

Application of KF/MgO as a heterogeneous catalyst in the production of biodiesel from rapeseed oil

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Abstract-Biodiesel was synthesized from rapeseed oil by transesterification over Magnesium oxide loaded with KF. The catalytic activity strongly depends on the loading amount of KF and calcined temperature. We found that the reaction reached a 79.37% yield when the loading amount was at 35 wt% and calcined at 500 °C. The simply dried 30% KF/MgO at 80 °C was found to give equally good results from the catalyst calcined at 500 °C, avoiding the usual activation at high temperature. The catalysts were characterized by the Hammett indicator method, BET, TG/DTG, XRD, NMR, EDS, and FT-IR. According to the instrumental analysis, the activity in the transesterification probably belonged to coordinately unsaturated F⁻ and liberation of hydroxide during preparation. The effects of methanol/oil ratio and catalyst amounts on the conversion were also studied in this paper.

Key words: Transesterification, Heterogeneous Catalyst, Loading of KF on MgO, Rapeseed Oil, Biodiesel

INTRODUCTION

Biodiesel is gaining more and more attention due to its environmental merits and the earth's diminishing fossil fuel resources. Having almost the same characteristics as diesel fuel, biodiesel can be used directly in diesel engines. Fuels from renewable biomass can lower the combustion emission of carbon monoxide, particulate matter, and sulfur compounds and limit greenhouse emissions because of the closed carbon dioxide cycle [1,2].

Transesterification is used to make biodiesel fuel as defined in Europe and in the USA [3]. Biodiesel is usually synthesized in the presence of homogeneous catalysts such as sodium methoxide, sodium or potassium hydroxide [4]. However, the formation of soap lowers the biodiesel yield and renders the separation of ester and glycerol, making the washing process difficult. To solve this problem, at present, more and more research works have focused on the use of heterogeneous catalysts. Heterogeneous catalysts have several advantages including easier operational procedures, catalyst separation, and reduction of environment pollutants, among others. Many heterogeneous catalysts have been used in the alcoholysis of vegetable oil. Acid-catalyzed process is often used for High FFA (Free Fatty Acid) oil [5]. As the catalytic activity of a base is higher than that of an acid, the base catalysis is preferred to acid catalyzed routes. Gryglewicz [6] reported that the transesterification of rapeseed oil by methyl alcohol could be catalyzed effectively by basic alkaline-earth metal compounds such as calcium oxide, calcium methoxide, and barium hydroxide. Watkins et al. [7] developed Li/CaO for transesterification of vegetable oils with methanol. Other catalysts such as the NaX zeolite, ETS-10 [8], SrO [9], Na/NaOH/ γ -Al₂O₃ [10], MgAl hydrotalcite [11], vanadyl phosphate [12], K₂CO₃/Al₂O₃ [13] and Eu₂O₃/Al₂O₃ [14], have also shown good catalytic activity. It has been proven that Magnesium oxide is a good catalyst

for the preparation of fatty methyl esters [15]. A kinetic model was developed by Dossin et al. [16]. However, the activity of MgO in transesterification of vegetable oils to biodiesel is low, so the reaction needs to be taken at high temperature.

To the best of our knowledge, there is no open literature giving details of Magnesium oxide loaded with KF as a catalyst for the transesterification of rapeseed oil, an important raw renewable material for biodiesel production. In this study, KF was loaded onto Magnesium oxide and adopted for the production of biodiesel from rapeseed oil. The aim was to investigate the catalyst performance on different prepared conditions and various reaction variables, as well as to have a better understanding of its catalytic activity through various characterizations. In addition, we found KF/MgO was also active after a simple drying at 80 °C. The activation procedure can be reduced to a drying at oven temperature, which could be meaningful for industrial application.

EXPERIMENT

1. Catalyst Preparation

MgO was obtained from the Beijing chemical factory. The catalyst was prepared by using the impregnation method. MgO was doped in the aqueous solution containing the desired amount of KF, air dried for six hours at 80 °C, and calcined at different temperatures (typically at 500 °C) in air for three hours.

2. Catalyst Characterization

The catalysts were characterized by using several techniques of the Hammett indicator, BET, XRD, NMR, FT-IR, TG, and EDS.

