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ORIGINAL PAPER

Preparation of Biodiesel by Transesterification of Rapeseed Oil with Methanol Using Solid Base Catalyst Calcined $K_2CO_3/\gamma\text{-}Al_2O_3$

Xianghua Liu · Xingyao Xiong · Canming Liu ·
Dengyou Liu · Anjun Wu · Qiulong Hu · Chunlin Liu

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Abstract We report here the preparation of biodiesel by transesterification of rapeseed oil with methanol using calcined $K_2CO_3/\gamma\text{-}Al_2O_3$ as a solid base catalyst. The prepared catalysts were characterized using SEM, IR and BET, and their catalytic activities were evaluated. The reaction conditions were optimized, and in particular, the conversion can be as high as 98.62% under the optimal reaction conditions. In addition, the effect of the presence of water in the reaction system on the catalytic activity was also studied.

Keywords Biodiesel · Methanol · Rapeseed oil · Solid base catalyst · Transesterification

Introduction

Biodiesel is a promising non-toxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [1]. It is usually produced by transesterification of vegetable oils or animal fats with methanol using homogeneous base or acid catalysts. Specifically, potassium hydroxide, sodium hydroxide, as well as their carbonate and potassium and sodium alkoxides such as $NaOCH_3$ are often used as catalysts in base-catalyzed processes [2–5], while sulfonic acid and hydrochloric acid are the usual acid catalysts [6, 7]. Generally, the catalytic activity of base catalysts in transesterification is higher than that of acid catalysts. However, removal of base catalysts from the reaction system is often technically difficult due to the formation of a stable emulsion as well as saponification as a result of aqueous quenching. To overcome this difficulty, a great variety of heterogeneous base catalysts have been developed to not only effectively catalyze the transesterification of vegetable oils with methanol but also provide the advantage that they can be easily separated from the reaction mixtures [8–22]. Examples include calcined Mg–Al hydrotalcites [8], $Na/NaOH/\gamma\text{-}Al_2O_3$ [9], $K/KOH/\gamma\text{-}Al_2O_3$ [10], Zn/I_2 [11], Ba–ZnO [12], KF/ZnO [13], KF/Al_2O_3 [14], Mg/Zr [15], KNO_3/Al_2O_3 [16], Ca and Zn mixed oxide [17], KI/Al_2O_3 [18], KOH/Al_2O_3 and KOH/NaY [19], Fe–Zn double-metal cyanide complexes [20], K_2CO_3/MgO [21], and KF/MgO [22]. Particularly, K_2CO_3/Al_2O_3 as well as some other solid base catalysts were used as heterogeneous catalysts in the transesterification of triolein, canola oil, or soybean oil with methanol [23–25].

In this work, we report the preparation of biodiesel by transesterification of rapeseed oil with methanol using calcined $K_2CO_3/\gamma\text{-}Al_2O_3$ as a solid base catalyst. The prepared catalysts were characterized by SEM, IR and BET, and their catalytic activity was evaluated based on the conversion of rapeseed oil to its methyl ester. In addition, the effects of reaction variables such as reaction temperature, catalyst amount, etc. on rapeseed oil conversion were examined. The effect of the presence of water on the catalytic activity of the prepared catalyst was also investigated.

X. Liu · C. Liu (✉) · D. Liu · A. Wu
College of Science, Hunan Agricultural University,
Changsha 410128, People's Republic of China
e-mail: liucanming55@163.com

X. Liu · X. Xiong · C. Liu
Key Laboratory of Plant Resource Utilization of Hunan
Province, Changsha 410128, People's Republic of China

Q. Hu
College of Horticulture and Gardening, Hunan Agricultural
University, Changsha 410128, People's Republic of China

Experimental

Materials

Rapeseed oil was kindly provided by the Hunan Jinjian Cereals Industry Co., Ltd (Changde, China). Potassium carbonate and methanol were purchased from the Beijing Chemical Works (Beijing, China). Alumina was purchased from the Shanghai Wusi Chemical Reagent Co., Ltd (Shanghai, China). Analytical grade *n*-hexane was purchased from the Yanfeng Chemical Reagent Factory (Changsha, China). The reference standard of the methyl esters of tridecanoic, palmitic, oleic, linoleic, linolenic, *cis*-11-eicosenoic, and *cis*-13-docosenoic acids were obtained from Sigma–Aldrich (St. Louis, MO, USA).

