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ORIGINAL PAPER

Transesterification of Rapeseed Oil for Synthesizing Biodiesel by K/KOH/γ-Al_2O_3 as Heterogeneous Base Catalyst

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Abstract The heterogeneous base catalyst, γ-Al_2O_3 loaded with KOH and K (K/KOH/γ-Al_2O_3) was first prepared and used in the transesterification of rapeseed oil with methanol to produce biodiesel. The prepared catalyst was characterized by X-ray diffraction, scanning electron microscopy, Brunauer–Emmett–Teller method, infrared spectroscopy and X-ray photoelectron spectroscopy. It was found that when γ-Al_2O_3 is loaded with KOH and K, the Al–O–K species is produced, resulting in an increase in the catalytic activity. The impacts of catalyst preparation conditions on the catalytic activities of K/KOH/γ-Al_2O_3 were investigated. The results demonstrate that the catalyst K/KOH/γ-Al_2O_3 has high catalytic activity when the added amounts of KOH and K are 20 and 7.5 wt% respectively. The transesterification of rapeseed oil to biodiesel with the prepared heterogeneous base catalyst was optimized. It was found that the yield of biodiesel can reach as high as 84.52% after 1 h reaction at 60°C, with a 9:1 molar ratio of methanol to oil, a catalyst amount of 4 wt%, and a stirring rate of 270 *g*.

Keywords Biodiesel · Transesterification · Heterogeneous base · Catalyst · Rapeseed oil · Methyl esters · Alumina XRD · IR · XPS

Introduction

Biodiesel, defined as the alkyl esters of long chain fatty acids, can be used as biodiesel fuel or can be used as an additive or extender to diesel fuel in compression-ignition engines with little or no modification [1]. In addition, biodiesel is a biodegradable and renewable fuel. It contributes no net carbon dioxide or sulfur to the atmosphere and emits less gaseous pollutants than normal petroleum diesel. Carbon monoxide, aromatics and polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced during combustion in vehicles operating on biodiesel compared with petroleum diesel [2]. Nowadays, biodiesel is being developed as one of the most suitable substitutions for fossil fuels in solving energy and related environmental problems.

The main composition of vegetable oil and animal fat is triglycerides. Biodiesel is usually obtained from transesterification of triglycerides with methanol. An activated catalyst is always added to the transesterification system to improve the reaction rate. The homogeneous base catalysts, such as potassium hydroxide, sodium hydroxide, potassium methoxide and sodium methoxide, are most frequently used in the industrial process to produce biodiesel due to their high catalytic activities [3]. However, in the transesterification process catalyzed by homogeneous catalyst, the vegetable oil should have an acid value less than one and all materials should be substantially anhydrous [4]. Furthermore, wastewater produced during separation of homogenous catalyst from the reaction system during product purification is another disadvantage to reactions employing homogeneous catalysts. As a consequence, there is an urgent need to explore other activated catalysts that can be used in the

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transesterification with mild conditions to produce biodiesel that can be easily recovered.

Heterogeneous catalysts have been investigated more and more in relation to biodiesel production as a means to overcome the problems caused by using homogeneous catalysts, and it is suggested that using heterogeneous catalysts can reach a favorable yield of biodiesel [5–7]. However, in the study of Furuta et al. [5], high reaction temperature of 250°C, long reaction time of 20 h and high molar ratio of methanol to oil of 40:1 were applied to achieve over 80% conversions of soybean oil by using catalysts of tungstated zirconia–alumina (WZA), TiO_2/ZrO_2, and Al_2O_3/ZrO_2. In the study of Ebiura et al. [6], the THF was added to the reaction system as a cosolvent, and a high molar ratio of methanol to oil of 24.8:1 was utilized to obtain the biodiesel yields of over 80% by using the catalysts of alumina loaded with K_2CO_3, $LiNO_3$ or NaOH. In Kitiyanan's study [7], high reaction temperature of 200°C and high pressure of 5.0×10^6 Pa were used in the reaction system to gain the yield up to 90.3 wt% of methyl esters from crude palm kernel oil and 86.3 wt% from crude coconut oil by using catalysts of SO_4^{2-}/ZrO_2. The above studies demonstrated that, when heterogeneous catalysts were used, strict conditions including high reaction temperature, long reaction time, high molar ratio of methanol to oil, high pressure or adding cosolvent were still needed. As a consequence, it is still necessary to explore new heterogeneous catalysts which have high catalytic activity for transesterification of vegetable oil with methanol at mild reaction conditions.