The Hammett indicator is used to determine the basic strength of the solid bases (H₋) [17]. About 200 mg of sample was shaken with 10 ml methanol solution of the Hammett indicator and left for one hour to achieve equilibration. The samples were titrated with benzoic acid dissolved in ethanol. The concentrations of 0.02 mol/L Bromthymol Blue (H₋=7.2), phenolphthalein (H₋=9.8), 2,4-dinitroaniline (H₋=15.0) and 4-nitroaniline (H₋=18.4) were used

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Table 1. Basic properties and rapeseed oil conversion with different loading amounts of KF/MgO after being calcined at 500 °C

Sample	Basic strength	H ₊ =7.2-9.8	H ₊ >9.8	Total basicity (mmol/g)	Conversion
5%KF/MgO	9.8<H ₊ <15.0	0.33	0.37	0.70	20.85%
10%KF/MgO	9.8<H ₊ <15.0	0.25	0.45	0.70	31.28%
15%KF/MgO	15.0<H ₊ <18.4	0.52	0.72	1.24	67.48%
20%KF/MgO	15.0<H ₊ <18.4	1.18	0.88	2.06	68.57%
25%KF/MgO	15.0<H ₊ <18.4	1.24	0.77	2.01	71.24%
30%KF/MgO	15.0<H ₊ <18.4	0.99	1.17	2.16	71.32%
35%KF/MgO	15.0<H ₊ <18.4	0.86	1.22	2.08	79.37%
40%KF/MgO	15.0<H ₊ <18.4	0.75	1.23	1.98	78.71%
45%KF/MgO	15.0<H ₊ <18.4	0.45	0.77	1.22	50.72%

for Hammett indicators. Methanol was used as a solvent [18].

The BET surface area and pore volume of the prepared catalysts were measured by using ASAP 2020 (Micromeritics Corporation).

The XRD measurements were performed on an XRD-6000 powder diffraction using Cu-K α radiation over a 2 θ range of 10-80° with a step size of 0.02° at a scanning speed of 4°/min. The data were analyzed with the DiffracPlus software, and phases were identified according to the Powder Diffraction (PDF) database (JCPDS, International Centre for Diffraction Date).

¹⁹F MAS NMR spectra were recorded at 21 kHz on a Varian InfinityPlus-400 spectrometer with a 2.5-mm NMR probe.

The Avatar 360 FT-IR was used for infrared analysis of the solids with the KBr pellet technique. The range of scanning was from 400 cm⁻¹ to 4,000 cm⁻¹.

Thermal analysis of the KF/MgO was carried out on an AET-ARAM SETSYS 16TG/DTA/DSC apparatus operating under a flow of air at a 10 K/min heating rate up to 1,073 K.

The content of Mg and K atoms on the surface was recorded on a Hitachi EDS X-650 instrument.

3. Reaction Procedures

The rapeseed oil was bought from a local store. The acid value was 2.1914 mg/g and the average molecular weight of 942.5 was calculated from the saponification value.

The reaction was conducted in a 250 ml one-neck flask equipped with a water-cooled condenser and a magnetic stirrer charged with 30 ml (27.66 g) of rapeseed oil, different volumes of methanol, and varied amounts of catalysts freshly prepared in different conditions. Each reaction was performed at a methanol reflux temperature with vigorous stirring for the required time.

4. Methods of Analysis

The samples were analyzed with a Varian-3900 gas chromatography with an automatic injection system. Data collection and analysis were performed with a Varian-3900 workstation. A capillary column (HP5, 30 m×0.32 mm×0.25 μ m) was used for separation. Nitrogen was used for the carrier gas and the split ratio was 20 : 1. Samples were prepared by dissolving about 0.3 g of biodiesel sample into a 10 ml *n*-Hexane. About 0.05 g methyl salicylate was added as a reference of crude biodiesel. Samples were placed in GC auto sampler vials and 1.0 μ l was injected for GC analysis. The oven temperature program consisted of the following: start at 120 °C (3 min), ramp at 30 °C/min to 170 °C (2 min), ramp at 30 °C/min to 265 °C (20 min). The purity of crude biodiesel was calculated based on the area of FAME over the reference by the following equation:

$$\text{purity (\%)} = \frac{\frac{\text{area of FAME}}{\text{area of reference}} \bullet \text{weight of reference}}{\text{weight of crude biodiesel}} \times 100$$

