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Nano KF/Al_2O_3 particles as an efficient catalyst for no-glycerol biodiesel production by coupling transesterification

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In this study, an efficient solid base catalyst, nano KF/Al_2O_3, for no-glycerol biodiesel production was prepared using nano γ-Al_2O_3 particles as support, and was used in the tri-component coupling transesterification of canola oil, dimethyl carbonate and methanol. The preparation optimum conditions (blending temperature, blending time, calcination temperature and calcination time) as well as the loading amount of KF were screened in detail. A yield of biodiesel, 98.8%, was obtained under the conditions of KF loading of 10.0 wt%, calcination temperature of 400 °C, 2 h of reaction time at 338 K, 5.0 wt% catalysts and molar ratio of methanol/oil/DMC of 8 : 1 : 1. This high conversion of vegetable oil to biodiesel is considered to be associated with the high surface to volume ratio and basicity of the catalyst surface.

Introduction

Biodiesel is a renewable fuel that can be produced from vegetable oils, animal fats, or recycled restaurant grease for use in diesel vehicles. Its physical properties are similar to those of petroleum diesel, but cleaner when being burnt, thus making biodiesel a good alternative fuel.[1,2] The prevailing method of biodiesel production in industry is transesterification of glycerol triglyceride with short-chain alcohols, such as methanol or ethanol, in the presence of soluble inorganic basic catalysts, such as sodium or potassium methoxides.[3] Although the reaction rates for this process are high, recovery of catalysts is difficult, and treatment of waste mixtures containing catalysts, water, glycerol and oils presents challenges. Problems can be reduced by using solid catalysts, which can be filtered off or centrifuged out of suspensions. However, heterogeneous catalysis produces glycerol[4,5] which needs an additional separation process, thus adding to the overall cost of biodiesel manufacture.[6] Glycerin is not very valuable as a by-product which simply adds to the over-supply of the commodity and thus contributes to a price depression.[7]

Generation of glycerol can be avoided through the reaction of vegetable oils and dimethyl carbonate (DMC) to produce glycerol carbonate (GC) as a secondary product, which does not require separation from the fatty acid esters.[8] A direct reaction between DMC and triglycerides can occur in the presence of sodium methoxide or potassium hydroxide (KOH) when refluxed at 90 °C for 6 h.[9] Ilham,[10] Saka[11] and Tan *et al.*[12] used DMC to produce biodiesel and GC at supercritical conditions in non-catalytic processes, while other researchers used enzymes to produce biodiesel with DMC as reactant.[13–15] In our previous research, an indirect reaction between DMC and triglycerides has been established by adding methanol as the third reaction component.[16] Although the tri-component transesterification improved the reaction rate to a relatively high level, it still didn't reach the theoretical maximum due to low diffusion rate between the three-phase systems made up by the three components. Reaction can only occur on the interfacial region between phases, and the only way to increase yield is to increase contact area.[17] Our previous study focused on the use of nanocrystalline calcium oxides catalyst for the transesterification reaction,[18] and obtained high biodiesel yield of 99% at room temperature. The high catalytic activity of the nano-based catalyst was deduced from its high surface/volume ratio.

As we know now, γ-Al_2O_3-supported catalysts have shown high activity in heterogeneous reactions including transesterification for biodiesel production.[19] Yield of biodiesel can be greatly enhanced by the enormous increase of surface area of γ-Al_2O_3-supported nano materials. KF-Impregnated commercial nanoparticles of γ-Al_2O_3 have been used as heterogeneous catalysts for the transesterification of vegetable oil with methanol for the synthesis of biodiesel. In this paper, we present the results of nano KF/Al_2O_3 catalyzed coupling transesterification of vegetable oil, dimethyl carbonate and methanol to produce biodiesel at moderate conditions. The catalytic activities and the effect of nano γ-Al_2O_3 preparation condition on the yield of biodiesel were studied as well.

Experiments

Materials

Refined rapeseed or canola oil was purchased from Xi'an coal Co., Ltd. Dimethyl carbonate (DMC), methanol, analytical

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reagent grade, calcium carbonate (CC) (99% purity) and calcium oxalate monohydrate (CO) (98% purity) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Beijing, China) and were used without further purification. Methyl heptadecanoate (gas chromatographic standard), nano γ-Al_2O_3 (95% purity) and surfactant OP-10 (octyl phenol with 10 moles per L of ethoxylate) were purchased from Sigma.