Catalyst Preparation

Alumina was first pretreated at 823 K for 4 h to eliminate chemical species adsorbed on the surface. Then, potassium carbonate was loaded onto the alumina surface from aqueous solution by an impregnation method. The potassium carbonate was loaded at a dose of 3.0 mmol/g support, in which the loading amounts of potassium carbonate were calculated on the basis of the amount of starting material. The loaded alumina was subsequently dried in air at 393 K for 12 h. Prior to reaction, the catalyst was calcined in air for 4 h.

Catalyst Characterization

Morphological characteristics of the catalysts were examined using a JSM-6380LV scanning electron microscope (SEM). The accelerating voltage was 10 kV.

The IR spectra of the catalysts were recorded by a WQF-310 spectrometer (Beijing, China) with 1.5 cm^{-1} resolution using the KBr pellet technique at room temperature. The scanning range was from 400 to 4,400 cm^{-1}.

The specific surface areas of the catalysts were determined by the BET method using an ASAP 2020 Automatic Micropore and Chemisorption Analyzer, in which nitrogen was used as the gas adsorbate. Prior to the measurements, the catalysts were dried in air at 393 K for 12 h.

Reaction Procedure

Commercial edible grade rapeseed oil containing palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid and erucidic acid was purchased from the market and dried before use to remove moisture. The acid value and saponification value of the rapeseed oil were 0.15 mg KOH/g and 183.37 mg KOH/g, respectively, while its average molecular weight was 918.57 g/mol as calculated from the acid value and saponification value.

A 100-mL conical flask charged with 2.0 g rapeseed oil and an appropriate amount of anhydrous methanol, catalyst and co-solvent *n*-hexane was placed into a shaker system equipped with a constant temperature water-bath. The reaction mixtures were then shaken at the desired temperature during the reaction. After the transesterification reaction, the solid base catalyst was removed from the reaction mixture via filtration, the glycerine was separated using a separating funnel and the residual methanol and *n*-hexane were separated from the liquid phase via evaporation.

Method of Analysis

The reaction products were analyzed using an SP-6890 gas chromatograph (Tengzhou, China) equipped with a capillary column (HP-innowax, 30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). The temperatures of both the injector and detector were maintained at 280 °C. The gas chromatograph (GC) oven temperature was programmed to initially remain at 170 °C for 0.5 min, then rise to 200 °C at a rate of 5 °C/min, and finally reach 240 °C at a rate of 15 °C/min and remain at that temperature for 5 min. The flow rates of hydrogen and air were 32 and 320 mL/min, respectively. Nitrogen (pressure 60 kPa) was used as the carrier gas, and tridecanoic acid methyl ester was used as an internal standard. Meanwhile, a stock solution of *n*-hexane with a known amount of tridecanoic acid methyl ester was prepared in advance and used for analysis. The biodiesel sample analysis was carried out by dissolving approximately 0.02 g biodiesel sample into 1 mL *n*-hexane and subsequently injecting 1 μL of this solution into the GC. The standard calibration curves for the methyl esters were prepared in advance using tridecanoic acid methyl ester as an internal standard, by which the integrated area percentage can be converted to the weight percentage for each component present in the sample. The conversion of oil to biodiesel was calculated from the methyl ester amount as analyzed by GC according to Conversion $= (X/Y) \times 100\%$, in which X and Y were the weights of fatty acid methyl esters prepared by transesterification of saponifiable matters in 1 g rapeseed oil under the reaction conditions in this paper and those in GB/T 17376-1998, respectively.

Results and Discussion

Catalyst Characterizations

The morphology as well as particle size distribution of several representative catalysts prepared in this work were examined using SEM. The SEM images are shown in