As previously described by Suzukamo et al. [8, 9], catalyst $K/KOH/\gamma\text{-}Al_2O_3$ is a solid superbase possessing base strength stronger than $H\_ = 37$ ($H\_$ is the base strength of the catalyst measured by Hammett indicator method). In the present study, the heterogeneous base catalyst, $\gamma\text{-}Al_2O_3$ loaded with KOH and K, was explored in the transesterification of rapeseed oil with methanol to produce biodiesel, which to date has not been explored. The catalyst $K/KOH/\gamma\text{-}Al_2O_3$ was prepared according to the procedure described by Suzukamo et al. [8] and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller method (BET), infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). The catalytic activities were evaluated in the transesterification of rapeseed oil with methanol. The impacts of catalyst preparation conditions, including amounts of KOH and metal potassium, on the catalytic activities of $K/KOH/\gamma\text{-}Al_2O_3$ were investigated. In addition, to optimize the reaction conditions, the variables of reaction time, the molar ratio of methanol to rapeseed oil, the amount of catalyst, reaction temperature and the stirring rate were investigated.

Experimental

Preparation of Catalyst $K/KOH/\gamma\text{-}Al_2O_3$

The catalyst $K/KOH/\gamma\text{-}Al_2O_3$ was prepared by the three steps method as follows [8]. Firstly, the 100 g $\gamma\text{-}Al_2O_3$ solid (Tianjin Research and Design Institute of Chemical Industry, China) with surface area of 200 m^2/g and size fraction of 75 ~ 80 μm was calcined at 500 °C for 360 min in a muffle furnace to remove the organic substances. Then the calcined $\gamma\text{-}Al_2O_3$ was cooled to ambient temperature in the furnace. Secondly, the calcined $\gamma\text{-}Al_2O_3$ with amount of 80 g (0.784 mol) was added to a stainless steel vessel equipped with a nitrogen flow line, a continuous stirring system and a temperature controlling system. The potassium hydroxide (AR; Kewei Reagent, Tianjin University, Tianjin, China) was also introduced into the vessel with weight percents of 10 ~ 40 wt% (8 ~ 32 g, 0.143 ~ 0.571 mol) relative to the weight of calcined $\gamma\text{-}Al_2O_3$. Then the vessel was closed and heated to 360°C under N_2 protection, and kept stirring at a constant temperature for 120 min. After that, the temperature of the vessel was decreased from 360 to 240°C by circulating chilled water. Thirdly, the metal potassium (AR; Tianjin Kermel Chemical Reagents Development Center, Tianjin, China) was added to the reaction system with weight percents of 2.5 ~ 10 wt% (2 ~ 8 g, 0.051 ~ 0.205 mol) relative to the weight of calcined $\gamma\text{-}Al_2O_3$, stirred at 240°C under N_2 protection for 1 h. After being cooled to ambient temperature by circulating chilled water, the prepared dark blue solid base catalyst $K/KOH/\gamma\text{-}Al_2O_3$ with an amount of 89.5 ~ 107.6 g (the average yield was 95.3%) was taken out of the vessel and placed in silica gel desiccator before characterization and using in transesterification reaction. Besides, the calcined $\gamma\text{-}Al_2O_3$ and $KOH/\gamma\text{-}Al_2O_3$ prepared in the step 1 and step 2, respectively, were also collected for the following characterization.

Characterization of the Catalyst

X-ray diffraction analyses were carried out by using an X'Pert PRD X-ray diffraction system (PANalytical, Almelo, Overijssel, Netherlands) with a Co-Kα radiation. The surface morphology of the prepared catalysts was investigated by a XL30 SEM (Philips, Eindhoven, North Brabant, Netherlands). The BET surface area, total pore volume and average pore size of the catalysts were analyzed by the BET nitrogen adsorption method at −196 °C using a Tristar 3000 instrument (Micromeritics, Norcross, GA, USA). IR measurements were performed with a Nicolet 560 spectrometer (Nicolet, Madison, Wisconsin, USA). And the infrared spectra were recorded at room temperature in the range of 4,000–400 cm^{-1}, with 300 scans and 4 cm^{-1} resolution. X-ray photoelectron spectroscopy analysis was performed with a PHI1600 XPS system (PerkinElmer, Waltham, Mass., USA) operated under Mg–Kα radiation at 1.2×10^{-8} Torr.