Catalyst preparation

Nano KF/γ-Al_2O_3 catalyst particles were prepared by the sol–gel method. Firstly, 5.0 g γ-Al_2O_3 was added into 50 mL of ethanol, and then a certain amount of KF·$2H_2O$ and 1 mL OP-10 was added in under stirring. The mixture was stirred for 2 h and a clear white gel was obtained. The white gel was kept at room temperature for 2 h. After that, the gel was heated up to 80 °C and kept for 2 h to vaporize water. Then the condensed gel was placed in a desiccator for 12 h to dry completely. The resulting dry gel was milled to white powder and calcinated under high temperature, and cooled to room temperature to complete the preparation procedure of catalyst KF/γ-Al_2O_3-OP. For comparison, the supported KF/γ-Al_2O_3 was prepared by impregnating KF over commercial γ-Al_2O_3 directly under same condition without ethanol.

Materials characterizations

Thermo gravimetric analysis (TGA) of catalyst sample was performed in the static air condition 20–1000 °C with a heating rate of 5 °C min^{-1}, using a thermo-gravimetric analyzer/simultaneous differential thermal analyzer (TGA/SDTA 851^e, Mettler-Toledo, Switzerland). Textural characteristics were investigated by means of surface area determined by BET including mean pore diameter and pore volume using desorption isotherms on a Micromeritics ASAP2000. The crystalline structures of the products of calcination were analyzed using an X-ray diffraction device (JDX-3530, JEOL, Japan) with an X-ray tube that has copper Cu as target and released K_α radiation when accelerated at 30 mA and 40 kV. Scanning Electron Microscopy (SEM) was used for the investigation of surface morphology of catalyst samples. Before submitted to SEM characterization, the solid sample was coated with gold in order to achieve sufficient conductivity. Temperature-programmed desorption patterns of carbon dioxide (CO_2-TPD) for the products were measured with an automated chemisorption analyzer (Autochem II 2920, Micromeritics, USA) at the temperature range from 40 to 800 °C with a heating rate of 10 °C min^{-1}.

Preparation and analysis of biodiesel

Prior to reaction, the oil was treated with sodium hydroxide, at a ratio of 1 mg KOH per g lipids, and with bentonite to, respectively, lower fatty acid and water concentrations below 1 mg g^{-1} of triglyceride. The reaction was performed in a three necked round bottomed flask equipped with a reflux condenser and a thermometer. A certain amount of KF/γ-Al_2O_3 and 8.01 g methanol were charged into the flask. Then 20.48 g rapeseed oil and 2.815 g DMC were added. The mixture was heated to and maintained at 65 °C with continuous stirring. Samples were taken from the reaction mixture for each hour, and quenched to room temperature. The catalyst was separated by centrifugation, and the excess methanol was distilled off under vacuum. Samples were quantitatively analyzed for composition on an HP-6890 gas chromatograph equipped with a flame ionization detector and a fused-silica capillary column (HP-5; 0.32 mm × 30 m, 0.1 μm film thickness) using methyl heptadecanoate as standard. The carrier gas was nitrogen with a flow rate of 20 mL min^{-1}. The oven temperature was kept constant at 280 °C. Yield was defined as a ratio of the weight of fatty acid methyl esters in samples, as determined using the GC, to the weight of equivalent fatty acid methyl esters contained in the oil used in the reaction.

Results and discussion

Characterizations of various samples

Thermo-gravimetric analyses (TGA). The thermal characteristics of support and the prepared KF/γ-Al_2O_3-OP and KF/γ-Al_2O_3 samples were investigated using TGA from room temperature up to 1000 °C (Fig. 1). The weight losses in the range from 30 to 200 °C is due to loss of physically adsorbed water and hydroxyl from catalyst's surface, while the second weight loss step occurred at higher temperature in the TGA curve may be related to crystallization and/or weight loss due to components' loss of the catalysts caused by certain reactions occurring at high temperature.[20] It can also be found that the weight loss in the higher temperature range was enhanced over KF/γ-Al_2O_3-OP indicating the stronger interaction of support and KF.

