titration with NaOH solution, and then the basicity was calculated based on the amount of acid consumed.

2.4 Transesterification Procedures

A 16 g of soybean oil (18.3 mmol, calculated from the average molecular weigh of the soybean oil), different volumes of anhydrous methanol and the freshly prepared catalysts were placed into a 250 mL round-bottom flask equipped with a water-cooled condenser and a magnetic stirrer. The transesterifications were allowed to perform at reflux of methanol for the required time. In order to minimize the mass transfer limitation, each mixture was stirred vigorously and refluxed throughout the duration of the reaction. After the course of reaction, the catalyst was separated by filtration and the residual methanol was recovered by a rotary evaporator under vacuum at 60 °C prior to the subsequent analyses.

The transesterification process consists of a sequence of three consecutive and reversible reactions transforming the triglyceride into a diglyceride, then into a monoglyceride, and finally into glycerin and the fatty acid methyl esters. Obviously, one molecule of methyl ester is produced for each molecule of methanol consumed, with the formation of one molecule of free hydroxyl group liberated in the transesterification reaction. Therefore, the increase of methyl ester amount results in the increase of hydroxyl content of the liquid phase with the same step if the excess methanol is absolutely removed. The conversion of soybean oil to methyl esters was determined by measuring hydroxyl content on the transesterified soybean oil as previously described in the literature [30].

To optimize the reaction conditions, experiments were performed by varying reaction parameters such as methanol/oil ratio, catalyst amount, and reaction time. The obtained results (data not shown) showed that the optimized conditions for the transesterification reaction were a methanol/oil molar ratio of 12:1, a catalyst amount of 6 wt%, and a reaction time of 5 h, which resulted in a 91.3% conversion of soybean oil at reflux of menthol.

3 Results and Discussion

3.1 Influence of Preparation Methods on the Catalyst Performance

The preparation method of the catalysts has an important influence on their catalytic performance. In this work, the impregnation, conventional co-precipitation, and modified co-precipitation method were used for the catalyst preparation.

For the co-precipitation method, ammonia or NaOH aqueous solutions are usually employed as the precipitating agent. When NaOH is used as a precipitating agent, the alkali metals can not be completely removed from the composites and the residual sodium metal is easily leached by dissolution in reaction media during the transesterification processes. The presence of leached basic species in the reaction medium may contribute the catalytic activity as a homogeneous pathway, thus eventually reducing the stability of the catalyst and also restricting the reusability of the catalyst [27]. During the preparation procedure with ammonia aqueous solution as precipitators and metal nitrate as precursors, the ammonia ion and nitrate ion can be decomposed and eliminated completely from the mixed metal oxides as the catalyst is calcined at a higher temperature, which can reduce the amount of leached basic species and thus probably enhances the catalyst stability. However, when the ammonia aqueous solution was employed as a precipitating agent, the calcium ions could not be precipitated and $Mg(OH)_2$ precipitates were mainly formed. For this reason, a modified co-precipitation method was developed in an attempt of obtaining the mixed metal oxides catalyst [28]. In this preparation method, the calcium and magnesium ions are firstly in the form of metal hydroxides upon adding ammonia aqueous solution into the precursor compound solution. After pH adjustment and ageing for 24 h, the gel solution was formed. As the $Mg(OH)_2$ precipitates were firstly produced and probably acted as a nucleus of the composites, the $Ca(OH)_2$ could be loaded onto the $Mg(OH)_2$ during the ageing and drying process. The mixed metal hydroxide solid could be obtained by drying the resulting gels, followed by a calcination step ultimately to produce mixed metal oxides.