Reaction

The transesterification of rapeseed oil (Xingwang Oil, Guanghan, China) with methanol to produce biodiesel using prepared catalysts was performed. The oil is immiscible with methanol, and the reactants initially form a three-phase system, triglycerides/methanol/catalyst. The upper layer is methanol, and the lower one is oil. A stirrer must be used to reduce the mass transfer resistance and increase the contact area of reactants. Otherwise, the reaction takes place only at the boundary between the two phases. A 250-ml flask, an electrical stirrer, a reflux condenser and an electric jacket with thermocouple and relay were used for the transesterification. Firstly, 100 g rapeseed oil (expeller pressed oil, with acid value of 1.4 mg KOH/g and with water content of 0.0374 wt%), and precalculated amount of methanol (according to the investigated molar ratio of methanol to rapeseed oil) were displaced into the 250-ml four-neck flask. The mixture was stirred and heated to preestablished temperature (30 ~ 65°C). Then, the prepared catalyst with scheduled amount (0.5 ~ 7.0 wt% relative to rapeseed oil) was introduced to the reaction system. The reaction was carried out for 360 min under a predefined stirring rate (0 ~ 360 *g*). A sample of 0.5 ml was collected by drip tube each time at 20-min intervals in the first hour, and then collected at 60-min intervals. Then the samples were washed 5 times with hot deionized water, dried over anhydrous sodium sulfate, and then dissolved in n-hexane to form 10 mg/ml solutions for gas chromatographic (GC) analysis.

Method of Sample Analysis

An HP 6890 Series Gas Chromatograph System equipped with a split/splitless injection system, a 5973N mass spectrum (MS) detector (Aglient, Palo Alto, California, USA) was used for the analysis of sample to determine the composition of the fatty acid methyl esters. The column was HP-INNO Wax capillary column (0.25 mm × 30 m, 0.25 μm) (J and W Scientific, Folsom, California, USA) with helium at 1.5 ml min^{-1} as carrier gas and a split ratio of 100:1. Samples (1 μl) were injected by a sampler at an oven temperature of 160°C. After an isothermal period of 2 min, the GC oven was heated at 5°C min^{-1} to 240°C, and held for 10 min to ensure that all material had eluted from the column. The injector temperature was 250°C. The mass range of the mass spectrometer was set to 10–500 amu, and the source and interface temperature were held at 150 and 230°C, respectively.

Calculated from the major fatty acid components, palmitic acid (3.30%), stearic acid (1.08%), linolenic acid (6.47%), linoleic acid (11.87%), oleic acid (27.32%), *cis*-11-eicosenoic acid (10.54%) and erucic acid (39.42%), the average molecular weight of the rapeseed oil is 934.2. Quantitative analysis was realized by external calibration using standard solutions of fatty acid methyl esters.

Results and Discussion

Catalyst Characterization

X-ray Diffraction

Figure 1 shows the XRD patterns of γ-Al_2O_3, KOH/γ-Al_2O_3 and K/KOH/γ-Al_2O_3. All of the catalysts own peaks were at near 43.56, 54.17 and 80.19°, which are attributed to the γ-Al_2O_3 crystal. Exclusive of the peaks for the support γ-Al_2O_3, the KOH/γ-Al_2O_3 has the sharp peaks at near 38.17 and 69.06°, which are ascribed to orthorhombic β-$KAlO_2$ species formed on the catalyst surface [10]. After metal potassium was subsequently added to form K/KOH/γ-Al_2O_3, the peaks of β-$KAlO_2$ species are intensified. It is very likely that the high activity of the catalyst, as evident in Figs. 4–7, may be partially due to this β-$KAlO_2$ phase since a relationship was observed between the high basicity of β-$KAlO_2$ species and the catalytic activity [11]. Besides,

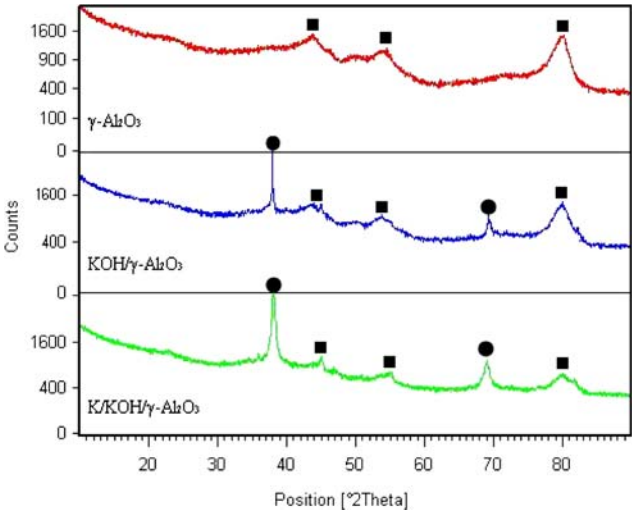


Fig. 1 XRD patterns of the prepared catalysts γ-Al_2O_3 (*filled square*), $KAlO_2$ (*filled circle*). The introduction amounts of KOH and K were 20 and 7.5 wt% (relative to the weight of calcined γ-Al_2O_3), respectively

there is no evidence of existence of potassium hydroxide or potassium on the catalyst surface, suggesting a good dispersion of KOH and K on alumina due to the solid-state reaction between the guest species (KOH and K) and the surface of the support in the catalyst preparation process.