X-Ray diffraction analyses. The X-ray diffraction patterns for support material γ-Al_2O_3, KF/γ-Al_2O_3 and KF/γ-Al_2O_3-OP are shown in Fig. 2. The plots show that all of samples have the characteristic peaks of Al_2O_3 at 2θ of 37.0, 46.0 and 67.0. An additional K_2O phase can be observed in both catalysts with the characterization diffraction peak at 30.0, 42.7 and 53.0. The intensities of these peaks over KF/γ-Al_2O_3 are not as high as those observed for KF/γ-Al_2O_3-OP, indicating the role of OP-

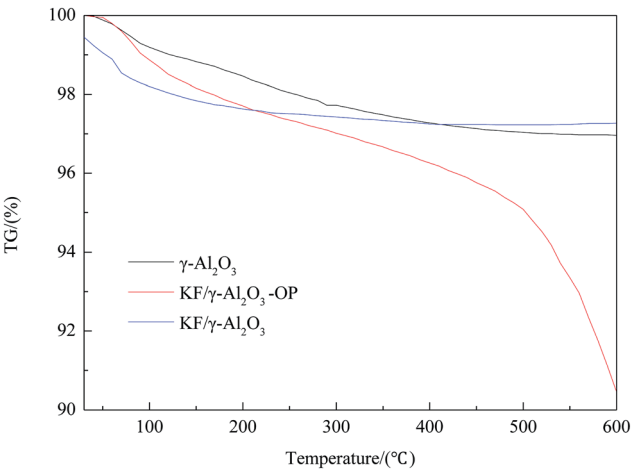

Fig. 1 TGA plot for KF/γ-Al_2O_3 prepared by different method.

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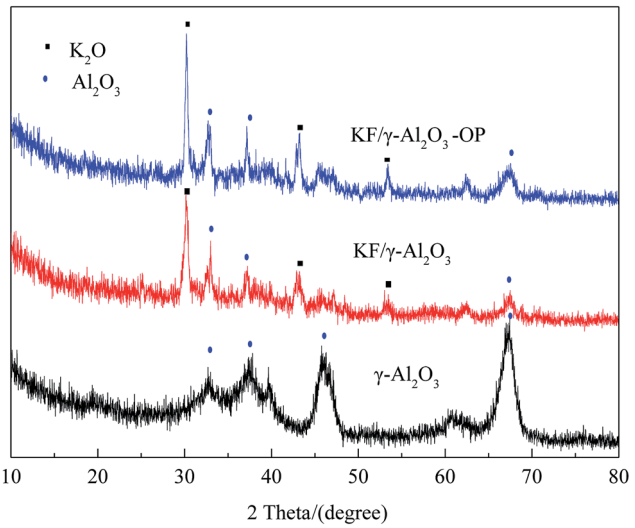

Fig. 2 XRD patterns for γ-Al_2O_3 and KF/γ-Al_2O_3 prepared by different method.

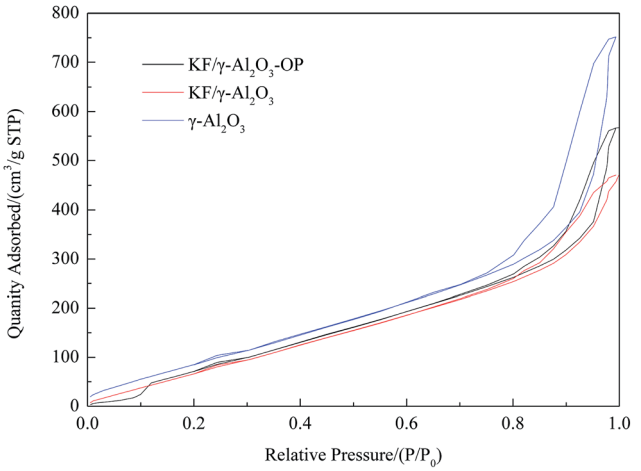

Fig. 3 Nitrogen adsorption curves of γ-Al_2O_3 and KF/γ-Al_2O_3 prepared by different method.

10 to improve the dispersion of Al_2O_3 in the mixture as suggested previously. Studies have discovered the relationship of the high catalytic activity of KF-impregnated alumina catalysts with the basicity of the surfaces, which is due to the formation of the K_2O and Al–O–K groups derived from the thermal decomposition of the loaded K compounds by salt–support interactions.[21]

Surface properties. The BET surface, pore size and average pore volume of KF/γ-Al_2O_3 obtained from different method are characterized and listed in Table 1. As shown in Table 1, the specific surface area S_{BET} of γ-Al_2O_3 decreased greatly from 396.3 $m^2\ g^{-1}$ to 278.5 $m^2\ g^{-1}$ after supporting KF with a large reduction of pore volume, whereas the BET surface area for KF/γ-Al_2O_3-OP still remains a high value of 389.9 $m^2\ g^{-1}$. This may be due to its smaller particle size and/or smaller pore diameter caused by second calcination under high temperature. The surface area and pore properties of KF/γ-Al_2O_3-OP were greatly enhanced compared with KF/γ-Al_2O_3, reflecting a significant role of ethanol as surfactant to prevent aggregation of nano-Al_2O_3 during preparation. Nitrogen adsorption–desorption isotherms obtained with all of the samples are shown in Fig. 3. The nitrogen adsorption isotherms of γ-Al_2O_3 and KF/γ-Al_2O_3 exhibit the typical type III isotherm, indicating that all of the samples were macroporous, and a low energy of adsorption as well. The capillary condensation of N_2 can be observed at relative high pressure.

