

## CONVERSION OF RAPESEED OIL TO BIODIESEL ON KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CATALYST

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*It is shown that the KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst obtained by the sol–gel method has a greater activity in the process of transesterification of methanol and rapeseed oil to biodiesel compared to KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by impregnation. The highest yield of biodiesel (96.5%) is achieved with use of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, prepared at molar ratio KF to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 1.3:1. High conversion of rapeseed oil to biodiesel is explained by the relatively high basicity and specific surface of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.*

**Keywords:** biodiesel, transesterification, nanosized solid base.

Biodiesel, an eco-friendly fuel that is not toxic and does not contain sulfur, is used as an alternative to classic diesel fuel. Nowadays, alkaline-earth metal oxides and supported solid bases are used most widely as the catalysts in production of such fuel [1, 2]. Among the alkaline-earth metal oxides, calcium oxide has high catalytic activity, and its use provides for FAME (fatty acid methyl esters) yields as high as 90% in 5 h [3]. On the other hand, such catalyst is hydrated and carbonated in a few minutes upon contact with air at ambient conditions due to chemisorption of significant amounts of H<sub>2</sub>O and CO<sub>2</sub>. In order to improve the catalytic activity, calcium oxide is modified by doping and addition of other components [4]. The use of KF/Al<sub>2</sub>O<sub>3</sub> as a solid catalyst for biodiesel production was recently described, but such catalyst suffered from low catalytic activity caused by low content of strong basic sites [5]. Nanosized materials have been attracting much attention in view of their unusual physical and chemical properties [6]. Enhancement in the reactivity of the nanosized oxides is associated with their large surface area, higher concentration of highly reactive edge sites, corner defect sites, as well as unusual crystal lattice planes [7]. Reddy et al. [8] found that the high activity of the nanosized calcium oxide allowed one to carry out the transesterification of soybean oil and poultry fat at room temperature. However, the deactivation of the catalyst was observed after eight cycles, which was mainly caused by the moisture in the reaction medium.

In this paper the results of the application of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with KF, performed by two different methods, for the catalytic process of vegetable oil and methanol transesterification for biodiesel production at

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moderate conditions are presented. In the study the catalytic activity was compared with the analogues, and the effect of  $\gamma$ - $\text{Al}_2\text{O}_3$  preparation condition on the biodiesel yield was investigated in detail.

## EXPERIMENTAL

**Materials.** Refined rapeseed or canola oil was purchased from Xi'an Coal Co., Ltd. Dimethyl carbonate (DMC), methanol of analytical reagent grade, calcium carbonate (99% purity), and calcium oxalate monohydrate (98% purity) were purchased from Sinopharm Chemical Regents Co., Ltd. (Beijing, China) and used without further purification. Methyl heptadecanoate (gas chromatography standard) and nanosized  $\gamma$ - $\text{Al}_2\text{O}_3$  (95% purity) were purchased from Sigma.

**Catalyst preparation.** KF/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was prepared by the sol-gel method. First, 5.00 g  $\gamma$ - $\text{Al}_2\text{O}_3$  was added to 50 mL of ethanol and then 1 g of  $\text{KF}\cdot 2\text{H}_2\text{O}$  and 1 mL of OP-10 (dodecylphenol polyoxymethylene ether) were added under stirring with a mechanical mixer. After 2 h a homogeneous white gel was obtained. The white gel was kept still for 2 h to completion of the reaction, then heated up to 80°C for 2 h for water evaporation and gel concentration. The concentrated gel was placed in a desiccator for 1 h to dry completely. The resulting dry gel was milled to formation of a white powder. The produced powder was put into the oven under high temperature. The catalyst is marked as KF/ $\gamma$ - $\text{Al}_2\text{O}_3$ -OP. For comparison, the supported KF/ $\text{Al}_2\text{O}_3$  catalyst was prepared by impregnation of the commercial  $\gamma$ - $\text{Al}_2\text{O}_3$  with KF in 100 mL of distilled water under the same conditions but without use of ethanol and OP-10.