Scanning Electron Microscopy

The SEM images of the catalysts are shown in Fig. 2. It can be observed that the γ-Al_2O_3 is a particle accumulation with a lot of smaller irregular particulates (see Fig. 2a). After KOH is added to the γ-Al_2O_3 and the reaction temperature is kept at 360°C, the support γ-Al_2O_3 is covered by potassium species, especially by orthorhombic crystals β-$KAlO_2$ evidenced by XRD (see Fig. 2b). Successively, after addition of metal potassium to the reaction system to form catalyst K/KOH/γ-Al_2O_3, more potassium species in form of orthorhombic crystals are well dispersed on the outer surface (see Fig. 2c).

Brunauer–Emmett–Teller method

The BET surface area, total pore volume and average pore size of the investigated catalysts are listed in Table 1. It can be seen that γ-Al_2O_3 is loaded with KOH, and the surface area and total pore volume are both reduced due to the potassium species forming and covering on the porous surface of γ-Al_2O_3. After KOH/γ-Al_2O_3 is further loaded with metal potassium, the surface area and total pore volume are both increased due to the increase of small regular crystals and its better dispersion as shown in Fig. 2c. However, the average pore sizes are in increasing order of γ-Al_2O_3 < KOH/γ-Al_2O_3 < K/KOH/γ-Al_2O_3. The possible reason is that the thin layers formed on the surface of γ-Al_2O_3 reduce the small pores, which have little effect on large pores, and finally make the catalyst pore sizes more equal, resulting in an increase in average pore size.

Infrared Spectroscopy

To further understand the interactions between the KOH and the support γ-Al_2O_3 and between metal K and KOH/γ-Al_2O_3 during the catalyst preparation process, characterization by IR was also carried out. All of the samples showed very intense bands centered at 714 and 588 cm^{-1}, which are attributed to the vibrations of Al–O, and the minor absorption band at about 1,637 cm^{-1} may be assigned to the δ_{OH} bending vibration mode of H_2O molecules absorbed from air [12]. In the support γ-Al_2O_3, a broad absorption band centered at approximately 3,602 cm^{-1} was observed due to the overlapping of bands

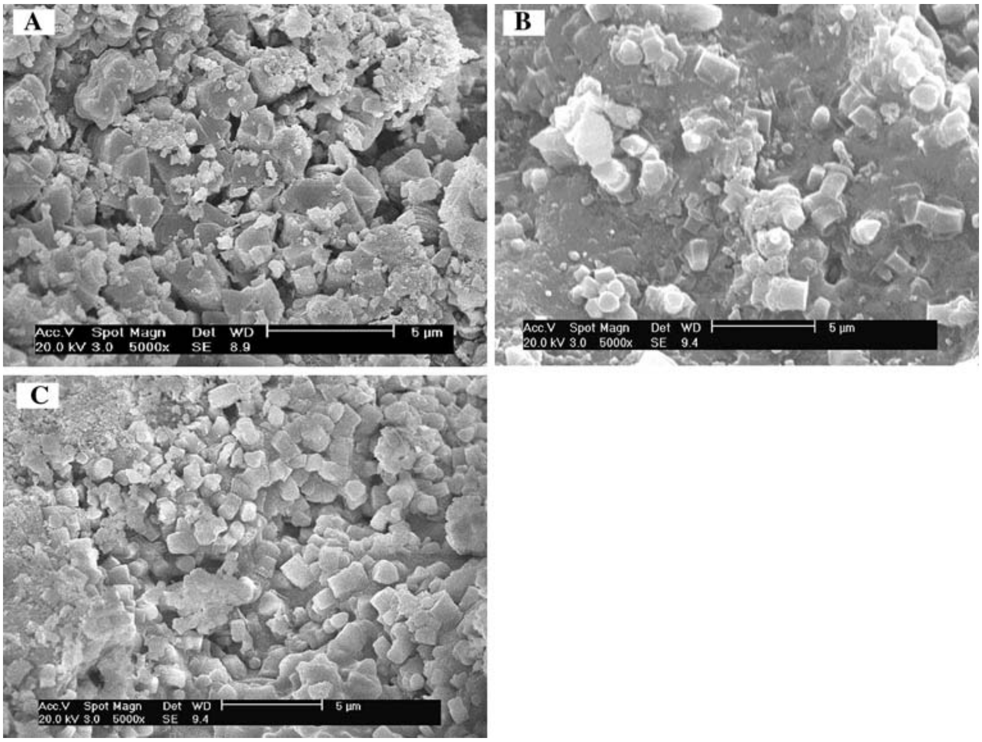


Fig. 2 SEM images of catalysts: **a** γ-Al_2O_3, **b** KOH/γ-Al_2O_3, **c** K/KOH/γ-Al_2O_3. The introduction amounts of KOH and K are 20 and 7.5 wt% (relative to the weight of calcined γ-Al_2O_3), respectively