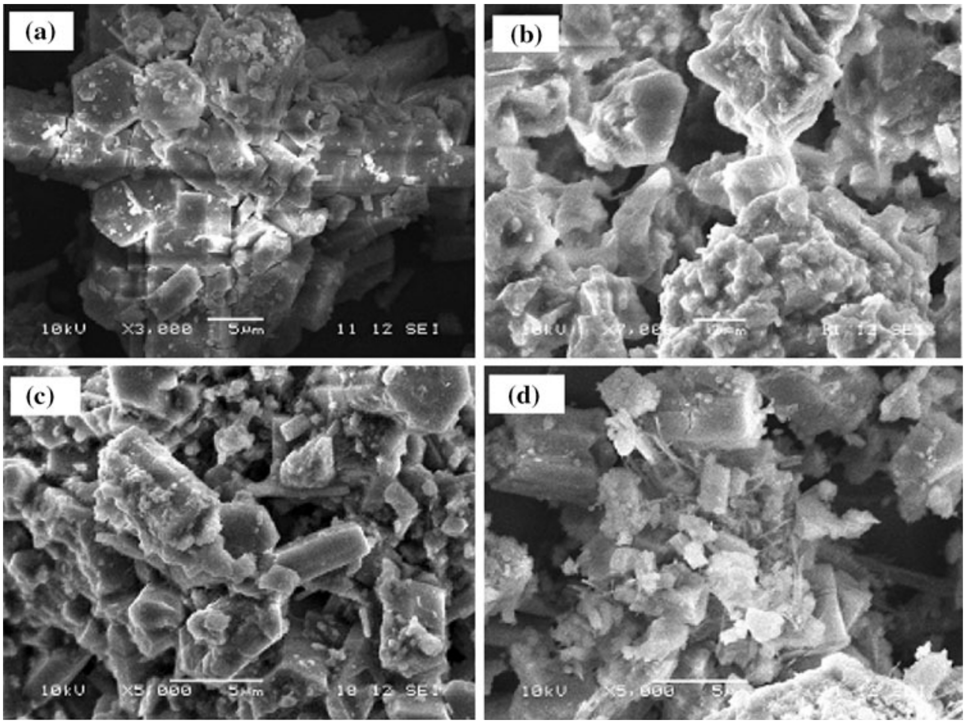

Fig. 1 SEM image of typical catalyst samples : **a** γ-Al_2O_3 calcined at 823 K, **b** K_2CO_3/γ-Al_2O_3 calcined at 623 K, **c** K_2CO_3/γ-Al_2O_3 calcined at 823 K and **d** K_2CO_3/γ-Al_2O_3 calcined at 1,023 K

Fig. 1. Specifically, as shown in Fig. 1, the catalyst particles were irregular-shaped as well as polydispersed with a particle size range from 0.2 to 10 μm. Particularly, all catalyst particles were composed of small irregular particulates. Although there was no obvious morphological difference among samples (a), (b) and (c), the morphology of sample (d) was quite different from the other three samples, which is attributable to the crystal structure collapsing and changing as well as the formation of new substances as the result of such a high temperature (1,023 K).

The IR spectra of prepared catalysts are shown in Fig. 2. Specifically, all samples exhibited several broad absorption bands in an approximate wave number range from 580 to 800 cm^{-1}, which can be attributed to the vibrations of the Al–O bond. Meanwhile, an evident IR absorption band around 1,404 cm^{-1} due to CO_3^{2-}can be observed in samples b, c, d, e and f, while they cannot be seen in the samples either without loading K_2CO_3 (sample a) or being calcined at a temperature above 1,000 K (samples g, h, and i). The appearance of this CO_3^{2-} band in samples b, c, d, e, and f is very likely due to incomplete decomposition of the carbonate at the calcination temperature from 623 to 923 K. On the other hand, the absence of CO_3^{2-} band in samples g, h, and i may indicate that the carbonate has been completely decomposed at the calcination temperature 1,023 K and higher. In addition, the observed absorption band around 1,660 cm^{-1} can be attributed to the O–H bending vibration of H_2O molecules absorbed onto the catalysts from the air. The amplitude of the 1,660 cm^{-1} band decreased with the increase in the calcination temperature and almost disappeared at the calcination temperature 1,023 K and higher (Fig. 2, curves g, h and i). Very interestingly, a broad absorption band centered at approximately 3,438 cm^{-1} that can be attributed to the stretching vibrations of surface hydroxyl groups attached to the Al_2O_3 was observed in γ-Al_2O_3 support (Fig. 2a). This band shifted with increasing calcination temperature and finally centered at about 3,460 cm^{-1} at the calcination temperature 1,223 K, which can be at least partly attributed to the stretching vibration of Al–O–K groups formed during the activation process.