**Materials characterizations.** Textural characteristics were studied from the data of nitrogen desorption isotherms, measured on a Micromeritics ASAP2000 instrument, by determining the surface area by BET, mean pore diameter, and pore volume. Thermogravimetric analyses (TGA) of catalyst samples were performed under static condition in air in the temperature range 20-1000°C with a heating rate of 5°C·min<sup>-1</sup> using a thermogravimetric analyzer simultaneously with a differential thermal analyzer (TGA/SDTA 851<sup>e</sup>, Mettler-Toledo, Switzerland). The crystal structures of the calcination products were analyzed using an X-ray diffractometer (JDX-3530, JEOL, Japan) with an X-ray tube with Cu anode, producing  $K_\alpha$  radiation at 30 mA current and 40 kV accelerating voltage. Scanning electron microscopy (SEM) was used for the investigation of surface morphology of the catalyst samples. Before SEM characterization, the solid sample was coated with gold in order to achieve sufficient conductivity. Temperature-programmed desorption patterns of carbon dioxide ( $\text{CO}_2$ -TPD) for the samples 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<sup>-1</sup>.

**Preparation of biodiesel.** The method for biodiesel production based on the traditional transesterification between methanol and rapeseed oil was used. Prior to the conversion process, the oil was treated with sodium hydroxide at a ratio of 1 mg NaOH/g lipids, and the water concentration was reduced to a level below 1 mg/g of triglyceride using raw bentonite. The reaction was performed in a three-necked round bottomed flask equipped with a reflux condenser. Methanol was charged into the flask, then 30 g of rapeseed oil was added. The mixture was heated and maintained at 65°C temperature with continuous stirring. The samples were withdrawn from the reaction mixture every 20 min, and the reaction was quenched by cooling to room temperature. After the reaction stopped, the catalyst was separated by centrifugation, and the excess of methanol was distilled off under vacuum. The composition of the samples collected was determined using 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 the standard. Nitrogen was used as the carrier gas at a flow rate of 20 mL·min<sup>-1</sup>. The oven temperature was kept constant at 260°C. The yield was defined as the ratio of the weight of fatty acid methyl esters in the samples, determined by the GC, to the weight of the equivalent fatty acid methyl esters that the oil used in the reaction would have contained.

## RESULTS AND DISCUSSION

### Effect of the Catalyst Preparation Parameters

**Effect of the KF amount.** The influence of the amount of active ingredient on the performance of KF/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst in the rapeseed oil transesterification was investigated at refluxing temperature (65°C) with a molar ratio of methanol to oil