Table 1 BET surface area, total pore volume and average pore size of the prepared catalysts

Catalyst[a]	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (Å)
γ-Al_2O_3	223.9	0.481	85.9
KOH/γ-Al_2O_3	91.0	0.235	103.5
K/KOH/γ-Al_2O_3	104.7	0.272	103.9

[a] The introduction amounts of KOH and K were 20 and 7.5 wt% (relative to the weight of calcined γ-Al_2O_3), respectively

from the stretching vibrations of surface hydroxyl groups attached to the Al [12]. However, after the support was loaded with KOH at 360°C, the broad band was shifted and centered at 3,504 cm^{-1}, which could be partly assigned to the stretching vibration of Al–O–K groups [13, 14]. According to the previous studies on K_2CO_3/γ-Al_2O_3 [14], KI/γ-Al_2O_3 [15] and KNO_3/γ-Al_2O_3 [16], on the surface of fully hydroxylated alumina, K^+ ions could replace the protons of the surface hydroxyl groups to form Al–O–K groups. It is noteworthy that the extent of the displacement reaction depends not only on the acidity of surface Al–OH groups (pK_a value = 3.8 [17]), but also on the basicity of the loading species. Accordingly, potassium hydroxide was much more basic than other potassium salts studied by previous researchers, resulting in formation of a more stable chemical bond Al–O–K. In addition, and confirmed by a new peak at 1,390 cm^{-1} in the infrared spectra of KOH/γ-Al_2O_3, $KAlO_2$ species appear on the catalyst surface [14], which is consistent with the XRD analysis discussed above.

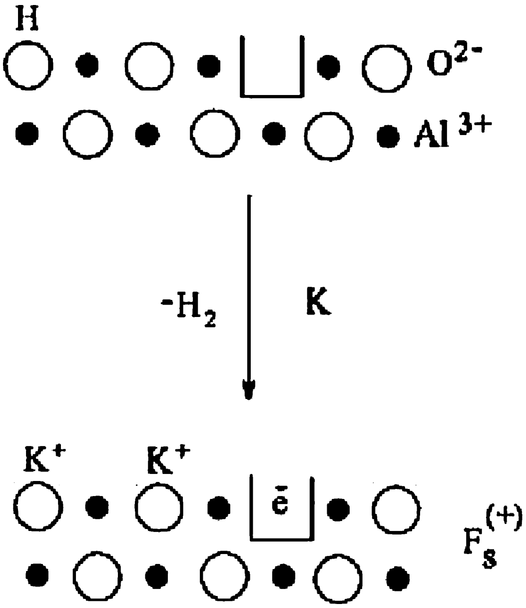
Furthermore, after metal potassium was subsequently loaded, forming catalyst K/KOH/γ-Al_2O_3 at 240°C, the colorless catalyst became dark blue and, in the infrared spectra, the peak area around 3,504 cm^{-1} was intensified. This can be explained by there being many defects or vacancies in the structure of γ-Al_2O_3 [14, 18], resulting from the dehydration of surface hydroxyl groups. The metal potassium could react with anionic vacancies on alumina surfaces at 240°C resulting in the formation of surface color centers of $F_s^{(+)}$ (Scheme 1), which were identified as the strongest one-electron donor sites [18, 19]. In addition to the reaction with anionic vacancies leading to color center formation, metal potassium underwent reactions with other types of surface electron acceptor centers, which were the holes trapped on oxygen anions near the cationic vacancies and surface hydroxyl groups illustrated by following reactions [19]

$$O^{-}[=] + K \rightarrow O^{2-}[=] + K^{+} \quad (1)$$

Hole trapped on the oxygen anion

$$2Al - OH_s + K \rightarrow Al - O - K_s + H_2O \quad (2)$$

Surface hydroxyls



Scheme 1 Synthesis of ion radical species on γ-alumina surface

$$Al - OH_s + K \rightarrow Al - O - K_s + 1/2H_2 \quad (3)$$

These result in forming an oxygen layer with high electron donating ability. In the transesterification of rapeseed oil with methanol, these oxygen anions are the active sites on the catalyst surface and can abstract protons from methanol to produce CH_3O^- anions, which further react with glycerides to synthesize biodiesel.

X-ray Photoelectron Spectroscopy

It can be found from XPS analytical results that the O1s binding energy on the surface of KOH/γ-Al_2O_3 is 529.40 eV, which is lower than that of γ-Al_2O_3 (531.28 eV), suggesting that the oxygen atoms on the surface of KOH/γ-Al_2O_3 have stronger electron donating ability. Moreover, since the O1s binding energy further decreased to 528.64 eV, the oxygen atoms on catalyst K/KOH/γ-Al_2O_3 have highest electron donating ability and are assumed to exhibit superbasicity [9]. All these are consistent with the IR analysis discussed above. As a consequence, the prepared catalyst K/KOH/γ-Al_2O_3 was used for the transesterifications of rapeseed oil to produce biodiesel.