Table 1 Pore structure properties of the catalyst

Sample	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1} \times 10^{-2}$)	Pore size (nm)
γ-Al_2O_3	396.34	0.9054	91.3801
KF/γ-Al_2O_3-OP	389.97	0.7230	75.3185
KF/γ-Al_2O_3	278.46	0.4328	50.3287

Basic properties. For solid basic catalysts, the amount of irreversibly adsorbed CO_2 reflects the population of base sites on exposed surfaces. The desorption temperature indicates the strength of adhesion at the base site. Results for temperature-programmed desorption were presented in Fig. 4. The profiles exhibit peaks between 400 °C and 700 °C associated with strong base for transesterification reaction.[22] The broad band associated with weak or medium strength interactions of CO_2 with the basic sites on catalyst particles moves to almost below 200 °C, indicating the weak basic sites. In the samples, KF/γ-Al_2O_3-OP showed higher and broader desorption peak around 600–650 °C attributed to the strong basic sites of O^{2-} anions, whereas KF/γ-Al_2O_3 showed a considerably smaller desorption peak with the maximum temperature of 598 °C. Consistent with previous findings,[23] the increased surface area and the basicity of the catalysts will benefit to their activities, so the FAME yield may be increased directly with increasing basicity of the high catalyst surface over KF/γ-Al_2O_3-OP.

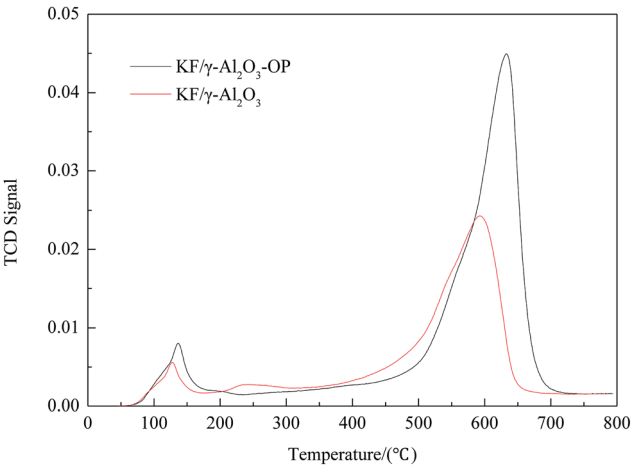

Fig. 4 CO_2-TPD curves of KF/γ-Al_2O_3 prepared by different method.

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Scanning electron microscopy (SEM). The SEM image of γ-Al_2O_3, KF/γ-Al_2O_3-OP and KF/γ-Al_2O_3 were shown in Fig. 5. These graphs showed a good dispersion of KF on the surface of γ-Al_2O_3, however, the surface morphology has been changed over KF–γ-Al_2O_3 and some degree of agglomeration is evident from the large particles. It was further confirmed that the dispersion function of ethanol during the preparation of KF/γ-Al_2O_3 using nano-γ-Al_2O_3 as support. It can be found that the particle size of KF/γ-Al_2O_3 was smaller than that of KF/γ-Al_2O_3-OP while the surface area of latter was larger. Generally, an inverse proportionality between BET area and particle size was deduced based on geometry. However, for the macroscopic material that may have been more capacity potentially leading to an artificial increase in the specific surface area, and a change in the apparent surface reactivity.[24]

Effect of preparation parameters

Effect of the amount of KF. As suggested by previous reports that K_2O was the main active sites for the transesterification of supported KF catalysts, hence a series of KF/γ-Al_2O_3-OP catalyst calcined at 400 °C for 2 h with loaded KF ranging from 0.5–3.0 mmol g^{-1} have been investigated under 65 °C at 2 h. Fig. 6 shows very high FAME yield as high KF loading amount, indicating the enhanced activity due to a concomitantly remarkable increase in surface basicity. In order to obtain the best catalytic performance, more KF were loaded under same reaction condition and achieved 98.8% of FAME yield for the KF(10%)/γ-Al_2O_3-OP, but the yield declined as KF amount exceeding 10.0%. These differences may be associated with the strong basic sites resulted from KF loading on Al_2O_3, which can also be covered by the excess KF. Drawing on the results, the optimum loading amount of KF was selected as 10.0%.