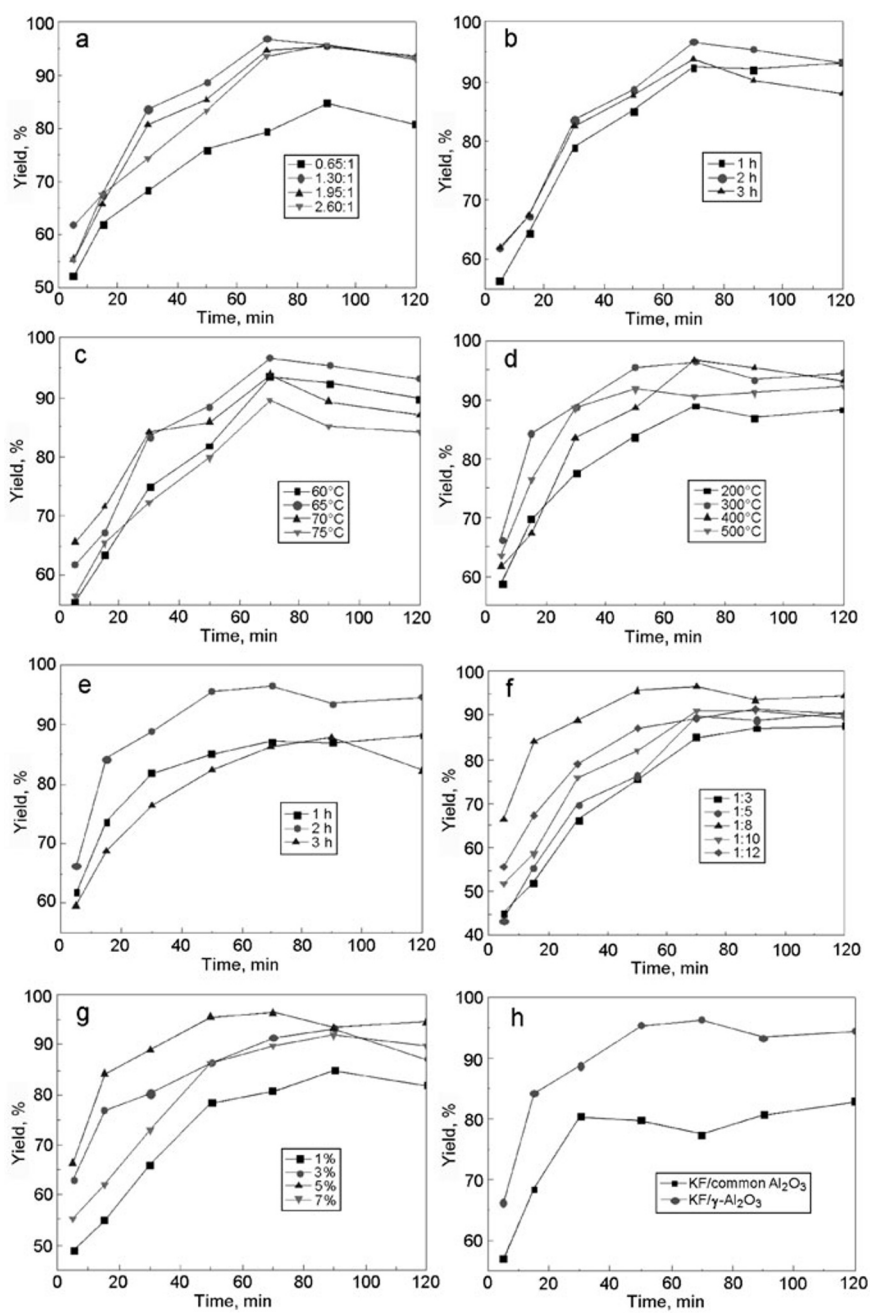


Fig. 1 Effect of the catalyst preparation conditions and the reaction conditions on biodiesel yield: KF amount (a); time of blending during catalyst preparation (b); reaction temperature (c); temperature of the catalyst calcinations (d); calcination time (e); amount of methanol (f); amount of the catalyst (g); performance comparison for KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by different methods (h).

equal to 8:1 upon addition of 5 wt.% of the catalyst. The results are shown on Fig. 1a. From these results, it is seen that the biodiesel yield varies depending on the amount of KF and reaches the optimal value of 96.5 % at a molar ratio of KF to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> equal to 1.30, which can be explained by the increase in surface-active sites as a result of increase in the KF amount. However, a decrease in biodiesel yield was found when excessive amounts of KF were used, which led to poor dispersion of active sites on the catalyst surface [9].

**Effect of blending time.** The influence of the blending time in the catalytic performance of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP was investigated at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1 upon addition of 5 wt.% of the catalyst. The results are shown on Fig. 1b. From these results, the FAME yield increases with blending time; however, with further increase in the blending time, a decrease in FAME yield was observed, indicating that the long blending time caused aggregation of the active component on the catalyst surface. Therefore, the best blending time for preparation of efficient KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was selected and found to be 2 h.

**Effect of the blending temperature.** Since the solubility of the surfactant is affected by temperature, catalysts prepared at different temperatures of KF,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and surfactant OP-10 blending were studied. The investigation was carried out at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1 upon addition of 5 wt.% of the catalyst. The results are shown on Fig. 1c. From the result, it is seen that the solid catalyst prepared at 65°C has the highest catalytic activity, and the FAME yield reaches 96.69% in 70 min. Thus, a relatively high blending temperature was required to achieve good solubility of the surfactant, while a much higher blending temperature caused an increase in the solution viscosity. So, in the further work the blending temperature 65°C was chosen.

**Effect of calcination temperature.** To obtain efficient basic sites on the surface of the KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP catalyst, the influence of the calcination temperature on the rapeseed oil transesterification was investigated. The study was performed at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1 in presence of 5 wt.% of the catalyst. The results are shown on Fig. 1d. After calcination at 300°C, the catalyst showed the highest activity in the transesterification of rapeseed oil, and the FAME yield exceeded 95% in 50 min. However, when the calcination temperature increased above 300°C, the catalytic activity gradually decreased, probably due to the agglomeration of the catalyst and reduction of the catalyst's surface area.

**Effect of the calcination time.** As is known, the calcination time has a significant effect on the interaction between the support and the active species. Thus, in our experiment the influence of the time of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP calcination on the transesterification of rapeseed oil was investigated by using KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP calcined for various times at 300°C as solid base. The transesterification was carried out at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1 in presence of 5 wt.% of the catalyst. The results are shown on Fig. 1e, where one can see that the best catalytic performance was obtained in the case of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP calcined for 2 h, while low FAME yields were observed for other calcination times, probably due to the lower activity of the sites or sintering of the catalytically-active surface.