The Impacts of Catalyst Preparation Conditions on the Catalytic Activity

The transesterifications of rapeseed oil to produce biodiesel were conducted at 60°C for 1 h with 9:1 molar ratio, 4 wt% catalyst and 270 *g* stirring rate. The introduction amounts of KOH and K were 20 and 7.5 wt% (relative to the weight of γ-Al_2O_3), respectively, in the process of catalyst preparation. It was found that, compared with the catalytic activity of γ-Al_2O_3 (3.17% yield), an obvious increase in catalytic activity is obtained by adding KOH to γ-Al_2O_3 (43.07% yield) due to the production of Al–O–K species, and a more obvious increase is obtained by adding metal potassium to form catalyst K/KOH/γ-Al_2O_3 (84.52% yield) due to the formation of superbasic sites. Obviously, there is a correlation between the catalytic activity and the basicity, which was evaluated in the IR and XPS analysis.

The impacts of catalyst preparation conditions, including the added amount of KOH and metal potassium, on the catalytic activities of K/KOH/γ-Al_2O_3 were investigated, and the results are shown in Fig. 3. It was found that when the added amount of metal potassium was kept 7.5 wt% (relative to the weight of γ-Al_2O_3), with increasing adding amount of KOH, higher catalytic activity is obtained, and thus the yield of biodiesel increases. There is no obvious change in biodiesel yield when the amount of KOH reaches 20 wt%, which is due to the saturation of KOH loaded on γ-Al_2O_3. When the adding amount of KOH was kept at 20 wt%, the similar phenomena are obtained in the investigation of the effect of adding percents of metal potassium on the biodiesel yields in the transesterification. When the added amount of metal potassium reaches 7.5 wt%, there is no obvious change in the yield of biodiesel, which may be due to the saturation of vacancies owned by the surface of catalyst KOH/γ-Al_2O_3. As discussed above, one can find that when catalyst K/KOH/γ-Al_2O_3 was prepared with 20 KOH and 7.5 wt% metal potassium, the catalyst has high catalytic activity and can be used in the transesterification of rapeseed oil with methanol to produce biodiesel.

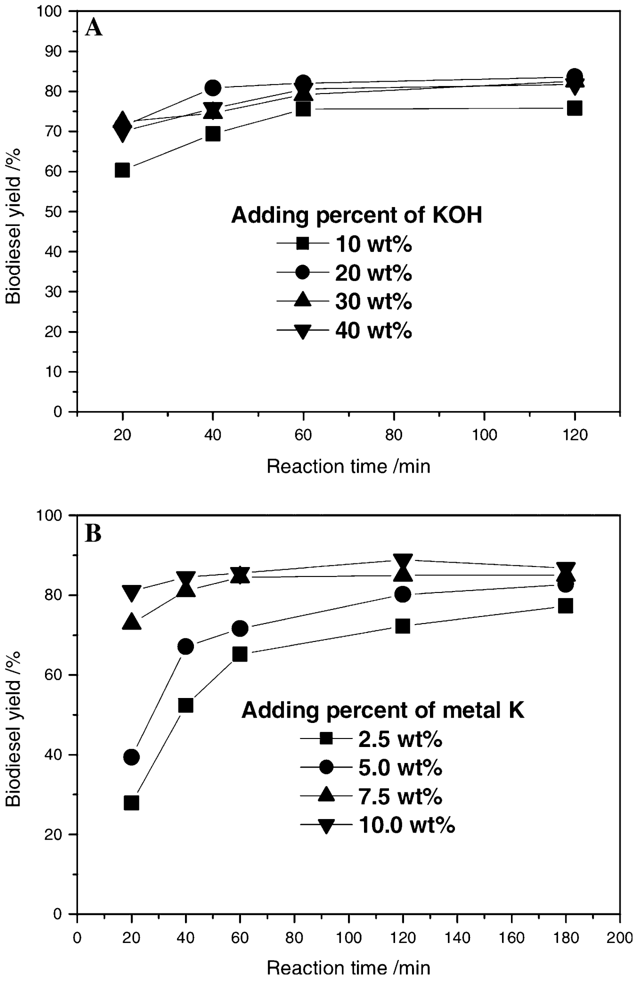


Fig. 3 Effect of the catalyst preparation conditions on the biodiesel yields in the transesterification of rapeseed oil at 60 °C with 9:1 molar ratio of methanol to rapeseed oil, 4 wt% catalyst and 270 rpm stirring rate: **a** effect of adding of KOH on the yield of biodiesel (the added percent of metal potassium was kept 7.5 wt%); and **b** effect of adding of metal potassium on the yield of biodiesel (the adding of KOH was kept 20 wt%)