The experimental results indicated that the differently prepared $Ca_xMg_{2-x}O_2$ catalysts exhibited high catalytic activities, with the soybean oil conversion higher than 90%. Over $Ca_xMg_{2-x}O_2$ (MP), $Ca_xMg_{2-x}O_2$ (CP) and $Ca_xMg_{2-x}O_2$ (IP) catalyst, the conversions were 91.3, 92.5 and 93.8%, respectively. However, for industrial applications, the reusability of catalysts is of great significance. After the transesterification reaction, the spent catalyst was separated by filtration, washed thoroughly with petroleum ether and methanol, and then heated at 120 °C overnight. Subsequently, a new transesterification reaction under the identical reaction conditions was carried out using the recovered catalyst. As can be seen from Fig. 1, the oil conversion over the recovered $Ca_xMg_{2-x}O_2$ (IP) catalyst was decreased obviously to 84.2% after three cycles and to 46.5% after five cycles, revealing that the recovered $Ca_xMg_{2-x}O_2$ (IP) catalysts exhibited a lower stability when they were subjected to fresh transesterification reaction. Although the deactivated $Ca_xMg_{2-x}O_2$ (IP) catalyst was regenerated by directly calcining it at a temperature of 800 °C, its catalytic activity was not recovered, which showed that the loss in the activity was probably caused by the leaching of calcium from the catalyst surface. Besides, over the recovered $Ca_xMg_{2-x}O_2$ (CP) catalyst, the conversion of soybean oil was 93.8, 91.3, 87.4, 83.2 and 72.7% when the catalyst was used for 1, 2, 3, 4, and 5 cycles, respectively, suggesting that the $Ca_xMg_{2-x}O_2$ (CP) catalyst was deactivated greatly after use for more than three cycles. Similar results were also reported in the literature [25]. The presence of trace of alkali metals was proposed as the origin of the leachable catalytic species in the $Ca_xMg_{2-x}O_2$ (CP) catalyst [27, 31]. Moreover, the data in Fig. 1 also showed that the $Ca_xMg_{2-x}O_2$ (MP) catalysts could be used for five times and still maintained the conversion over 85%. As a result, the $Ca_xMg_{2-x}O_2$ (MP) catalyst has a high operational stability with no appreciable

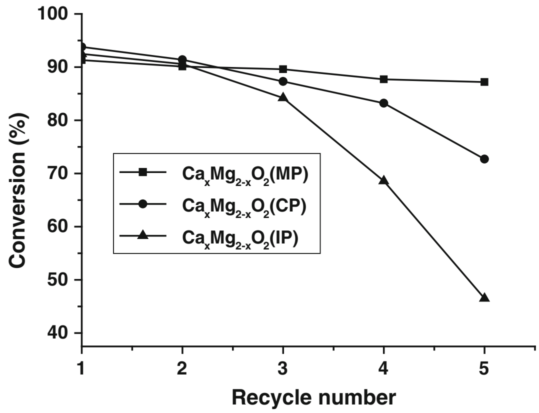

Fig. 1 The stability of the $Ca_xMg_{2-x}O_2$ catalyst prepared by different methods. Reaction conditions: methanol/oil molar ratio 12:1, catalyst amount 6 wt%, reaction temperature 65 °C

loss in catalytic activity even after five successive cycles and performs a good reusability. This observation could be attributed to the interaction of CaO and MgO in the solid solution formed during the calcination processes, which strongly anchors the basic sites on the catalyst surface and results in a high stability of the $Ca_xMg_{2-x}O_2$ catalyst. In an attempt to confirm the stabilization effect the additional experiment was carried out. Firstly, 0.96 g of $Ca_xMg_{2-x}O_2$ (MP) catalyst was stirred with 10 g of methanol at reflux of methanol for 5 h. After the catalyst was removed by filtration, the supernatant was mixed with 16 g soybean oil and then the reaction was conducted under optimized conditions as described above. If the catalyst was lixiviated, the oil conversion should be observed due to the homogeneous contribution. The experimental results showed that only insignificant conversion of 2.1% was obtained for the supernatant solution which confirmed that the solid catalyst did not leach out during the transesterification reaction. Such experiments have been already used in the previous literature and demonstrated that the leached species from the CaO catalysts were responsible of the homogeneous reaction [32]. By drawing on the results, the $Ca_xMg_{2-x}O_2$ (MP) catalyst exhibits a higher activity and better stability, and therefore is chosen for the subsequent study in this work.