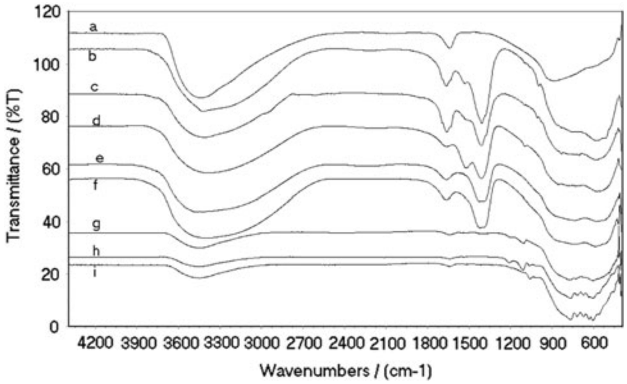

Fig. 2 IR spectrum of samples: **a** γ-Al_2O_3 calcined at 823 K, **b** K_2CO_3/γ-Al_2O_3 (not calcined), **c** K_2CO_3/γ-Al_2O_3 calcined at 623 K, **d** K_2CO_3/γ-Al_2O_3 calcined at 723 K, **e** K_2CO_3/γ-Al_2O_3 calcined at 823 K, **f** K_2CO_3/γ-Al_2O_3 calcined at 923 K, **g** K_2CO_3/γ-Al_2O_3 calcined at 1,023 K, **h** K_2CO_3/γ-Al_2O_3 calcined at 1,123 K, **i** K_2CO_3/γ-Al_2O_3 calcined at 1,223 K

Table 1 BET surface area of samples

Catalyst	BET surface area (m^2/g)
γ-Al_2O_3 calcined at 823 K	128.86
K_2CO_3/γ-Al_2O_3 (not calcined)	48.81
K_2CO_3/γ-Al_2O_3 calcined at 623 K	49.28
K_2CO_3/γ-Al_2O_3 calcined at 823 K	31.10
K_2CO_3/γ-Al_2O_3 calcined at 1,023 K	36.27

Table 2 Effect of calcination temperature on the conversion of rapeseed oil to methyl esters

Catalyst	Conversion (%)
γ-Al_2O_3 calcined at 823 K	0.00
K_2CO_3/γ-Al_2O_3 calcined at 623 K	52.70
K_2CO_3/γ-Al_2O_3 calcined at 723 K	80.09
K_2CO_3/γ-Al_2O_3 calcined at 823 K	98.62
K_2CO_3/γ-Al_2O_3 calcined at 923 K	64.05
K_2CO_3/γ-Al_2O_3 calcined at 1,023 K	2.16
K_2CO_3/γ-Al_2O_3 calcined at 1,123 K	1.30
K_2CO_3/γ-Al_2O_3 calcined at 1,223 K	0.76

Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

The BET specific surface areas of the prepared catalysts are listed in Table 1. As can be seen, the specific surface area of K_2CO_3/γ-Al_2O_3 samples showed a minimum at the calcination temperature 823 K, indicating a loss of specific surface area that is very likely due to the decomposition of CO_3^{2-} on the catalyst surface. However, this loss of specific surface area did not affect the catalytic activity. On the contrary, the specific surface area of γ-Al_2O_3 calcined at 823 K was very large (Table 1), while it did not show any catalytic activity in transesterification of rapeseed oil with methanol (Table 2).

The Effect of the Calcination Temperature on the Conversion of Rapeseed Oil to Methyl Esters

The effect of the calcination temperature on catalyst activity is summarized in Table 2. As shown in Table 2, the calcination temperature can significantly affect catalytic activity. Specifically, the conversion of rapeseed oil to methyl esters initially increased with the temperature and reached a maximum of 98.62% at the calcination temperature 823 K. Then, the conversion gradually decreased with a further increase in the calcination temperature. The conversion was almost negligible at the calcination temperatures 1,023, 1,123 and 1,223 K. Therefore, 823 K is obviously the optimal calcination temperature for K_2CO_3/γ-Al_2O_3.

The Effect of the Reaction Time on the Conversion of Rapeseed Oil to Methyl Esters

The variation of rapeseed oil conversion as a function of the reaction time is shown in Fig. 3. Specifically, the rapeseed oil conversion increased steadily from 87.64 to 98.62% as the reaction time increased from 0.5 to 3 h, whereas, the conversion decreased slightly with any further increase of reaction time, and is very likely due to the occurrence of side reactions. Maximum conversion of 98.62% was obtained at a reaction time 3 h.