Optimization of Reaction Conditions

It needs to be pointed out that in the presence of solid base catalysts in transesterification, the reaction mixture is a three-phase oil/methanol/catalyst system. The methoxide species, which are thought to be the active species in transesterification reaction, are formed upon adsorption of methanol on the catalyst surface, and the transesterification reaction becomes mass transfer-controlled [16, 20]. As the methanol/oil ratio increases, the driving force for methanol adsorption increases as well, thus favoring the transesterification reaction. From the reaction formula, the stoichiometric ratio of methanol to rapeseed oil is 3:1. In this work, therefore, the effects of the molar ratios of methanol to rapeseed oil in the range of 3:1 ~ 24:1 on the yields of biodiesel were studied, and the results are shown in Fig. 4. It was found that, with increasing molar ratio of methanol to rapeseed oil, resulting in an increase in the reaction rate of transesterification of rapeseed oil with methanol, a high yield of biodiesel was observed. As the molar ratio is high enough, the methanol adsorption is probably not the rate-determining step. Therefore, further increase in molar ratio from 9:1 to up to 24:1 had no effect on yield. When the molar ratio reaches 9:1, the yield of biodiesel reaches as high as 84.52% after 60 min reaction.

The impact of catalyst amount in the range of 0.5 ~ 7.0 wt% (relative to weight of rapeseed oil) on the yield of biodiesel in the transesterification of rapeseed oil was investigated and the results are shown in Fig. 5. By increasing the amount of catalyst used in the transesterification, the total amount of basic sites and their contacting chances with reactants increase, and thus an obvious increase in the yield of biodiesel was observed. When the

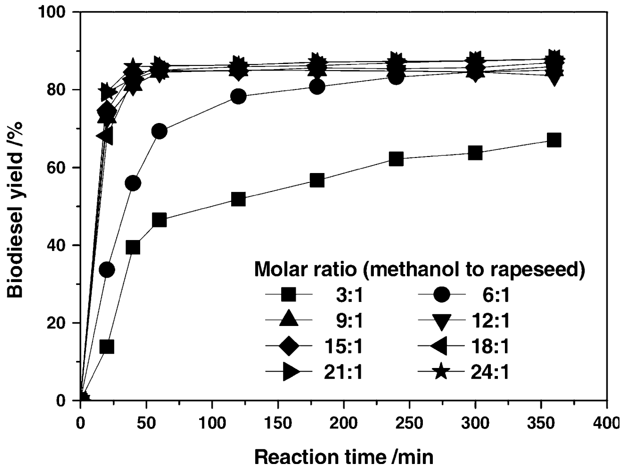


Fig. 4 Effect of molar ratio of methanol to rapeseed oil on the biodiesel yield in the transesterification of rapeseed oil at 60°C with 4 wt% K/KOH/γ-Al_2O_3 catalyst and 270 *g* stirring rate

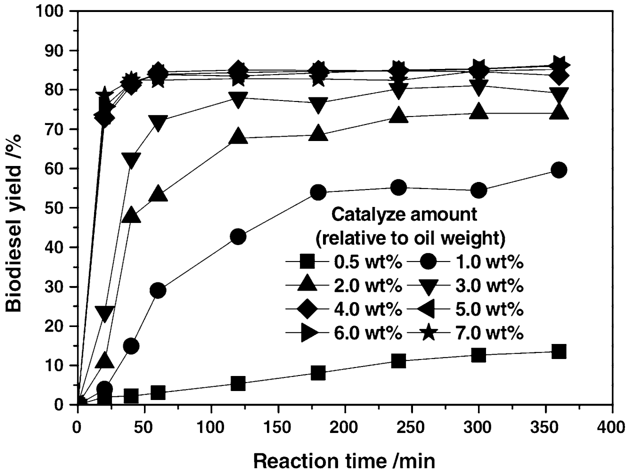


Fig. 5 Effect of the amount of K/KOH/γ-Al_2O_3 catalyst on the biodiesel yield in the transesterification of rapeseed oil at 60°C with 9:1 molar ratio and 270 *g* stirring rate