Fourier transform infrared spectroscopy was employed to investigate the catalyst prepared by the modified co-precipitation methods. Before the FT-IR measurements, the sample was pretreated at a temperature of 800 °C. In spite of this, it is unavoidable that the catalyst contacts air during the IR measurement process. As shown in Fig. 2, all the sample showed an intense absorption band at approximately 3,590 cm^{-1} that could be assigned to the stretching vibration of the hydroxyl groups attached to CaO and MgO [33]. Besides, the minor absorption peak at about 1,620 cm^{-1} could be ascribed to the bending vibration mode of H_2O molecules adsorbed from air [33]. Moreover, the two absorption peaks at 1,130 and 1,550 cm^{-1} attributable to the vibrations of carbonates were observed in the IR spectra of the catalysts, thus, revealing the presence of surface carbonate [33]. Since the IR measurement was not an in situ operation, the carbonates were supposed to be formed by the reaction of metal oxides with carbon dioxide during the sample preparation in air [22]. Additionally, there was very strong absorption peak at 500–700 cm^{-1} that could be principally attributed to Ca–O or Mg–O stretching vibration [34]. As reported previously, the basic sites in the alkaline-earth metal oxides can be explained due to the presence of the M^{2+}–O^{2-} ion pair in different coordination environments. Various oxygen anions O^{2-} of low coordination number on the metal oxides are considered to be responsible for the basicity [19]. The amount of surface oxygen depends on the chemical composition of the mixed metal oxides and the calcination temperature. In general, metal oxide catalysts are usually carbonated in air and hence probably inert. However, in the in situ activation prior to reaction, the contamination of CO_2 from atmosphere could be avoided.

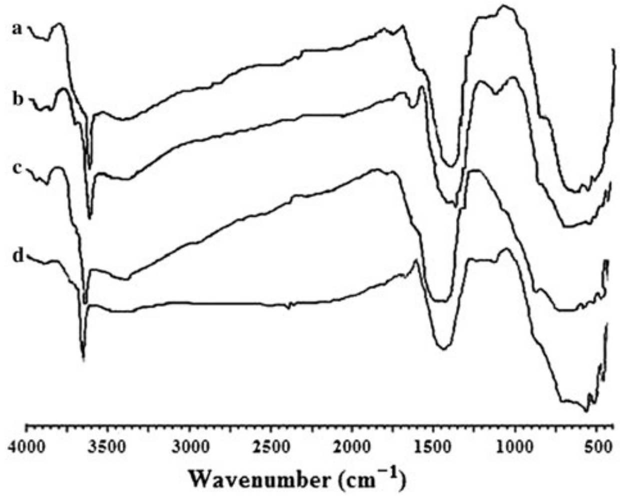

Fig. 2 IR spectra of the $Ca_xMg_{2-x}O_2$ (MP) catalyst. *a* Ca/Mg ratio 1.0 calcined at 700 °C; *b* Ca/Mg ratio 1.0 calcined at 800 °C; *c* Ca/Mg ratio 1.5 calcined at 800 °C; *d* Ca/Mg ratio 1.0 calcined at 900 °C

The thermal behavior of $Ca_xMg_{2-x}O_2$ (MP) catalyst is illustrated in Fig. 3. As can be seen, the TG profile showed three-stages of weight losses. The initial 1.2% weight loss in the temperature range of 30–200 °C, which was accompanied by an endothermic event, could be considered due mostly to the loss of weakly adsorbed water. The second stage weight loss of 30.1%, overlapping a broad endothermic DTA peak in a wide temperature range of 300–600 °C, was probably attributed to the decomposition of calcium and magnesium hydroxide. The final weight loss in the range above 600 °C was considered to be induced by the $CaCO_3$ decomposition. In the light of the results together with other characterization results, it can be