**Effect of the methanol to oil molar ratio.** The molar ratio of methanol to oil is one of the most important parameters that affect the FAME yield. The influence of the molar ratio of methanol to oil on the transesterification of the rapeseed oil was investigated under the same reaction conditions as given above: at refluxing temperature (65°C) in presence of 5 wt.% of the catalyst, as shown on Fig. 1f. The results agree well with those reported previously: that excess of methanol shifts the equilibrium towards the direction of ester formation because the transesterification of triglyceride is a reversible reaction. In our experiment, an increase in the molar ratio of methanol to oil from 3:1 to 8:1 resulted in a significant effect on the FAME yield, and the best yield, at the level of 96.47%, was obtained at 8:1 molar ratio of methanol to oil. Further increase in the methanol content resulted in a decrease in the fatty acid methyl ester yield because of dilution by the excess alcohol [10].

**Effect of the catalyst amount.** The influence of the amount of catalyst on the rapeseed oil transesterification was investigated at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1; the result is shown in Fig. 1g. As it can be seen in Fig. 1g, at the beginning with increase in the amount of catalyst from 1% to 7% (weight relative to oil weight), the yield of FAME markedly increased and reached the maximum value when 5% of the catalyst was used. However, with further increase in the catalyst content, the FAME yield decreased due to the formation of soap, which increased the viscosity of the reactant and adhered to its diffusion to the catalyst surface. Therefore, the optimal content of the KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP catalyst used in this study was 5% [11].

## Comparative Study

The catalytic activity of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP obtained by the two different methods is shown on Fig. 1h. The investigation was carried out at refluxing temperature (65°C) with a molar ratio of methanol to oil equal to 8:1 in presence of 5 wt.% of the

TABLE 1. Performance Comparison for Biodiesel Preparation Catalyzed by Different Types of Catalysts

Catalysts	Reaction temperature, °C	Methanol-to-oil ratio	Amount of catalyst, %	Reaction time, h	Yield, %
SrO-CaO-Al <sub>2</sub> O <sub>3</sub> [12]	65	18:1	7,5	3	98,16
ZnO/CuO [13]	55	10.5:1	1.66	1.88	94.53
KOH [14]	63.3	7.5:1	0.95	1.54	98.48
Sulfated ZrO <sub>2</sub> (CN/SZ) [15]	65	3:1	0.2	2	98.8
Algal biochar/CaO/K <sub>2</sub> CO <sub>3</sub> [16]	65	18:1	4	3.3	98.83
ZnCuO/N-doped graphene (NDG) [17]	180	15:1	8	10	97.1
Prepared KF/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	65	8:1	5	1.11	96.5

TABLE 2. Characteristics of the Porous Structure of the Samples

Sample	BET Surface area, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g·10 <sup>-2</sup>	Pore size, nm
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	396.3	0.9054	91.3801
KF/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -OP	389.9	0.7230	75.3185
KF/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	278.5	0.4328	50.3287

prepared catalysts. As can be seen from the results, in the case of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP prepared by the blending method, the yield of FAME was 96.5% after 60 min, while only 80% yield of FAME could be obtained in the presence of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by the ordinary volume impregnation method using commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support. Furthermore, a comparison of the performance of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP with the data reported in the literature for other efficient catalysts for this process, which are shown in Table 1, shows the benefits of the proposed catalyst, such as fast conversion to achievement of high FAME yields under the same reaction conditions. To explain the reason for these results, the structures of these catalysts were investigated in detail.

### Characterizations of Samples

**Surface area.** The results of examination of textural properties of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared by different methods are presented in Table 2. As can be seen from the table, the BET surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reaches 396.3 m<sup>2</sup>·g<sup>-1</sup>, and this compound has a large pore volume equal to 0.9054 cm<sup>3</sup>/g·10<sup>-2</sup> and pore size 91.4 nm. After deposition of KF, these values gradually decreased due to calcination at high temperature. KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP had a relatively large average pore diameter compared to