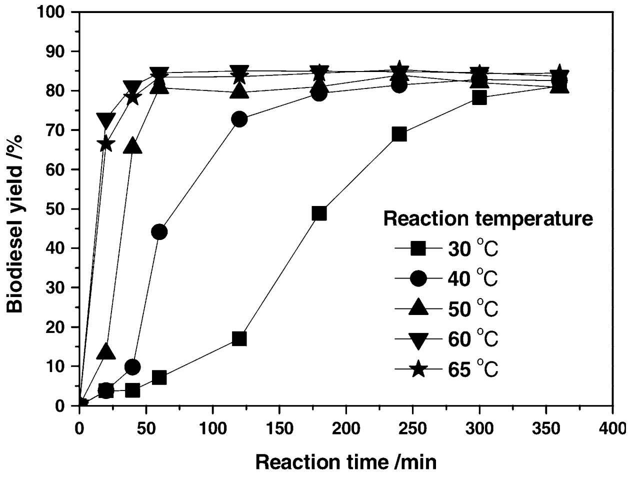


Fig. 6 Effect of reaction temperature of transesterification on the yield of biodiesel with 4 wt% K/KOH/γ-Al_2O_3 catalyst, 9:1 molar ratio and 270 *g* stirring rate

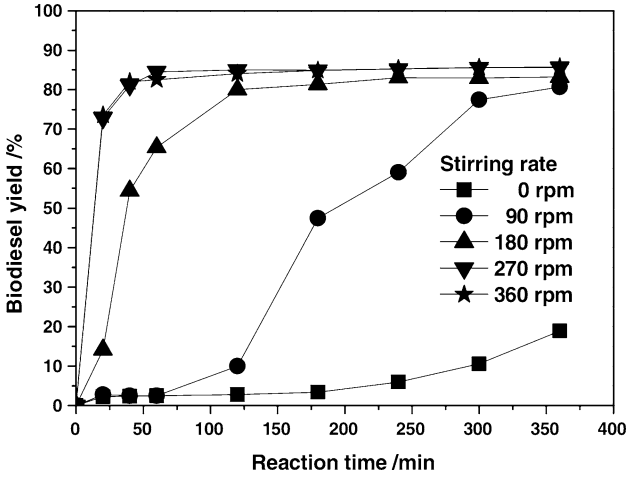


Fig. 7 Effect of stirring rate on the yield of biodiesel at 60°C with 4 wt% catalyst and 9:1 molar ratio

amount of catalyst arrives at 4 wt%, the yield of biodiesel reaches 84.52% in 60 min.

The impact of reaction temperature of the transesterification in the range of 30 ~ 65°C on the yield of biodiesel was examined. As shown in Fig. 6, with increasing temperature, due to the higher energy state of the molecules resulting in more fruitful collision, and higher solubility of the reactants at elevated temperatures, the reaction rate increases. At the reaction temperature of 60°C, the yield of biodiesel reaches 84.52% in 60 min reaction.

As shown in Fig. 7, since the heterogeneous reaction of transesterification takes place among three-phase system, the reaction may become diffusion-controlled when there is no agitation or the stirring rate is not high enough. With increasing stirring rate, the mass transfer resistance can be reduced and the contact area may increase, and thus an obvious increase in the yield of biodiesel in a short time of reaction is obtained. When stirring rate reaches 270 *g*, after only 60 min reaction, the yield of biodiesel reaches as high as 84.52%, and then there is no obvious increase in the yield of biodiesel with elevated stirring rate. As the stirring rate is high enough, the triglycerides and methanol have favorable contact area, and the transfer resistance is not still the controlling factor. So, further increase in stirring rate had no effect on yield.

In view of these results, it was found that when the heterogeneous catalyst K/KOH/γ-Al_2O_3 was used in the transesterification of rapeseed oil with methanol to produce biodiesel, high production efficiency was obtained with mild reaction conditions, i.e., the biodiesel yield as high as 84.52% was obtained with a molar ratio of methanol to rapeseed oil of 9:1, a catalyst amount of 4 wt%, a reaction temperature of 60°C, a stirring rate of 270 *g* and a reaction time of 1 h.

This catalyst K/KOH/γ-Al_2O_3 can be easily recovered by simple filtration. In an attempt to investigate the catalytic activity of the recycled K/KOH/γ-Al_2O_3, the transesterification of rapeseed oil with the same batch of supported catalyst under optimized conditions was performed. After a recycled experiment (with total reaction time of 12 h), it was found that the biodiesel yield decreases to 37.6%, and the catalyst loses weight of 10.8%, illustrating the relatively low stability of the catalyst. The decrease in catalyst activity after 12 h reaction was due to leaching of active species to the methanol phase, as evidenced by Alonso [12]. Assuming that the $KAlO_2$-like species (or Al–O–K species) would be formed at the surface of the solid, the following leaching process can be proposed

$$KAlO_2 + CH_3OH \rightarrow AlOOH + K^+ + CH_3O^- \qquad (4)$$

where the dissolved CH_3O^- species would be responsible for the homogeneous reaction. Consequently, the leaching potassium species to the methanol phase would be ascribed to the decrease in the catalyst activity. Therefore, from a practical point of view, further investigation should be done to intensify the stability and increase the lifetime of the catalyst.

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