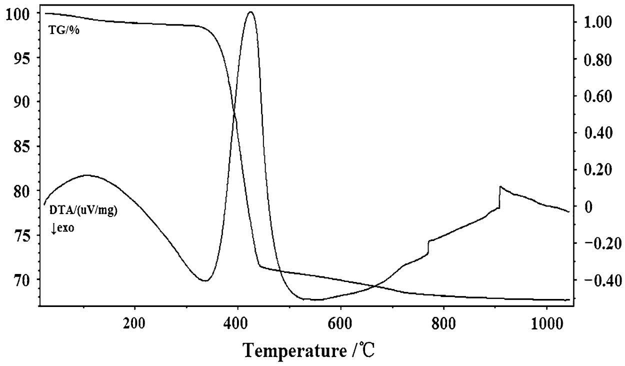

Fig. 3 TG–DTA curves of the non-calcined $Ca_xMg_{2-x}O_2$ (MP) sample

inferred that the formation of catalytic activity sites most likely results from the decomposition of calcium and magnesium compounds.

3.2 Influence of Preparation Conditions on the Catalyst Performance

Since the $Ca_xMg_{2-x}O_2$ (MP) catalyst prepared by a modified co-precipitation method exhibited promising performances in the soybean oil transesterification, the influence of preparative parameters, such as the calcination temperature and Ca/Mg molar ratio, were studied to optimize the catalyst performance.

The basicity of the $Ca_xMg_{2-x}O_2$ (MP) catalysts and their catalytic activity are shown in Table 1 as a function of calcination temperatures. It is shown that the basicity and the catalytic activity of the catalysts are significantly affected by the calcination temperature. Without the calcination, the catalyst was inactive in the transesterification reaction. With the increase of calcination temperature from 500 to 800 °C, the basicity was gradually increased, though the basic strengths of the different $Ca_xMg_{2-x}O_2$ (MP) catalysts were of equal strength ($9.8 < H\_ < 15.0$), and in consistence with this, the corresponding conversion to methyl esters was thus improved. However, with further increasing the calcination temperature higher than 800 °C, the basicity was slightly reduced, and mostly due to this, leading to a decrease of the conversion to methyl esters. The decrease in the basicity with further increase in calcination temperature is probably due to a reduction of surface area originating from the sintering of fine crystals, which leads to the inferior catalytic activity of the catalyst [26, 28]. Obviously, the optimal calcination temperature for the catalyst was observed at 800 °C. At this calcination temperature, both the highest basicity and the best conversion were achieved. Further, the basicity changes with the calcination temperature for the catalyst are in agreement with the changes in the catalytic activity toward the soybean oil transesterification reaction. Since $Ca(OH)_2$–$Mg(OH)_2$ is inactive for this reaction, the activity variation of the catalysts calcined at different temperatures is owing to the different precursor decomposition extents. The thermal treatment at a calcination temperature of 800 °C is necessary for the catalyst to get higher catalytic activity. According to TG/DTA curves, the transformation of the alkaline-earth metal hydroxide to the metal oxides occurred between 300 and 600 °C. However, the prepared $Ca_xMg_{2-x}O_2$ (MP) catalyst is easily contaminated by the CO_2 contained in air to form a stable carbonate salts, and mostly because of this, the need to heat to 800 °C is due to the need to decompose the calcium carbonate. This phenomenon is consistent with the XRD measurements and previous work [26, 35]. Therefore, the crystalline magnesium and calcium oxides formed by decomposition of metal compounds are expected to be the main catalytically active sites, in accordance with the result of similar published studies [25].

In order to explain the difference in catalytic activities, it is important to characterize the catalysts by physico–chemical techniques. Figure 4 shows the XRD patterns of