Effect of blending time. The dispersion of hydrophobic Al_2O_3 particles in the KF solution was greatly influenced by the amount of surfactant, OP-10, employed during the process of catalyst preparation. The optimum blending time for the preparation of supported Al_2O_3 was determined by performing reaction at varying reaction time in the range of 1–3 h. The experimental results, reported in Fig. 7 indicated that the FAME yield increased with blending time between 1 h and 2 h of complete mixing, while long blending time caused low yield, probably due to increasing viscosity. Thus, the maximum FAME yield of 98.8% was achieved after 2 h of blending time.

Effect of blending temperature. In order to improve the solution of OP-10, blending temperature during catalyst preparation process was screened in the temperature range from 60 to 75 °C and summarized in Fig. 8. From the result, it was believed that the relatively high blending temperature improved the mutual oil–methanol–DMC miscibility, resulting in an increase of the FAME yield. The maximum FAME yield of 98.8% was achieved when the mixture was stirred at 65 °C. However, extremely high blending temperature caused a decrease in the yield of FAME, which possibly owing to

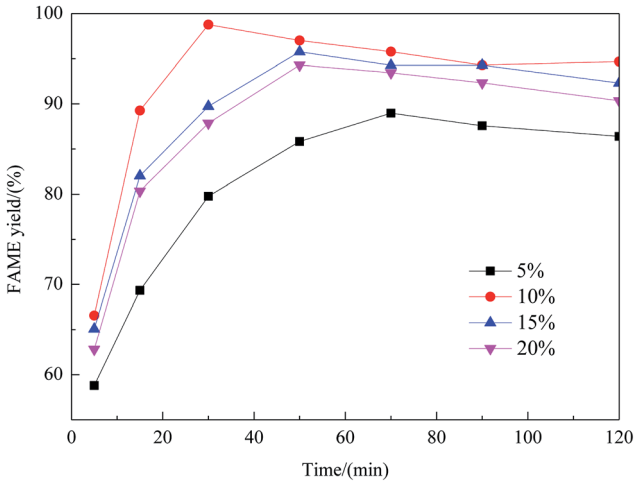


Fig. 6 Effect of amount of KF on the performance of KF/γ-Al_2O_3-OP.

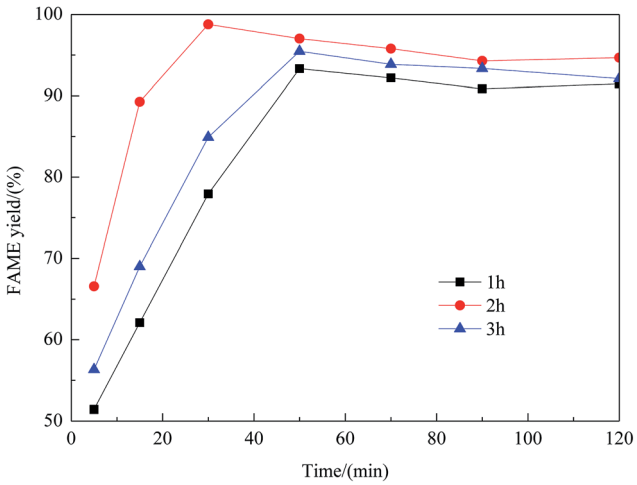
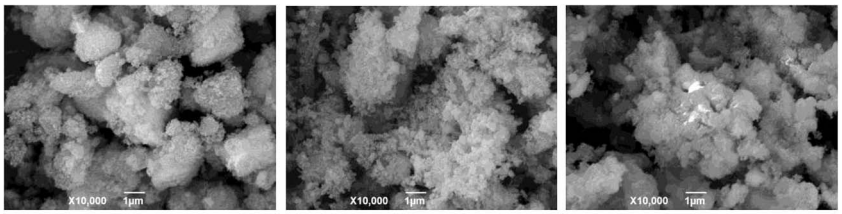


Fig. 7 Effect of blending time on the performance of KF/γ-Al_2O_3-OP.



a. γ-Al_2O_3 b. KF/γ-Al_2O_3 c. KF/γ-Al_2O_3-OP

Fig. 5 SEM photographs of γ-Al_2O_3 and KF/γ-Al_2O_3 prepared by different method.