The Effect of the Amount of Catalyst on the Conversion of Rapeseed Oil to Methyl Esters

In Fig. 4, the rapeseed oil conversions are plotted versus the catalyst amount in a catalyst amount range of 2.0–6.0 wt.%

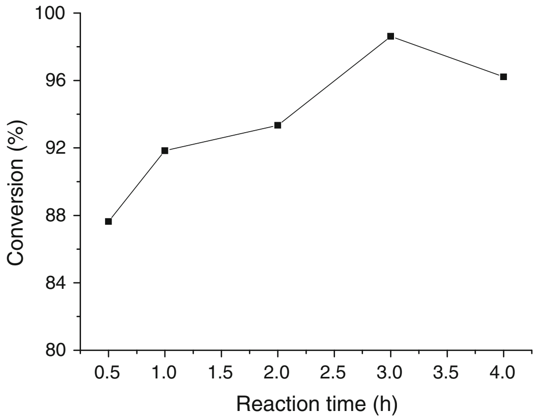

Fig. 3 Effect of reaction time on the conversion of rapeseed oil to methyl esters. Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

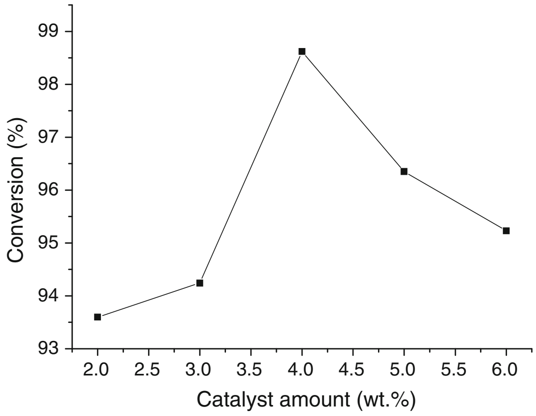

Fig. 4 Effect of catalyst amount on the conversion of rapeseed oil to methyl esters. Reaction conditions: reaction temperature 323 K, molar ratio of methanol/oil 15:1, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

(relative to the weight of rapeseed oil). As shown in Fig. 4, the conversion of rapeseed oil to methyl esters increased from 93.60 to 98.62% as the catalyst amount increased from 2.0 to 4.0 wt.%, then decreased with the further increase in the amount of catalyst, which can be attributed to the deterioration of mixing as the amount of solid base catalyst increased. In this study, maximal conversion is achieved by using a catalyst amount of 4.0 wt.%, the reaction mixture remained clear and liquid like and the catalyst amount in subsequent transesterification reactions in this work were all subsequently fixed at 4.0 wt.%.

The Effect of the Molar Ratio of Methanol to Oil on the Conversion of Rapeseed Oil to Methyl Esters

The stoichiometric methanol to rapeseed oil ratio in transesterification reaction was 3:1. However, because transesterification is a reversible reaction, the rapeseed oil conversion can be increased by simply introducing excess amount of methanol to shift the equilibrium toward the products side. The effect of changing methanol to rapeseed oil molar ratio on rapeseed oil conversion was investigated in a molar ratio range from 9:1 to 21:1. The results are shown in Fig. 5. Specifically, the rapeseed oil conversion increased from 87.59 to 98.62% as the methanol to rapeseed oil molar ratio increased from 9:1 to 15:1. However, with a further increase in the molar ratio, the rapeseed oil conversion began to decrease slightly. The maximum conversion was obtained at a molar ratio of 15:1. Although the excess methanol is usually recovered and reused in the industrial process after purification, an excessive amount of methanol can still inevitably lead to an increase in its recycling cost. Therefore, the choice of an optimal molar ratio has to take the increase in process expense into consideration.

The Effect of the Reaction Temperature on the Conversion of Rapeseed Oil to Methyl Esters

The effect of the reaction temperature on rapeseed oil conversion is shown in Fig. 6. Specifically, the conversion increased significantly from 89.64 to 98.62% as the reaction temperature increased from 303 to 323 K and remained nearly constant with any further increase in the reaction temperature. The maximum conversion 98.62% was achieved at the reaction temperature 323 K with a reaction period of 3 h.