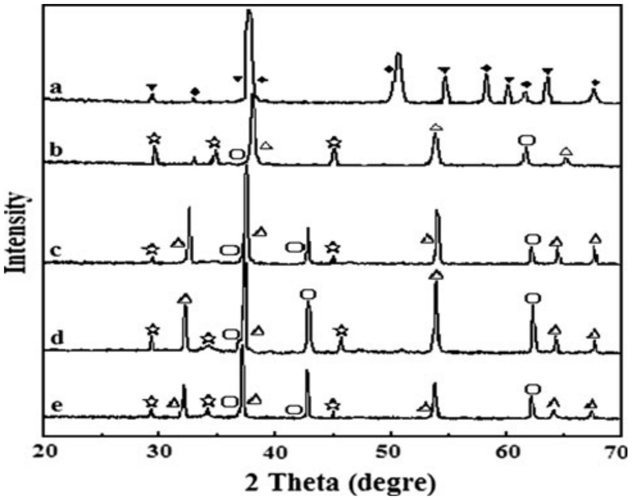

Fig. 4 XRD patterns for the $Ca_xMg_{2-x}O_2$ (MP) catalyst prepared by modified co-precipitation methods with different calcination temperatures. *a* non-calcination; *b* at 700 °C; *c* at 800 °C; *d* at 900 °C; *e* the recovered catalyst. Symbols: (*open circle*) MgO, (*open triangle*) CaO, (*open star*) $CaCO_3$, (*filled diamond*) $Mg(OH)_2$ and (*filled inverted triangle*) $Ca(OH)_2$

Table 1 The basicity and conversion over the $Ca_xMg_{2-x}O_2$ catalyst prepared by modified co-precipitation method with different calcination temperatures

Calcination temperature (°C)	Basicity (mmol/g)		Total basicity (mmol/g)	Conversion (%)
	$H\_ = 7.2–9.8$	$H\_ = 9.8–15.0$		
Non-calcination	0.64	0.17	0.81	1.6
500	1.06	0.31	1.37	25.3
600	1.42	0.82	2.24	36.7
700	1.63	1.42	3.05	72.1
800	1.95	2.28	4.23	91.3
850	1.98	2.12	4.10	90.1
900	1.89	2.04	3.93	88.4

the $Ca_xMg_{2-x}O_2$ (MP) catalysts prepared by the modified co-precipitation method with the calcination temperatures altered from 700 to 900 °C. In the absence of calcination, the sample as prepared only exhibited $Mg(OH)_2$ and $Ca(OH)_2$ phases. After the calcination, the characteristic diffraction peak of cubic CaO appeared at 2θ angles of 32.3°, 37.5°, 53.9° and 64.2° (JCPDS File No. 37-1497), and the characteristic diffraction peak of hexagonal MgO at 2θ angles of 37.3°, 43.0°and 62.3° was also observed (JCPDS File No. 4-0829), indicating that the $Ca_xMg_{2-x}O_2$ (MP) catalyst consisted of a mixture of each metal oxide. As a consequence, the improved catalytic activity may be due to the synergism effect between CaO and MgO. Besides, the low diffraction peaks at 2θ angles of 29.8° and 45.2° corresponding to $CaCO_3$ (JCPDS File No. 41-1475) were registered in the diffraction patterns of the calcined samples, suggesting that the CaO formed by calcination at higher temperatures could absorb atmospheric CO_2 with the formation of $CaCO_3$ phase [16]. Moreover, with the increase of calcination temperature from 700 to 900 °C, both CaO and MgO diffraction peaks became more intensive. In addition, as depicted in Fig. 5, the characteristic CaO and MgO peaks for the recovered catalyst were decreased slightly in their intensity. This phenomenon is in agreement with the measurements of basicity and activity, as indicated above.

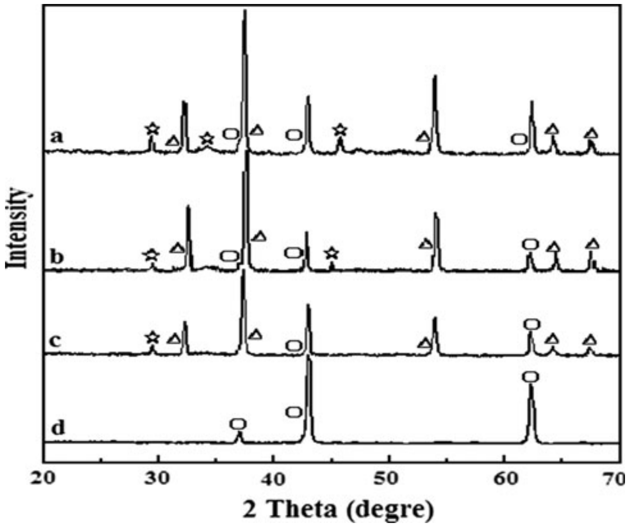

Fig. 5 XRD patterns for the $Ca_xMg_{2-x}O_2$ (MP) catalyst by modified co-precipitation methods with different Ca/Mg molar ratios. *a* Ca/Mg ratio 1.5; *b* Ca/Mg ratio 1.0; *c* Ca/Mg ratio 0.5; *d* MgO. Symbols: (*open circle*) MgO, (*open triangle*) CaO and (*open star*) $CaCO_3$

