Catalysis Letters Vol. 107, Nos. 1–2, February 2006 (© 2006)
DOI: 10.1007/s10562-005-9731-0

Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst

Wenlei Xie* and Xiaoming Huang

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, 450052, P.R. China

Received 1 October 2005; accepted 24 November 2005

Biodiesel was produced by transesterification of soybean oil with methanol using ZnO loaded with KF as a solid base catalyst. It was found that the catalyst with 15 wt.% KF loading and calcined at 873 K showed the optimum activity. XRD, IR and Hammett indicator method were employed for the catalyst characterization. The results showed the activity of the catalysts was correlated with their basicity. The influence of various reaction variables on the conversion was also discussed.

KEY WORDS: methyl esters of fatty acids; heterogeneous catalyst; transesterification; biodiesel.

1. Introduction

Over the past couple of decades alternative fuels for diesel engines are becoming increasingly important due to the limited resources of fossil fuel, increasing prices of crude oil and environmental concerns [1]. Methyl esters of fatty acids, better known as biodiesel, are nontoxic, biodegradable and an excellent substitute for conventional diesel fuels. The energy content, cetane number and viscosity of biodiesel are similar to those of petroleum-based diesel fuel. Moreover, biodiesel is essentially sulfur-free and the engines fueled by biodiesel emit significantly fewer particulates, unburnt hydrocarbons and less carbon monoxide than operating on conventional diesel fuels [1–3].

Methyl esters of fatty acids are usually produced by transesterification of triglyceride to methyl esters using sodium or potassium hydroxide dissolved in methanol as homogeneous catalysts; however, in this conventional method removal of these catalysts is technically difficult and a large amount of waste water was produced to separate and clean the catalyst and the products [4–6]. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst should be introduced. Heterogeneous catalysts could improve the synthesis methods by eliminating the additional processing costs associated with homogeneous catalysts and minimizing the production of pollutants. Many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils to prepare fatty acid methyl esters. For example, modified zeolites, anionic clays (hydrotalcites-like), calcium carbonate rock, EST-4, Li/CaO andNa/NaOH/γ-Al_2O_3 have been found to be efficient heterogeneous catalyst for transesterification of vegetable oils with methanol [7–12]. However, they are quite expensive or complicated to prepare or sensitive to water and acid, which limited their industrial application. Thus, it is desirable to find more efficient and cheap catalysts for transesterification of triglyceride with methanol in the application of commercial production.

It has been reported that KF-loaded alumina (KF/Al_2O_3) shows an efficient solid base catalyst for promoting versatile chemical transformations, such as the Micheal addition, N-, O- and S-alkylation reactions, the Knoevenagel condensation, aldol condensation, Witting–Horner reactions and alkene isomerization [13–19]. To the best of our knowledge, there is no open literature concerning the solid base of ZnO loaded with KF (KF/ZnO). In this work, KF/ZnO heterogeneous base catalyst was firstly adopted for the production of biodiesel. The catalytic efficiency in this reaction was studied regarding the conversion of soybean oil to methyl esters. XRD, IR, DTA-TG and Hammett indicator method were employed for the catalyst characterization. Besides, the effect of reaction variables such as the ratio of methanol to oil, the reaction time and the catalyst amount on the conversion to methyl esters was investigated. Furthermore, a correlation between the basicity of the catalysts and their catalytic activity towards the transesterification of soybean oil was also proposed.

2. Experimental

2.1. Catalyst preparation

Zinc oxide used as a support was obtained from Luoyang Chemical Regent Factory (Luoyang, China). The supported catalyst was prepared by an impregna-

---

* To whom correspondence should be addressed.
E-mail: xwenlei@163.com

tion method with an aqueous solution of an alkali metal compound. The resulting solid was dried under air for 24 h at 393 K. Prior to the reaction, the catalysts thus obtained were calcined at desired temperatures (typically at 873 K) in air for 5 h. Unless otherwise noted, the alkali metal salts of 15 wt.% were loaded on ZnO.