RESULTS AND DISCUSSION

1. Basicity and Conversion Using Different Loading Amounts

The base strengths of the catalysts were determined by using the Hammett titration method. When the 2,4-dinitroaniline indicator was added into the methanol solution of samples, the color just very slightly changed. In our opinion, the samples contained very few basic sites of H₊>15.0 on the surface. Because it is difficult to detect the accurate basic amounts, we limited our discussion in this work to the amounts of two different surface basic sites, 9.8>H₊>7.2 and H₊>9.8.

Table 1 provides a summary of the base strengths of the catalysts with various loading amounts calcined at 500 °C. The support MgO, with a low base strength, was regarded as a base strength of 9.8<H₊<15.0. Loading amounts of the samples below 15% have the same base strength. The results suggest that strong base sites are harder to create with low loading amounts. The color of the 2,4-dinitroaniline (H₊=15.0) could turn from yellow to mauve when the loading amounts were more than 15 wt% (contained 15 wt%), but it failed to change the color of the 4-dinitroaniline (H₊=18.4). These samples (H₊>15.0) could be regarded as strong bases according to the definition of acids and bases by Tanabe [19]. The basicity increased with increasing KF content, a maximum basicity of 2.16 mmol/g was observed at 30% loading KF/MgO, further increase of the loading amount of KF beyond 30%, led to the decrease of the basicity. The basicity of 30% KF/MgO is much less than the original KF, suggesting that basic sites have a very specific environment. At a low loading of KF, the active sites are more dispersed on the magnesia surface. However, if magnesia is loaded with too much KF, the KF cannot disperse properly and the excess KF could cover the active sites on the composite surface. The catalyst of 35% KF/MgO achieved the highest conversion rate of 79.37%. From the table, we can see the yield was consistent with the change of the basicity.

2. Basicity and Conversion with Different Calcined Temperatures

Calcined temperature is an important parameter in catalyst preparation. It is very interesting to find that a sample after simply drying at 80 °C almost has the same activation as the 500 °C calcined

Table 2. Basic properties and rapeseed oil conversion of 30%KF/MgO with different calcined temperatures

Sample (CP)	Basic strength	H ₋ =7.2-9.8	H ₋ >9.8	Total basicity (mmol/g)	Conversion
80 °C	15.0<H ₋ <18.4	0.29	1.11	1.40	70.87%
300 °C	15.0<H ₋ <18.4	0.24	1.02	1.36	66.17%
400 °C	15.0<H ₋ <18.4	0.15	0.99	1.14	46.35%
500 °C	15.0<H ₋ <18.4	0.99	1.17	2.16	71.32%
600 °C	15.0<H ₋ <18.4	0.98	0.61	1.59	50.89%
700 °C	15.0<H ₋ <18.4	0.13	0.52	0.65	37.61%

one as shown in Table 2. This result indicated the catalyst was not sensitive to the atmosphere. It is a known fact that oven temperature alone is not enough to induce a decarbonation of the catalyst; thus, its activity must be assigned to fluoride anions. As the calcined temperature increased from 80 to 400 °C, the basicity decreased. And then the basicity increased to its maximum at the calcination temperature of 500 °C. After being calcined above 500 °C, a lower level of basicity was observed.

From the result, we can see that the catalyst activity was correlated closely with the thermal treatment. The reason may be because fluoride anions transform among different states when the thermal treatment temperature is changed. A similar dependence of the basicity on the conversion to that with the relationship of the loading and basicity was observed.

3. Surface Area and Porous Structure Investigation

The measured BET surface area, pore volume, and pore diameter are shown in Table 3. The BET surface area and the pore volume decrease to about half of the MgO when it is loaded with 30 wt% KF. The KF should be well dispersed, allowing the fluorides to in-

teract strongly with the support. The sample calcined at 500 °C after simple drying at 80 °C induces a slight increase of the area from 13.31 to 13.70 m²/g. It must be due to a dehydration in the Mg(OH)₂ lattice with an increase of pore volume from 0.0726 to 0.0784 cm³/g.