The effects of Ca/Mg molar ratio on the basicity and the catalytic activity of the catalysts were studied and the results are summarized in Table 2. It can be seen that the soybean oil conversion is greatly dependent on the Ca/Mg ratio. With the rise of Ca/Mg molar ratio from 0 to 1.0, both the basicity and the corresponding oil conversion were enhanced remarkably, and the best conversion of 91.3% together with the highest basicity of 4.23 mmol/g were attained at Ca/Mg molar ratio of 1.0, though the basic sites in various $Ca_xMg_{2-x}O_2$ (MP) samples with different Ca/Mg molar ratios were of equal strength ($9.8 < H\_ < 15.0$). However, the further increasing the Ca/Mg molar ratio led to a drop of the basicity, and subsequently a decrease of the conversion to methyl esters. The same relationship between the catalytic activity and the Ca/Mg molar ratio was also observed by other researches [25]. Further loading of calcium content with the residual bulk phase of CaO may result in saturation or filling of pores in the mixed oxides, which leads to the conversion reduction [26]. Given the present results, the $Ca_xMg_{2-x}O_2$ (MP) catalyst with the Ca/Mg ratio of 1.0 is the most suitable catalyst for the reaction.

Power XRD patterns for the catalysts with various Ca/Mg molar ratios are presented in Fig. 5. As illustrated in this figure, with increasing the Ca/Mg molar ratio of the catalyst from 0 to 1, the diffraction lines associated to CaO and $CaCO_3$ became more intense. The further increasing the Ca/Mg molar ratio to 1.5 did not result in the increase in the relative intensity of diffraction peaks for CaO and MgO. Such changes in the intensity of the diffraction peaks were coincident with the variability of catalytic activity and basicity in the $Ca_xMg_{2-x}O_2$ catalyst.

In the present work, the oil conversion of 91.3% can be achieved by using the solid base catalyst. However, to drive the transesterification reaction toward completion of methyl ester formation, a large excess of menthol (a molar ratio of methanol to oil of 12:1) is required. Evidently, excessive methanol is not favorable for industrial applications, since more energy is needed for recovering the excessive of methanol. Therefore, for the industrial

Table 2 The basicity and conversion over the $Ca_xMg_{2-x}O_2$ catalyst prepared by modified co-precipitation method with different Ca/Mg molar ratios

Ca/Mg molar ratio (mol/mol)	Basicity (mmol/g)		Total basicity (mmol/g)	Conversion (%)
	$H\_ = 7.2–9.8$	$H\_ = 9.8–15.0$		
0	1.12	0.85	1.97	56.5
0.5	1.59	2.00	3.59	86.3
1.0	1.95	2.28	4.23	91.3
1.5	1.83	1.94	3.77	86.8
2.0	1.77	1.90	3.67	85.3

production of biodiesel, the activity of the catalyst is expected to be further improved considerably in the near future so that an appropriate amount of methanol is employed for a good conversion.

4 Conclusions

In the present study, the $Ca_xMg_{2-x}O_2$ (MP) mixed oxide has been prepared with the aim of being used as heterogeneous catalysts for the production of biodiesel. The performances of the catalyst for the transesterification of soybean oil with methanol are largely dependent on the catalyst preparation methods and conditions. The catalyst prepared by a modified co-precipitation method, with the Ca/Mg ratio of 1.0 and calcined at 800 °C, was found to be the optimum catalyst, which could give the best catalytic activity. The high catalytic activities are shown to arise from the high basicity of the catalyst. The maximum soybean oil conversion of 91.3% was obtained when the reaction conditions were set at reflux of methanol with a molar ratio of methanol to oil of 12:1, a reaction time of 5 h and a catalyst amount of 6 wt%. The catalyst thus obtained shows a long-term stability with no appreciable loss in catalytic activity after five cycles.