2.2. *Catalyst characterisation*

Basic strength of the solid bases (H_) was determined by using Hammett indicator. About 50 mg of sample was shaken with appropriate volume of a methanol solution of Hammett indicator and left to equilibrate for 2 h after which no further color changes were observed. The base strength is quoted as being stronger than the weakest indicator which exhibits a colour change, but weaker than the strongest indicator that produces no change. In these experiments, the following Hammett indicators were used: dimethylaminoazobenzene (H_ = 3.3), phenolphth (H_ = 8.2), 2,4-dinitroaniline (H_ = 15), nitroaniline (H_ = 18.4) and 4-chloroaniline (H_ = 26.5). To measure the basicity of the catalysts, the method of Hammett indicator–benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) titration was used [20–22]. The Hammett indicator method can give qualitative information of the basic properties of the solid catalysts. Otherwise, it should always be considered that diffusion problems of the indicator molecules into the micropores might occur [23]. Nevertheless, the basicities obtained by using Hammett indicator method are in good agreement with the catalytic findings.

XRD patterns of the samples were recorded on a Rigaku D/MAX-3B powder X-ray diffractometer with the Cu Kα radiation using an acceleration voltage of 40 kV and a current of 20 mA, over a2θ range of 3–70° at a scanning speed of 5°/min. The data were processed with the DiffracPlus software. The phases were identified using the Power Diffraction File (PDF) database (JCPDS, International Centre for Diffraction Date).

Thermal decomposition of the KF/ZnO sample was evaluated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) carried out on a Shimadzu DT-40 instrument operating under a flow of air at a 10 K/min heating rate up to 1183 K.

KBr pellet technique was applied for determining IR spectra of the samples. Spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer with 4 cm^{-1} resolution. The scanning range was from 400 to 4600 cm^{-1}

2.3. *Transesterification procedure*

Commercial edible grade soybean oil was obtained from market and was refined again to reduce free fatty acid and water content any further. The fatty acid composition consisted of, palmitic acid 12.3%, stearic acid 5.8%, oleic acid 26.5%, linoleic acid 49.4% and linolenic acid 5.9%, according to GC (Shimadzu DC-9A) analysis [24].The acid value was less than 0.1 mg KOH/g, and the average molecular weight of 874 g/mol was calculated from the saponification value (S_v = 193 mg KOH/g).

A 250 mL one-necked glass flask with a water-cooled condenser was charged with 16.0 g (18.3 mmol, calculated from the average molecular weight of soybean oil) of soybean oil, 5.87 g of anhydrous methanol and an appropriate amount of catalyst. The mixture was vigorously stirred and refluxed for the required reaction time. After the transesterification reaction finished, the mixture was filtered and the residual methanol was separated from the liquid phase via rotary evaporation.

For NMR analysis, the reaction mixture, after complete separation of methanol, was washed three times with a saturated aqueous NaCl solution for removal of the formed glycerin. The separated organic phase was dried with anhydrous $MgSO_4$ and, then submitted to NMR analysis (Bruker, DPX-400) in $CDCl_3$ using TMS as internal standard. The conversion of the soybean oil to methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of the methyl esters) and 2.30 ppm (α-carbon CH_2 groups of all fatty acid derivatives) as described by Gelbard [25].

3. Results and discussion

3.1. *Catalytic activities of ZnO loaded with potassium compounds*

Table 1 summarizes the basic strength of various ZnO-supported catalysts, which were prepared by loading 15 wt.% potassium compounds on ZnO followed by calcination at 873 K. The parent ZnO was acidic and converted the color of dimethylaminoazobenzene (H_ = 3.3) from yellow to red. After the loading of KF, KOH and K_2CO_3 and their calcination at higher temperature, the modified ZnO samples exhibited a high base strength regardless of the kinds of potassium salts. They could change the color of 2,4-dinitroaniline (H_ = 15) from yellow to mauve, but failed to convert 4-nitroaniline (H_ = 18.4) to its conjugate base form, and therefore their base strength could be tentatively denoted as 15.0 < H_ < 18.4. According to the definition of Tanabe [21], these samples can be regarded as strong bases. Besides, the main basic sites with H_ in the range of 9.8–15.0 and the other basic sites with H_ in the range of 7.2–9.8 were observed (data not shown), thus suggesting that the catalysts contain different types of surface basic sites as far as the basicity is concerned.