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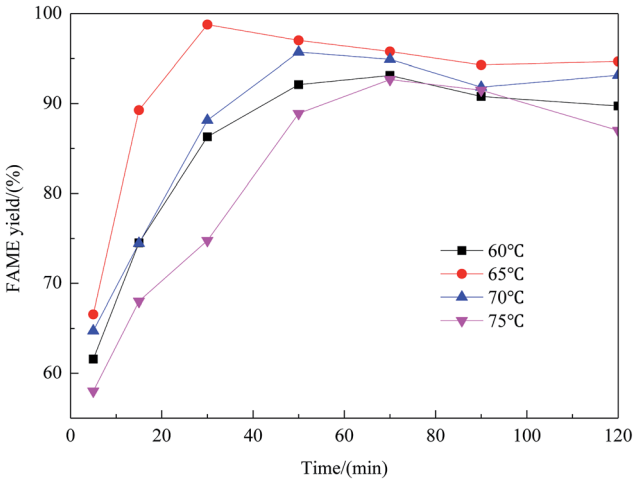

Fig. 8 Effect of blending temperature on the performance of KF/γ-Al_2O_3-OP.

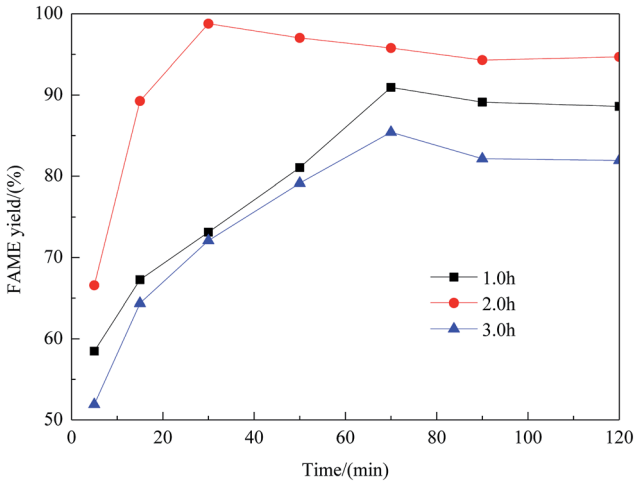

Fig. 10 Effect of calcination time on the performance of KF/γ-Al_2O_3-OP.

a miscibility problem involving OP-10 and Al_2O_3 particles under high temperature. Accordingly, the preparation condition for nano-KF/γ-Al_2O_3 was studied under blending temperature of 65 °C.

Effect of calcination temperature. As we are aware, the calcination temperature plays an important role in the catalytic activity of solid catalyst by producing much active site of mixed oxides and the KF decomposition extent. Therefore, the KF/γ-Al_2O_3-OP was calcined at different temperature (200 °C, 300 °C, 400 °C and 500 °C) in order to seek for better activity. From the results summarized in Fig. 9, it can be found that the yield of FAME increased with calcination temperature until 400 °C, which contributed to the appearance of basic active site from the decomposition of KF, and the maximum FAME yield of 98.8% can be obtained over the catalyst calcined at 400 °C. However, slight descending of FAME yield appeared when further increasing calcination temperature to 500 °C. This was possibly due to agglomeration of catalyst surface area and loss of potassium species by sublimation or penetration into the subsurface, an influential factor for the reaction rate especially for the heterogeneous reaction.

Effect of calcination time. Since the activity variation of KF/γ-Al_2O_3-OP catalyst should be attributed to the distribution of potassium on the alumina support which were calcined at different time, the calcination time of KF/γ-Al_2O_3-OP was investigated from 1 h to 3 h. From the results summarized in Fig. 10, it can be concluded that an appropriate calcination time was at 400 °C for 2 h to obtain the maximum FAME yield of 98.8%. Overlong calcination time caused the decrease of yield of FAME due to loss of active sites as a result of agglomeration of catalyst surface. Therefore, calcination time of 2 h was suitable for obtaining high yield of FAME.

Effect of reaction parameters. Transesterification was preceded using three components of rapeseed oil, methanol and DMC at mild conditions as our previous publication referred.[17] Methanol first reacted with the triglyceride to produce FAME and glycerol. In the coupling process, the

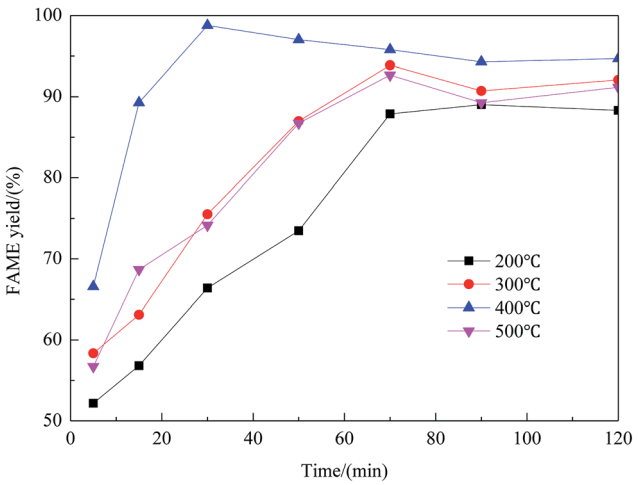

Fig. 9 Effect of calcination temperature on the performance of KF/γ-Al_2O_3-OP.