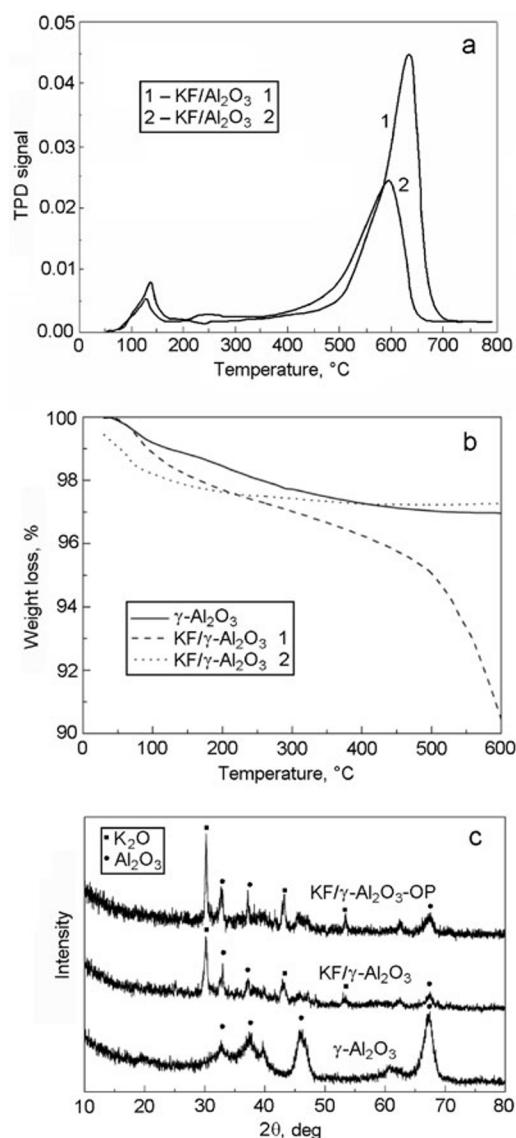


Fig. 2 Characterizations of the KF/γ-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by different methods: a) CO<sub>2</sub>-TPD; b) TG curves; c) XRD patterns.

KF/γ-Al<sub>2</sub>O<sub>3</sub>, which is the primary requirement for an ideal solid base catalyst for the transesterification process, because the presence of large interconnected pores minimizes diffusion limitations for molecules having long alkyl chains [18].

### Temperature-Programmed Desorption of CO<sub>2</sub>

The results of the temperature-programmed desorption of CO<sub>2</sub> are presented in Fig. 2a. The profiles exhibit peaks between 400°C and 700°C associated with strong basic sites, required for the transesterification reaction. The broad band associated with the weak or medium strength interactions of CO<sub>2</sub> with the basic sites on catalyst particles shifts to the low temperature range, below 200°C. In the case of KF/γ-Al<sub>2</sub>O<sub>3</sub>-OP samples, the largest broad desorption peak is observed in the temperature region of 600-650°C; such peak is attributed to the strong basic sites of the O<sup>2-</sup> anions. In the case of KF/γ-Al<sub>2</sub>O<sub>3</sub>, a considerably smaller desorption peak is observed with the same maximum temperature of 598°C [19], indicating that the