The transesterification reaction was carried out over the solid base catalysts with a molar ratio of methanol to soybean oil of 10:1 at reflux of methanol for 9 h, and the conversions of soybean oil are listed in table 1, in which are also included the basicities of the catalysts measured by Hammett indicator method. ZnO and KF, when separately used, showed no catalytic activity, while the KF/ZnO sample exhibited a high catalytic activity for

Table 1
Catalytic activities and basic properties of various solid bases

Catalysts	Conversion of soybean oil (%)	Basic strength (H_)	Basicity (mmol/g)
KF/ZnO	87	15.0–18.4	1.62
KOH/ZnO	82	15.0–18.4	1.47
K_2CO_3/ZnO	74	15.0–18.4	0.99

the reaction. Thus it is essential to support KF on ZnO followed by calcination at high temperature to generate catalytic activity, suggesting that the active sites are possibly generated by the reaction of KF with the surface ZnO. Among the catalysts examined, KF/ZnO and KOH/ZnO exhibited high activities; the conversions exceeded 80% for these catalysts. K_2CO_3/ZnO exhibited moderate activity giving a conversion of 74%, though it is a strongly basic catalyst. In regard to basicity, when potassium salts was loaded on the surface of ZnO, the basicity of the modified ZnO increased significantly. In particular, the order of catalytic activity KF/ZnO > KOH/ZnO > K_2CO_3/ZnO for theses three catalysts corresponded to their relative basicity as shown in table 1. By drawing on the results, it seems that there is a relationship between the catalytic activity and the intrinsic basicity of the catalysts for the reaction, and due to this, the higher activity may be responsible for the higher basicity.

Ando *et al.* stressed the importance of coordinatively unsaturated F^- ions for the catalytic activity of KF/Al_2O_3 catalyst, though they did not deny the participation of the hydroxide species [26]. Our experimental results showed that the catalytic activities of KOH/ZnO and K_2CO_3/ZnO were lower than that of KF/ZnO, implying that the catalytic activity of KF/ZnO could be probably associated with F^- ions rather than O^{2-} ions, which may be catalytically active sites on KOH/ZnO and K_2CO_3/ZnO.

3.2. *Influence of the amount of KF loaded on support*

Table 2 shows the dependence of the catalytic activity of KF/ZnO on the loading amount of KF for the reaction. The transesterification reaction conditions are the same as described above. As expected, the parent ZnO has no or very weak catalytic activity with a conversion of 1.8% under the reaction conditions, most likely owing to its lack of strong basic sites on which the transesterification occurred. However, the basicity of the catalysts together with their catalytic activity was increased significantly when ZnO was loaded with KF and was activated at high temperature. Moreover, as illustrated in table 2, the conversion was increased with increasing the amount of KF loaded on ZnO, accompanied with the increase in the basicity of the catalysts. A maximum conversion of 87% and the highest basicity of 1.47 mmol/g were obtained at 15 wt.% KF loading. However, further increase of the loading amount of KF beyond 15 wt.% led to the decrease in the resulting basicity of the composite and thus caused a decrease in the oil conversion as seen in table 2. On the basis it is very likely that the higher amount of KF loading may result in agglomeration of active KF phase occurred during calcination and/or the cover of basic sites by the exceeded KF, and hence lower the surface areas of active components and lower the catalytic activity; but a further investigation is needed to explore the mechanism in detail.

Table 2
Influence of loading amount of KF on the basicity and soybean oil conversion over KF/ZnO catalysts

Entry	Amount of loaded KF (%)	Conversion of soybean oil (%)	Basicity (mmol/g)
1	5	58	0.79
2	10	76	1.02
3	15	87	1.47
4	20	83	1.40

3.3. *Influence of calcination temperature*

As described earlier, the catalytic activity of KF/Al_2O_3 catalyst depends very much on the calcination temperature [27]. Therefore, we also investigated the dependences of the catalytic activity of KF/ZnO on the calcination temperature for the transesterification reaction. The transesterification was carried out under the same conditions as mentioned above, and the results are listed in table 3. Obviously, the catalytic activity strongly depended on the calcination temperature. As shown in table 3, the conversion to methyl esters increased from 42 to 87% with increasing calcination temperature from 378 to 873 K and reached its maximum value (87%) at around a calcination temperature of 873 K. This results show that high-temperature calcination is essential for obtaining the high catalytic activity. However, the conversion gradually decreased as the calcination temperature increased beyond 873 K. A similar dependence of the catalytic activity of KF/Al_2O_3

Table 3
Influence of calcination temperature on the basicity and soybean oil conversion over KF/ZnO catalysts

Entry	calcination temperature (K)	Conversion of soybean oil (%)	Basicity (mmol/g)
1	378	42	0.81
2	673	59	0.93
3	773	68	1.08
4	873	88	1.47
5	973	66	1.06
6	1073	42	0.81

on calcination temperature was also observed in the previous literature [14].