The Effect of the Amount of Solvent on the Conversion of Rapeseed Oil to Methyl Esters

In this study, the rapeseed oil, methanol and the catalyst actually formed a three-phase reaction mixture due to the immiscibility of methanol with rapeseed oil as well as the solid catalyst phase. Consequently, the reaction rate could be limited by a diffusion process of the reactants. Therefore, it would be beneficial to introduce an appropriate co-solvent into the reaction mixture, which would enhance the reaction rate as well as increase the rapeseed oil conversion. In this work, *n*-hexane was adopted as the co-solvent, and the effect of the amout of co-solvent on rapeseed oil conversion was studied. The results are shown in Fig. 7. Specifically, the conversion increased significantly with the amount of *n*-hexane, and in particular, the minimum conversion 74.19% was observed in the absence of *n*-hexane. The conversion reached its maximum value of 98.62% at an *n*-hexane amount of 98.85 wt.% (relative to rapeseed oil), then decreased slightly with any further increase in the amount of *n*-hexane.

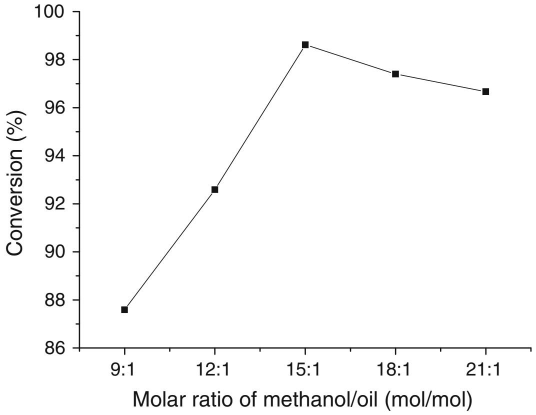

Fig. 5 Effect of the molar ratio of methanol to rapeseed oil on the conversion of rapeseed oil to methyl esters. Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), reaction time 3 h, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

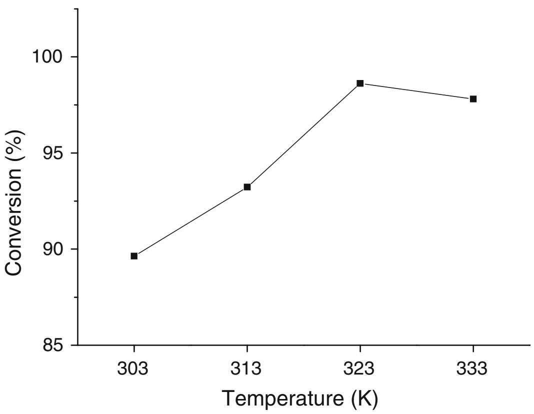

Fig. 6 Effect of reaction temperature on the conversion of rapeseed oil to methyl esters. Reaction conditions: catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, reaction time 3 h, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

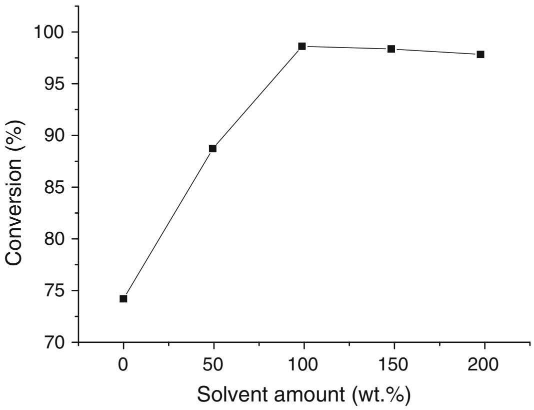

Fig. 7 Effect of the *n*-hexane amount on the conversion of rapeseed oil to methyl esters. Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, reaction time 3 h, rapeseed oil 2 g, shaking rate 150 rpm

The Effect of the Presence of Water on the Conversion of Rapeseed Oil to Methyl Esters

The catalytic activity of alkali catalysts can be significantly lowered by the presence of water in the reaction system. In this work, the effect of the presence of water on rapeseed conversion by directly adding water into the reaction mixtures was examined in detail. The results are shown in Fig. 8. Clearly, as shown in Fig. 8, the presence of water in the reaction system led to significant decrease in the conversion of rapeseed oil to methyl esters, which is very likely due to the inhibition of the catalytic activity of calcined $K_2CO_3/\gamma\text{-}Al_2O_3$. Specifically, the conversion decreased gradually from 95.39 to 86.72% as the weight percentage of water increased from 1.0 to 4.0% (relative to the weight of rapeseed oil), compared to the conversion of 98.62% without adding water. The decrease in the conversion can be attributed to the occurrence of a hydrolysis reaction induced by the addition of water and the reactants should be thoroughly dried or dewatered before the reaction.