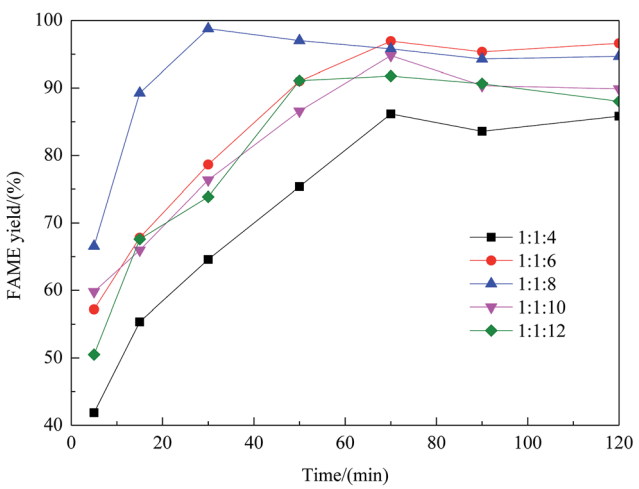

Fig. 11 Effect of molar ratio on the performance of KF/γ-Al_2O_3-OP.

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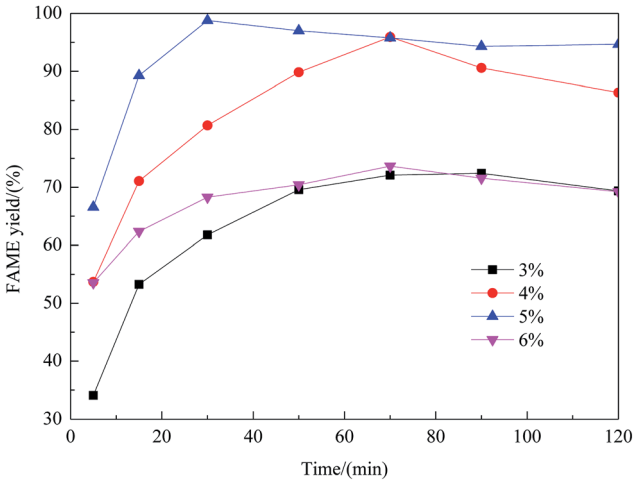

Fig. 12 Effect of catalyst content on the performance of KF/γ-Al_2O_3-OP.

produced glycerol reacted with dimethyl carbonate to form glycerol carbonate and methanol. From prior work, the optimal proportion of the feed reactants, on a molar basis, was 1 : 1 : 8 of oil : DMC : methanol under refluxing. For obtaining maximum reaction rate of the transesterification process, an overall optimization is necessary, and the reaction parameters which affect the yield of FAME have been itemized in detail.

Effect of molar ratio. As we know, the transesterification reaction between rapeseed oil and methanol generally requires a large excess of methanol to shift the equilibrium favorably, so the molar ratio of methanol to oil should be investigated. Fig. 11 graphically illustrates the FAME yield changing with the molar ratio of methanol to oil, under 1 : 1 molar ratio of rapeseed oil to DMC. As shown in this figure, with an increase of the methanol amount, the yield of FAME enhanced considerably. The maximum yield of FAME, 98.8%, was obtained as the molar ratio reached 8 : 1. However, beyond the molar ratio of 8 : 1, excessive methanol caused the yield to decrease, which was possibly due to the mixing difficulty caused by mass transfer hindrance involving excess reactants, products and solid catalyst. Therefore, the optimum molar ratio of methanol to rapeseed oil was determined as 8 : 1.

Effect of catalyst amounts. The dependence of the yield of FAME on the catalyst amount was studied in the presence of KF–γ-Al_2O_3-OP at 65 °C. The catalyst amount varied in the range of 3.0–6.0% (w/w) of oil. The reaction profile summarized in Fig. 12 indicated that the FAME yield was strongly dependent with catalyst percentage. Due to insufficient active sites, low addition of catalyst was unable to lead to high yield of FAME until it reached to 5.0%. While increased reaction rate can be observed in initial reaction time, indicating relatively high activity of supported catalyst. When the amount of catalyst increased from 3% to 5%, the yield of FAME at 30 min increased from 62.1% to 98.8%. Further increase in the catalyst amount leaded to the decrease of the yield of FAME. The reason for this decreasing trend was the mixing problem in presence of high amount of catalyst, which increased the viscosity of the reactants and lowered the yield of FAME. This result also implied that the transesterification of KF–γ-Al_2O_3-OP was strongly dependent on the amount of basic sites.