4. Thermal Analysis

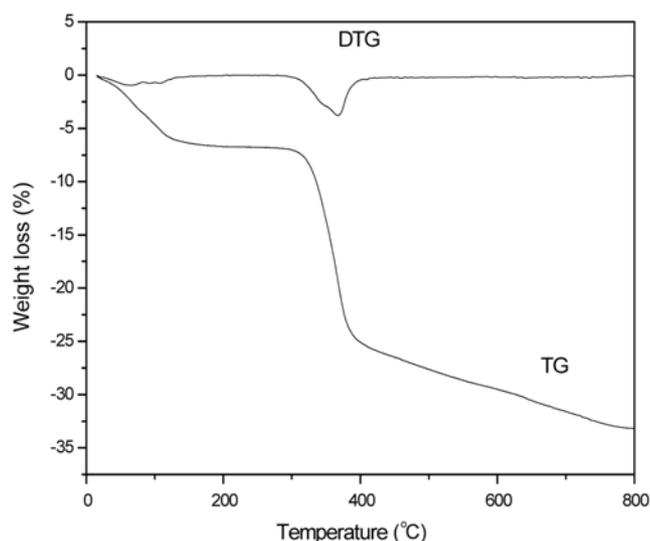
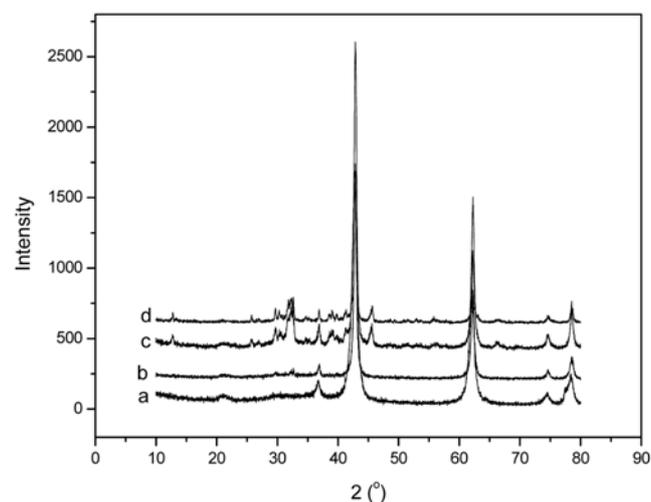
The TG-DTG trace of KF/MgO is reported in Fig. 1. Three main peaks are observed. One is at 80-120 °C, accompanied by a mass loss of about 7.5% and corresponding to the elimination of a surface that loosely held water without a collapse of the MgO structure. Another is at around 370 °C, with a weight loss above 17.5%, composed of water between the Mg(OH)₂ lattice. The third broad peak is from 400 to 800 °C, attributed to a solid-state reaction of the fluorides with the support.

5. XRD Analysis

The XRD patterns of KF/MgO with different loading amounts are shown in Fig. 2. All the samples were calcined at 500 °C first, in order to avoid the influence of carbonation and hydration. In the sample with a very low loading of 5 wt%, only the characteristic peaks of MgO appeared on the XRD patterns. New phases of K₂MgF₄

Table 3. BET surface area, pore volume, and pore diameter

Catalysts	BET area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
MgO	25.51	0.1479	228.4
30%KF/MgO (80 °C dried)	13.31	0.0726	219.1
30%KF/MgO (500 °C calcined)	13.70	0.0784	233.2

**Fig. 1. TG-DTG trace of KF/MgO.****Fig. 2. XRD patterns of KF/MgO with different loading amount: (a) 5%, (b) 15%, (c) 30%, (d) 45%.**

(PDF 76-38) ($2\theta=13.4, 30.3, 31.8, 34.6, 41.1, 42.2, 45.6$) were formed when the loading climbed to 15 wt%. There should also be a small fragment of KMgF_3 (PDF 86-2480) ($2\theta=31.8, 39.2, 45.6, 66.4$) in high loading samples. Their intensities grew to their highest with a 30 wt% loading. When the loading amount achieved 45 wt%, the intensities lowered a little. It was thought that the surface of the catalyst was covered with excess KF. There was no KF (33.6°) peak detected in all these samples. The lack of a KF diffraction pattern would seem to suggest that KF is well dispersed. The high activity of KF/ α -alumina was thought to be fluoride anions in the Michael addition of cyclohexene-2-one with nitroalkanes [20]. Thus, it is likely that in the reaction of transesterification from rapeseed oil, the active sites of the catalysts could partly belong to the coordinately unsaturated F^- ions on the reagent surface. The basicity and conversion have a good correlation with the peak change of X-ray patterns as shown in Fig. 2.