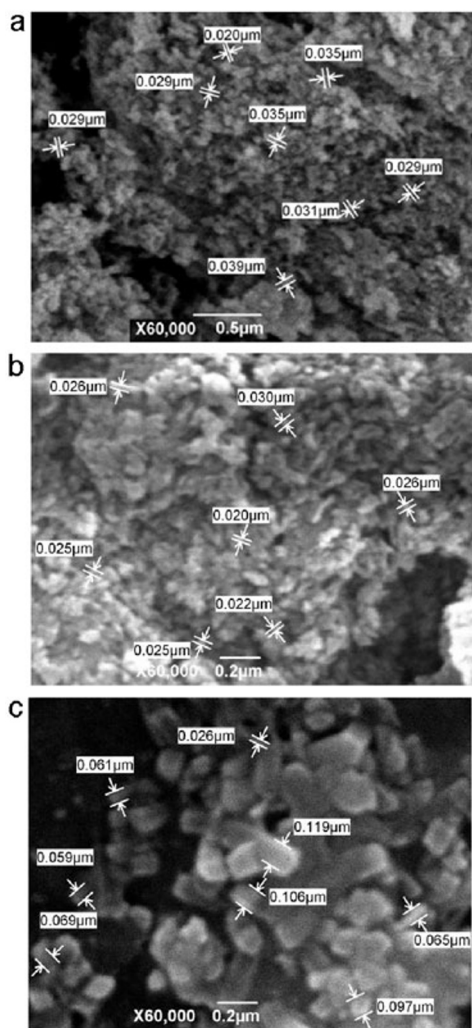


Fig. 3. SEM photographs of  $\gamma$ - $\text{Al}_2\text{O}_3$  and different  $\text{KF}/\gamma\text{-Al}_2\text{O}_3$  samples: a)  $\gamma\text{-Al}_2\text{O}_3$ ; b)  $\text{KF}/\gamma\text{-Al}_2\text{O}_3$ ; c)  $\text{KF}/\gamma\text{-Al}_2\text{O}_3\text{-OP}$ .

quantity of basic sites beneficial for the reaction is insufficient. Consistent with the earlier findings, the increasing surface area is strongly correlated with the basicity values of the synthesized catalysts and their activities, so the FAME yield increases directly with increasing basicity and the surface of  $\text{KF}/\gamma\text{-Al}_2\text{O}_3\text{-OP}$  catalyst.

### Thermogravimetry and Differential Thermal Analysis

The thermal behavior of the prepared samples was investigated using TGA and DTA from room temperature up to  $800^\circ\text{C}$  (Fig. 2b). We observed an endothermic process and an exothermic one in parallel with two weight loss steps on the curves. The endothermic peak from  $30$  to  $200^\circ\text{C}$  is caused by the loss of physically adsorbed water and the hydroxy groups on the catalyst surface. The high-temperature exothermic peak in the case of  $\text{KF}/\gamma\text{-Al}_2\text{O}_3\text{-OP}$  and  $\text{KF}/\gamma\text{-Al}_2\text{O}_3$  samples may be related to crystallization and/or weight loss due to component loss of the catalysts caused by certain reactions occurring at the high temperature [20]. It can also be seen that the weight loss in the high-temperature range is higher in the case of  $\text{KF}/\gamma\text{-Al}_2\text{O}_3\text{-OP}$ , indicating the stronger interactions of the support and KF.

## Scanning Electron Microscopy

The SEM images of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP are shown in Fig. 3. It can be seen from these images that there was a good dispersion of KF on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 3a) and KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after calcination at high temperature, as shown in Fig. 3b. However, the surface morphology of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP, as well as the degree of crystallinity, changed, since the large particles could be found on the SEM image, and the presence of such particles was further confirmed by XRD; there were sharp diffraction peaks on the XRD pattern of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP. The role of ethanol and OP-10 in the crystallization of the particles in the preparation of KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP was further confirmed [21].

## X-ray Diffraction

The XRD patterns of the two KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples, as well as the support, are shown in Fig. 2c. There are the characteristic peaks of Al<sub>2</sub>O<sub>3</sub> at  $2\theta$  of 37.0°, 46.0° and 67.0° in the plots of all samples shown. An additional K<sub>2</sub>O phase with strong basic properties is observed in both KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with characteristic diffraction peaks at 30.0°, 42.7°, and 53.0°, suggesting the clear relationship between the catalytic activity and catalyst basicity. The diffraction intensities increased greatly moving from KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-OP; this finding gives grounds to conclude that OP-10 plays an important role in improving the crystallization of Al<sub>2</sub>O<sub>3</sub> during the catalyst preparation. This conclusion agrees with the explanation suggested above. In the earlier studies the high catalytic activity of KF-impregnated alumina catalysts was associated with the basicity of the surface, and such basicity was related to the formation of K<sub>2</sub>O and Al-O-K groups from the thermal decomposition of the K-containing compounds, as well as from salt-support interactions [22].

In this work, KF- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have been successfully prepared. Such systems exhibited high catalytic activity in the reaction of rapeseed oil and methanol transesterification in the production of biodiesel. The preparation parameters for the KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> have been optimized, and it was found that the highest yield of FAME was achieved when 5% KF/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, prepared by the sol-gel method with a calcination temperature of 573 K, was used. From the results of our study it can be concluded that the high FAME yield reflects the benefits of relatively high basicity and large pore volume in the use of the catalyst.