Table 3 The produced fuel properties over KF/γ-Al_2O_3-OP

Fuel property	Unit	Prepared FAME	EU (EN14214)
Density (15 °C)	g mL^{-1}	0.88	0.86–0.90
Kinematic viscosity (40 °C)	mm^2 s^{-1}	3.18	3.5–5.0
Pour point	°C	−9.4	—
Cold filter plugging point	°C	−10.0	—
Flash point	°C	144.0	≥101
Free glycerol	% (m m^{-1})	0.018	<0.02

The comparison study

The catalytic performances of KF–γ-Al_2O_3-OP for biodiesel production with or without DMC have been investigated, and the properties of the product were studied. As presented in Table 2. Nearly 98.9% yield of FAME was obtained within 30 min using the proposed coupling transesterification under the optimized condition (65 °C, 1 : 1 : 8 molar ratio of methanol, oil to DMC), while transesterification between methanol and rapeseed oil resulted in 96.5% yield of FAME within 70 min. The main reason for high FAME yield over KF–γ-Al_2O_3-OP containing DMC should be contributed to the integration of two transesterifications of methanol/rapeseed oil and glycerol/DMC, which resulted in promoting the transesterification between rapeseed oil and methanol towards the favored direction as suggested in our previous results. As a result, the

Table 2 Catalytic performance of prepared catalysts

		KF/γ-Al_2O_3-OP		KF/γ-Al_2O_3
Reaction condition	Unit	Without DMC	With DMC	With DMC
Reaction time	min	70	30	120
Reaction temperature	°C	65	65	65
Molar ratio	—	1 : 8	1 : 1 : 8	1 : 1 : 8
Amount of catalyst	%	5	5	5
Yield of FAME	%	96.5	98.8	37.3
Yield of glycerol carbonate	%	—	98.6	37.2

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conversion of rapeseed oil was enhanced by activating and converting glycerol to glycerol carbonate, which shifted the transesterification of methanol and rapeseed oil favorably to give high FAME yield. The comparison study on the catalytic activity of KF/γ-Al_2O_3-OP and KF/γ-Al_2O_3 was carried out under the optimum reaction condition obtained above: 65 °C, 1 : 1 : 8 molar ratios of oil/DMC/methanol, 5 wt% of catalyst. From this study it can be seen that the yield of FAME was enhanced to near to 98.8% in the presence of KF/γ-Al_2O_3-OP at 30 min, while with KF/γ-Al_2O_3 it needed 120 min to obtain only 37.3%. In view of the characteristic results of the catalysts, it is obvious that the activity change of the catalysts was well correlated to the change of their basicity. Besides, the surfactant can also improve the dispersion of active species over support as it greatly enhanced the forming of both K_2O species and Al–O–K groups in the composite.

The quality of produced oil

For the aim of being commercial applicable, the produced biodiesel must be characterized using specified analytical methods to ensure it meeting the international standards. Therefore, some properties, including viscosity, density, flash point and free glycerol value were investigated and listed in Table 3. The specifications of both biodiesel are close to the European standard, EN14214 and the literature data.[25] It should be noted that the free glycerol in biodiesel obtained from the new method is within the range of European standard, thus indicates that the coupling transesterification eliminated glycerol efficiently as we suggested before. The viscosity of obtained biodiesel is lower than the limit of EN14214 due to the presence of glycerol derivates, and this property may improve the spray injection behavior of the fuel.

Conclusion

In this research, nano-KF/γ-Al_2O_3 was prepared by blending powdered nano-γ-Al_2O_3 with an aqueous solution of KF followed by calcination at a high temperature in air. The dispersed nano-γ-Al_2O_3 increased the surfactivity greatly, and the K_2O species formed during the thermal decomposition of loaded KF was probably the main reason for the high catalytic activity. Nearly 99.0% yield of FAME was obtained within 30 min using the proposed coupling transesterification under the optimized condition (65 °C, 1 : 1 : 8 molar ratio of methanol, oil to DMC). Furthermore, the reaction reduced the free glycerol content in biodiesel product to make it a great advantage of avoiding the risk of plug in fuel filters.

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