The influence of calcination temperature and dried temperature is illustrated in Fig. 3. The phases of K_2MgF_4 and KMgF_3 appeared after the sample was dried at 80°C , and then became very weak after being dried at 120°C . At a low calcination temperature of 300°C , the lines were similar to the sample dried at 80°C . It showed strongly after the 500°C thermal treatment, which was thought to be the best temperature to form a crystalline structure. When the temperature was higher than 500°C , the lines turned weak again. Because the phase of K_2MgF_4 (13.4, 30.3, 41.1, 42.2) is detected even at the 900°C calcination temperature, with the sample having almost no activity for reaction, the result confirms unsaturated F^- ions as active sites. The active sites would be lost with over drying higher than 700°C .

6. ^{19}F NMR Investigation

The spectra of the F species were recorded by using a MAS NMR. The sample was at 30 wt% loading, dried at 353 K, and calcined at 773 K. The spectra, reported in Fig. 4, show three different relaxation times (T_1) and intensities: a line at -161.3 ppm, attributed to surface F^- ; a line at -169.5 ppm, attributed to KMgF_3 ; and a line at

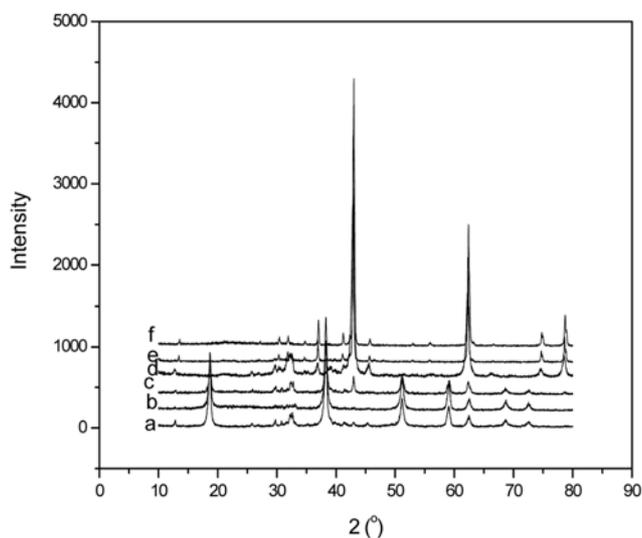


Fig. 3. XRD patterns for samples: (a) died at 80°C (b) died at 120°C (c) calcined at 300°C (d) calcined at 500°C (e) calcined at 700°C (f) calcined at 900°C .

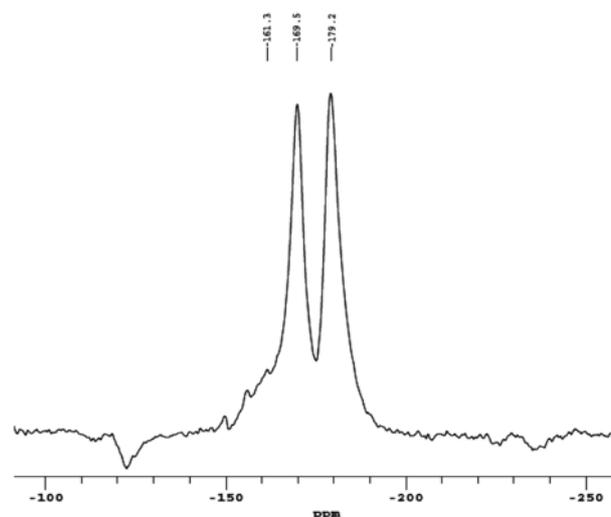


Fig. 4. ^{19}F NMR spectra of KF/MgO with 30 wt% loading and calcined at 500°C .