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## REFERENCES

1. K. A. Avinash, *Prog. Energy Combust. Sci.*, **33**, No. 3, 233-271 (2007), doi: <http://dx.doi.org/10.1016/j.peecs.2006.08.003>.
2. S. Majhi and S. Ray, *Environ. Sci. Pollut. Res.*, **2016**, No. 23, 9251-9259, doi:10.1007/s11356-015-4824-9.
3. M. Thawatchai, K. Sibudjing, and W. Chi-Hwa, *Energy Convers. Manag.*, **92**, 234-243 (2015), doi:<http://dx.doi.org/10.1016/j.enconman.2014.12.057>.
4. A. J. Dassey, S. G. Hall, and C. S. Theegala, *Algal Res.*, **4**, 89-95 (2014), doi: <http://dx.doi.org/10.1016/j.algal.2013.12.006>.
5. B. Xu, G. Xiao, L. Cui, et al., *Energy Fuel*, **21**, No. 63, 109-3112 (2007), doi: 10.1021/ef7005035.
6. D. Wei and R. D. R Pfeffer, *J. Nanopart. Res.*, **4**, 21-41 (2002), doi: 10.1023/A:1020184524538.
7. S. Yimer and O. Sahu, *Sust. Energy*, **3**, 81-84 (2014), doi: <http://dx.doi.org/10.1080/15567036.2015.1040899>.
8. L. Wen, T. Wang, and D. Lu, *Fuel*, **89**, 2267-2271 (2010), doi: <http://dx.doi.org/10.1016/j.fuel.2010.01.028>.



9. M. Agarwal, Garima Chauhan, S. P. Chaurasia, and K. Singh, *J. Taiwan Inst. Chem. Eng.*, **43**, 89-94 (2012), doi: <http://dx.doi.org/10.1016/j.jtice.2011.06.003>.
10. I. A. Musa, *Egypt. J. Pet.* **25**, 21-31 (2016), doi: <http://dx.doi.org/10.1016/j.ejpe.2015.06.007>.
11. P. L. Boey, G. P. Maniam, and S. A. Hamid, *Chem. Eng. J.*, **168**, 15-22 (2011), doi: <http://dx.doi.org/10.1016/j.cej.2011.01.009>.
12. Y. Zhang, S. Niu, K. Han, and C. Li, *Renew. Energy*, **168**, 981-990 (2020), doi: <https://doi.org/10.1016/j.renene.2020.12.132>.
13. M. Tuan, S. Chandrakantha, and Y. Manawadevi, *React. Kinet. Mech. Catal.*, 1-32 (2021), doi: [10.1007/S11144-021-01958-1](https://doi.org/10.1007/S11144-021-01958-1).
14. P. Singh, A. Sharma, N. Kumar, and Y. Singh, *Fuel*, **291** 120218 (2021), doi: <https://doi.org/10.1016/j.fuel.2021.120218>.
15. S. Sunita, M. Deboshree, D. Srikanta, et al., *Renew. Energy*, **158**, 656-667 (2020), doi: <https://doi.org/10.1016/j.renene.2020.05.146>.
16. R. Foroutan, R. Mohammadi, J. Razeghi, and B. Ramavandi, *Renew. Energy*, **168**, 1207-1216 (2021), doi: <https://doi.org/10.1016/j.renene.2020.12.094>.
17. M. Kuniyil, K. Shanmukha, A. Farooq, et al., *Arab. J. Chem.*, **14**, 102982 (2021), doi: <https://doi.org/10.1016/j.arabjc.2020.102982>.
18. H. Fukuda, A. Kondo, and H. Noda, *J. Biosci. Bioeng.*, **92**, 405-416 (2001), doi: [10.1016/S1389-1723\(01\)80288-7](https://doi.org/10.1016/S1389-1723(01)80288-7).
19. R. Santorio, O. Veloso Claudia, and C. A. Henriques, *J. Mol. Catal. A*, **422**, 234-247 (2016), doi: <http://dx.doi.org/10.1016/j.molcata.2015.12.006>.
20. L. Gao, S. Wang, W. Xu, and G. Xiao, *Appl. Energy*, **146**, 196-201 (2015), doi: <http://dx.doi.org/10.1016/j.apenergy.2015.02.068>.
21. X. Zheng, W. Fan, W. Kong, et al., *Kinet. Catal.*, **55**, 592-598 (2014), doi: [10.1134/S002315841405005X](https://doi.org/10.1134/S002315841405005X).
22. P. Qiu, B. Yang, C. Yi, and S. Qi, *Catal. Lett.*, **137**, 232-238 (2010), doi: [10.1007/s10562-010-0354-8](https://doi.org/10.1007/s10562-010-0354-8).