The basicity of KF/ZnO samples calcined at different temperatures was examined and is also shown in table 3. As can be seen, the basicity change with calcination temperature parallels with the change of the catalytic activity. Furthmore, this result is agreement with the fact that the XRD line intensity of the crystals of KF increases with calcination temperature but decreases beyond the temperature of 873 K, as seen from the evolution of the XRD line of figure 2, showing that the KF species giving this XRD signal is directly related to the catalytic activity.

3.4. XRD analysis

Figure 1 displays the XRD patterns of ZnO and KF/ZnO samples with different amount of KF loaded on ZnO. With the loading amount of KF below 10 wt.%, the composite only showed XRD patterns of ZnO($2\theta = 31.8°$, 34.4°, 36.3°, 47.5°, 56.6°, 62.8°, 66.4°, 67.9° and 69.1°) with neither characteristic peaks of KF nor new species (curves b and c in figure 1), indicating the well dispersion of KF on ZnO. However, when the amount of loaded KF was raised up to 15 wt.%, the characteristic XRD peaks of KF($2\theta = 33.6°$ and 48.2°) emerged on the XRD patterns (curve d in figure 1), thus suggesting a residual phase of KF remained on the composite. As the loading amount of KF increases to 20 wt.%, the small decrease of the characteristic peak intensity was observed (curve e in figure 1), corresponding to the small decrease in the conversion and in the basicity, as demonstrated in table 2. Based on these XRD results, it is likely that the spontaneous dispersion capacity of KF on ZnO was between 10 wt.% and 15 wt.%. Indeed,the XRD-undetectable phase of KF may have well dispersed onto the surface of ZnO as a monolayer [28,29]. For those loaded with KF at more than the spontaneous dispersion capacity on ZnO, the residual bulk phase of KF remained on the composite and, the appearance and the increase of KF species were associated with the variation of catalytic activity for the reaction as observed in table 2. Therefore, KF loading higher than that required for monolayer coverage was needed for high catalytic activities and high basicities, though it was unclear if the KF dissolved and how the KF species migrated on the surface of ZnO. By drawing on the results, the beneficial effect on activity observed in the cases by the dispersion of KF on the support and calcination at high temperature, suggesting that the catalytically basic sites could be identified to the KF species, in larger number on small KF crystallites.

XRD patterns of KF/ZnO samples calcined at different temperature are shown in figure 2. On KF/ZnO stored at room temperature, XRD was unable to detect KF species whatever the loading, revealing that KF is well dispersed and no large clusters are present in the monolayer coverage. However, when the calcination temperature was increased to 673 K, KF characteristic XRD lines appeared on the patterns, showing its presence and crystallization on the sample (curve c in figure 2). On the other hand, the characteristic peaks of ZnO was almost unchanged with respect to different calcination temperatures and different loading amounts of KF as evident in figures 1 and 2, indicating that loading of KF on ZnO followed by calcination did not cause considerable distortion in the bulk structure of ZnO, even when the sample was calcined at 1073 K. Besides, the high relative intensity and symmetry of

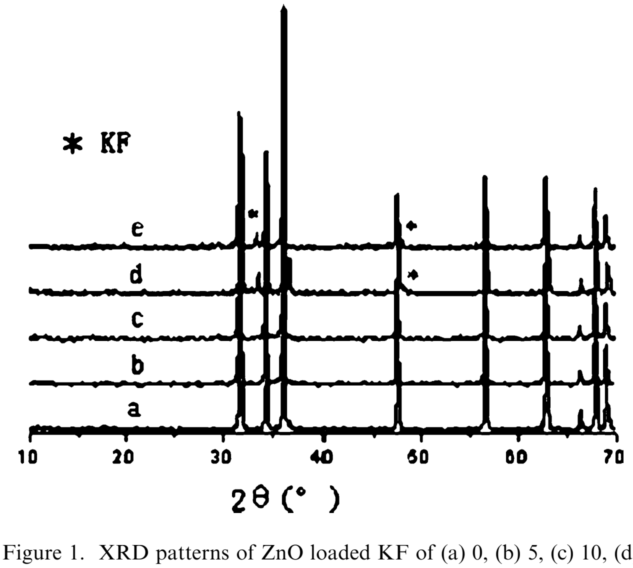

Figure 1. XRD patterns of ZnO loaded KF of (a) 0, (b) 5, (c) 10, (d) 15, (e) 20 wt.%.