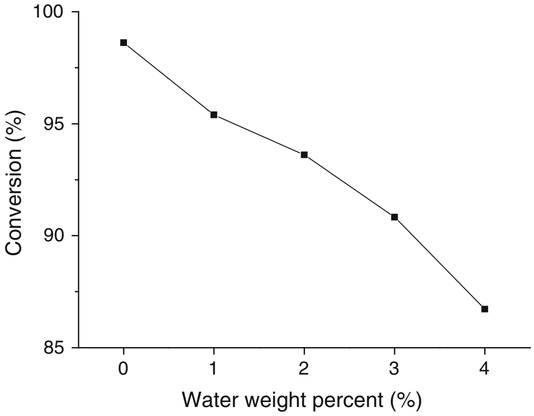

Fig. 8 Effect of the presence of water on the conversion of rapeseed oil to methyl esters. Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, reaction time 3 h, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

Table 3 Reusability of catalysts

Catalyst	Conversion (%)
$K_2CO_3/\gamma\text{-}Al_2O_3$ calcined at 823 K	98.62
Regenerated catalyst by washing and drying at 333 K	29.97
Regenerated catalyst by washing and calcination at 823 K	60.08

Reaction conditions: reaction temperature 323 K, catalyst amount 4.0 wt.% (relative to rapeseed oil), molar ratio of methanol/oil 15:1, rapeseed oil 2 g, *n*-hexane amount 98.85 wt.% (relative to rapeseed oil), shaking rate 150 rpm

Regeneration and Reusability of Catalyst

Heterogeneous catalysts have the potential to be recovered, regenerated, and reused. In this work, the spent catalyst ($K_2CO_3/\gamma\text{-}Al_2O_3$ calcined at 823 K) was recovered by simple filtration and subsequently regenerated by two types of regeneration procedure. In the first regeneration procedure, the recovered catalyst was washed with *n*-hexane and then dried in air at 333 K for 12 h. In the second regeneration method, the recovered catalyst was calcined in a muffle furnace at 823 K for 4 h after washing with *n*-hexane. The catalytic activities of the catalyst regenerated by these two methods were evaluated, and the results are summarized in Table 3. The catalytic activity of catalysts decreased significantly after regeneration. The rapeseed oil conversion decreased to 29.97 and 60.08%, for the catalyst regenerated by the first and second method, respectively, which was much lower than that of fresh prepared catalyst, i.e., 98.62%, indicating a relatively low stability and poor reusability of the prepared catalysts. Therefore, a future study aimed at improving the stability and lifetime of the catalyst is desirable.

Conclusions

Based on above study, we can conclude that: (1) The prepared catalysts were characterized using SEM, IR, and BET methods. (2) The catalyst $K_2CO_3/\gamma\text{-}Al_2O_3$ calcined at 823 K for 4 h was found to be optimal, by which the best catalytic activity for the transesterification of rapeseed oil with methanol can be achieved. (3) The optimal transesterification conditions were: a reaction temperature of 50 °C, a catalyst amount of 4.0 wt.% (relative to rapeseed oil), a molar ratio of methanol to rapeseed oil 15:1, the amount of co-solvent *n*-hexane is 98.85 wt.% (relative to rapeseed oil) and the reaction time 3 h. The oil conversion can be as high as 98.62% under the optimal reaction conditions. (4) *n*-Hexane as a co-solvent can promote the miscibility of rapeseed oil with methanol and improve the mixing of reactants thereafter increasing the conversion of rapeseed oil to methyl esters. Moreover, the boiling point of *n*-hexane is close to that of methanol. *n*-Hexane, can therefore be co-distilled with methanol. (5) The conversion of rapeseed oil decreased in the presence of water, indicating that water can inhibit the catalytic activity of calcined $K_2CO_3/\gamma\text{-}Al_2O_3$. So the reactants should be dried or dewatered before the reaction. (6) Further investigation is needed to intensify the stability and improve the lifetime of the catalyst.

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