-179.2 attributed to K_3MgF_5 . As seen from the XRD analysis, different fluorinated phases of KMgF_3 and K_2MgF_4 are found but no KF phase is observed in the catalysts. The differences in chemical shifts of -161.3 ppm F^- on the surface of magnesia from -123 ppm pure KF indicate that the F^- is in close proximity to both the surface hydroxyl group and cations, and the fluoride ion may be coordinately unsaturated [21].

Therefore, it is suggested that the species giving a peak at about -161.3 ppm are relevant to the catalytic activities.

7. Infrared Analysis of the Solid

Two obvious band absorptions of the FT-IR spectra are found at $1,500\text{ cm}^{-1}$ and $3,500\text{ cm}^{-1}$, which are similar to the absorptions of KF/ZnO in earlier research [22]. Some basic sites may be attributed to the O-H band on the surface, such as KF/ZnO, because catalysts contain different types of basic sites as mentioned above. However, it is more probable that most of the active sites can be ascribed to surface hydroxyl groups, as the absorption is at $3,500\text{ cm}^{-1}$, which

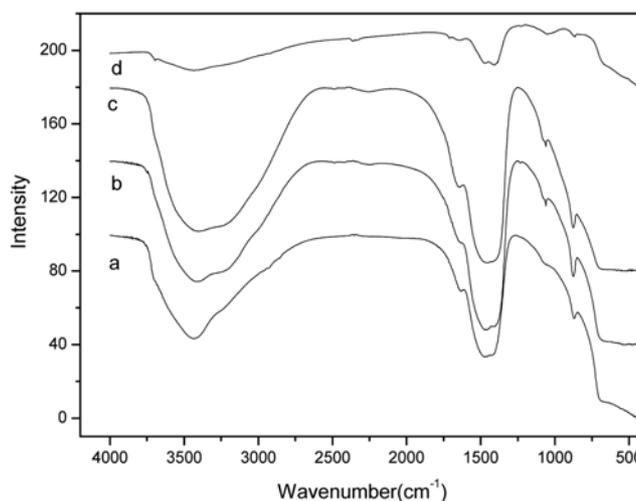


Fig. 5. FT-IR spectra of samples: (a) 5% loading (b) 15% loading (c) 30% loading (d) calcined at 500°C .

turned out to be weak after being calcined at 500 °C as shown in Fig. 5. On the pretreatment at 400 °C, the surface of MgO is considered to be covered mostly with OH groups [23]. Drawing on the results, the absorption could be assigned to the O-H stretching vibration on the surface of the MgO. We did not believe that there were K₂O species as decomposition products of KF at oven temperature. We can conclude that KF would interact with magnesia, and produce large amounts of hydroxide like KF on alumina [24]. The results indicate that OH⁻ on support's surface plays an important role in determining the activity of the reagents. The F⁻ ion may be strongly H-bonded to the hydroxylated surface of magnesia (Mg-[OHF]) which is similar with F⁻ on alumina [25].

8. Surface Investigation by EDS

The surface compositional investigation by EDS with different loadings and thermal treatments is reported in Table 4. The potassium content on the surface is parallel to the increasing loading amount but it deviates from the prepared ratio of origin materials. No potassium is lost during calcination at 500 °C, because the sample contained almost the same potassium content when dried at 80 °C and calcined at 500 °C; the catalysts are shown in Table 4. However, at higher temperatures of 900 °C, potassium loss is significant. The results suggest that most of the KF cover on the surface of the catalysts and potassium leaches from the surface at very high temperatures.

Table 4. Weight percent and atomic percent of Mg and K

Sample	Mg (wt%)	K (wt%)	Mg (at%)	K (at%)
5%KF/MgO (Calcined 500 °C)	94.48	5.52	96.49	3.51
15%KF/MgO (Calcined 500 °C)	79.20	20.80	85.96	14.04
30%KF/MgO (Calcined 500 °C)	73.10	26.90	81.38	18.62
45%KF/MgO (Calcined 500 °C)	64.81	35.19	74.76	25.24
Dried 80 °C (30% loading)	73.78	26.22	81.91	18.09
Calcined 500 °C (30% loading)	73.10	26.90	81.38	18.62
Calcined 900 °C (30% loading)	92.96	7.04	95.50	4.50