Acknowledgments This work was financially supported by research grants from National Science Foundation of China (Project No. 21076062) and Program for Innovative Research Team in Universities of Henan Province in China (2012IRTSTHN009).

References

1. Ma F, Hanna MA (1999) Bioresour Technol 70:1
2. Shumaker JL, Crofcheck C, Tackett SA, Santillan-Jimenez E, Crocker M (2007) Catal Lett 115:56
3. Li H, Xie W (2008) J Am Oil Chem Soc 85:655
4. Darnoko D, Cheryan M (2000) J Am Oil Chem Soc 77:1263
5. Jitputtia J, Kitiyanana B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P (2006) Chem Eng J 116:61
6. Di Serio M, Tesser R, Pengmei L, Santacesaria E (2008) Energy Fuel 22:207
7. Encinar JM, Gonzalez JF, Reinares AR (2005) Ind Eng Chem Res 44:5491
8. Wilson K, Hardacre C, Lee AF, Montero JM, Shellard L (2008) Green Chem 10:654
9. Ilgen O (2011) Fuel Process Technol 92:452
10. Xie W, Yang Z, Chun H (2007) Ind Eng Chem Res 46:7942
11. Cantrell DG, Gillie LJ, Lee AF, Wilson K (2005) Appl Catal A 287:183
12. Xie W, Yang Z (2007) Catal Lett 117:159
13. Gai PL, Montero JM, Lee AF, Wilson K, Boyes ED (2009) Catal Lett 132:182
14. Semwal S, Arora AK, Badoni RP, Tuli DK (2011) Bioresour Technol 102:2151
15. Xu C, Enache DI, Lloyd R, Knight DW, Bartley JK, Hutchings GJ (2010) Catal Lett 138:1
16. Castro CS, Cardoso D, Nascente PAP, Assaf JM (2011) Catal Lett 141:1316
17. Umdu ES, Tuncer M, Seker E (2009) Bioresour Technol 100:2828
18. Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R (2011) Biomass Bioenergy 35:827
19. Anderson JA, Beaton A, Galadima A, Wells RPK (2009) Catal Lett 131:213
20. Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In S (2009) Renew Energy 34:1145
21. Liu X, He H, Wang Y, Zhu S, Piao X (2008) Fuel 87:216
22. Yoosuk B, Udomsap P, Puttasawat B (2011) Appl Catal A 395:87
23. Alba-Rubio AC, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Martín-Alonso D, Jiménez-López A, Maireles-Torres P (2008) Appl Catal A 334:35
24. Granados ML, Alonso DM, Sádaba I, Mariscal R, Ocón P (2009) Appl Catal B 89:265
25. Yan S, Lu H, Liang B (2008) Energy Fuel 22:646
26. Taufiq-Yap YH, Lee HV, Yunus R, Juan JC (2011) Chem Eng J 178:342
27. Albuquerque MCG, Azevedo DCS, Cavalcante CL Jr, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Rodríguez-Castellón E, Jiménez-López A, Maireles-Torres P (2009) J Mol Catal A 300:19
28. Thitsartarn W, Kawi S (2011) Green Chem 13:3423
29. Xie W, Li H (2006) J Mol Catal A 255:1
30. Xie W, Li H (2006) J Am Oil Chem Soc 83:869
31. MacLeod CS, Harvey AP, Lee AF (2008) Chem Eng J 135:63
32. Granados ML, Poves MDZ, Alonso DM, Mariscal R, Galisteo FC, Moreno-Tost R, Santamaría J, Fierro JLG (2007) Appl Catal B 73:317
33. Mustrowski P, Chmielarz L, Bozek E, Sawalha M, Roessner F (2004) Mater Res Bull 39:263
34. Nakamoto K (1970) Infrared spectra of inorganic and coordination compounds. Wiley, New York
35. Anderson JA, Rochester CH (1986) J Chem Soc, Faraday Trans 82:1911