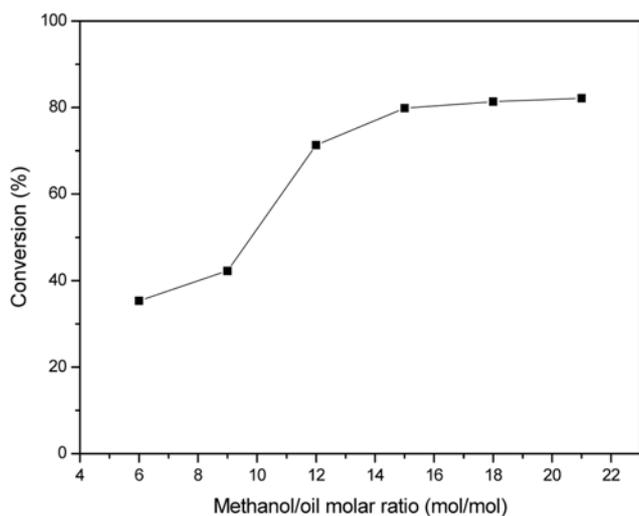


Fig. 6. Effect of methanol/oil molar ratio on the conversion. Reaction conditions: catalyst amount 3%, reaction time 5 h, methanol reflux temperature.

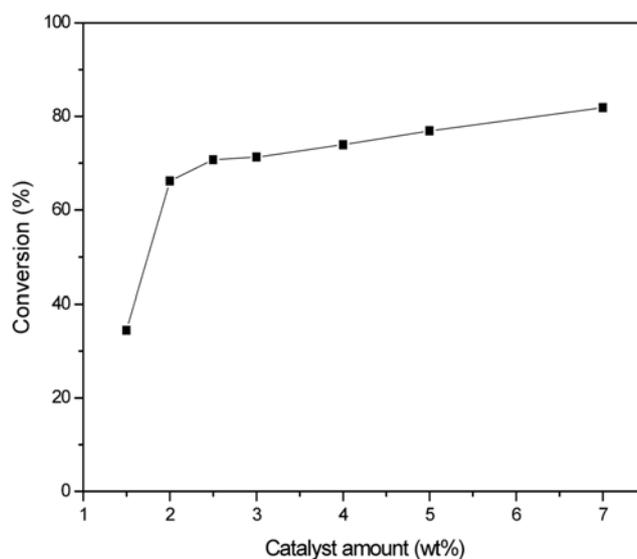


Fig. 7. Effect of catalyst amount on the conversion. Reaction conditions: methanol/oil molar ratio 12 : 1, reaction time 5 h, methanol reflux temperature.

Thus, the decrease in catalytic activity at very high temperatures probably resulted from the leaching of the potassium content.

9. Catalytic Properties

The effects of methanol/oil ratio and catalyst amount were studied. The 30%wt KF/MgO catalysts calcined at 500 °C were used for the investigation of catalytic properties. The influence of the methanol/oil ratio is shown in Fig. 6. In heterogeneous catalysis, mass transfer and reactant adsorption on catalyst are very important; thus an amount bigger than the stoichiometric molar ratio of methanol is needed for the reaction. When the methanol/oil molar ratio reached 15 : 1, the maximum conversion was obtained. The excessive use of methanol had no significant effect on the production yield.

The influence of catalyst amount on the conversion is illustrated in Fig. 7. The conversion was greatly dependent on the catalyst applied. When the catalyst amounts are as low as 1.5%, a high conversion could not be reached. On the other hand, the catalyst would have less efficiency with an increased amount of loading catalyst that is more than 2.5%. The production yield increased quickly along with the addition of amounts from 1.5% to 2.5%, and it reached the highest yield of 81.87% at 7%.

CONCLUSION

KF loaded on MgO prepared by the impregnation method showed high catalytic activities for the transesterification reaction. The 35% KF/MgO sample calcined at 500 °C reached 79.37% yield. On the other hand, after thermal treatment at 500 °C, the conversion of 30% KF/MgO reached 79.82% with a 3% catalyst and 15 : 1 methanol/oil ratio. A very interesting point is the high activity KF/MgO just dried at 80 °C, avoiding the usual activation at high temperature. At least two mechanisms apparently give rise to the high basicity based on the instrumental analysis: coordinately unsaturated F⁻ and liberation of hydroxide during preparation.

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