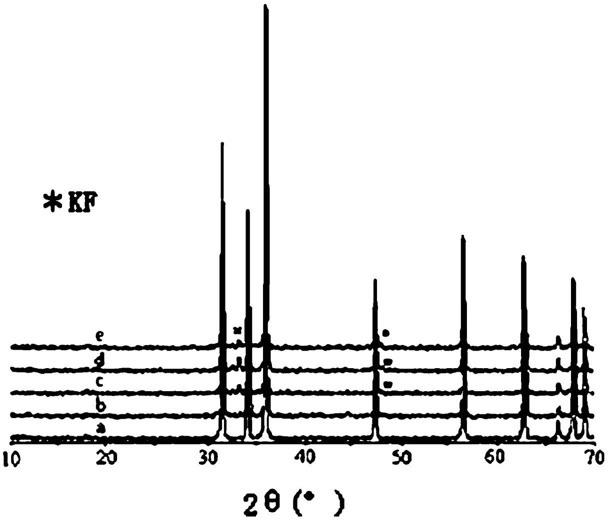

Figure 2. XRD patterns for samples: (a) ZnO; (b) KF/ZnO without calcination; (c) KF/ZnO calcined at 673 K; (d) KF/ZnO calcined at 873 K; (e) KF/ZnO calcined at 1073 K.

these peaks confirmed the good crystallinity of the composites. Moreover, the intensity of the KF diffraction line with 2θ of 33.6° reached the maximum value when the calcination temperature was 873 K (curve d in figure 2); but further increase in calcination temperature resulted in a decrease in its intensity (curve e in figure 2). Thus, it is clear that the increase in KF species could be consistent with an increase in number of basic sites present, and also in line with the Hammett basicity measurement, and due to this, resulting in the increase in the conversion, as shown in table 3. These results further confirmed that the KF species was catalytically active site and the activity of the catalysts was correlated closely with their basicity.

3.5. *FTIR analysis*

The investigation of the KF/ZnO catalysts was conducted via IR spectroscopy as shown in figure 3. For the support ZnO, there are two absorption bands at 3440 and 1640 cm^{-1} assigned to the physically absorbed water. For the KF/ZnO catalyts, the intensity of the band at 1640 cm^{-1} which is due to the bending vibration of water molecular, became weaker and finally disappeared with the increase of calcination temperature, which indicates gradual loss of physisorbed water. It has been proposed that KF could simply introduce hydroxyls at the surface of alumina, and this hypothesis was investigated by infrared spectrometry on KF/Al_2O_3 samples [30]. ZnO has practically no hydroxyls, whereas KF/ZnO has a strong OH band at 3350 cm^{-1} as illustrated in figure 3, even after calcination at 573 K. This O–H band absorption was not totally attributed to the stretching vibration of water molecular but partly assigned to the absorption of surface hydroxyl groups, because it still remained and even became stronger when the absorption peak at 1640 cm^{-1} due to water bending vibration became weaker and even disappeared. Accordingly, it seems that the surface hydroxyls may be the other active sites when KF is supported on ZnO, which conforms to the fact the catalysts contain different types of basic sites as mentioned above. In addition, for all the samples the strong adsorption peaks at 400–600 cm^{-1} could be attributed to Zn–O stretching vibration.

3.6. *Thermal analysis of KF/ZnO*

DTA-TG profiles of KF/ZnO is reported in figure 4 and show two DTA peaks in the range 303–1183 K. The first endothermic DTA peak around 362 K,which was accompanied by a mass loss of 7.8%, corresponded to the elimination of the surface loosely held water without collapse of the ZnO structures. Besides, a very broad endothermic band in the temperature of above 843 K, overlapping a small mass loss of about 1.5%, was also observed in the DTA-TG profiles. In our opinion, this DTA peak may be tentatively attributed mainly to a solid-state interaction of the fluorides with the support, and for this reason, resulting in catalytically active sites.

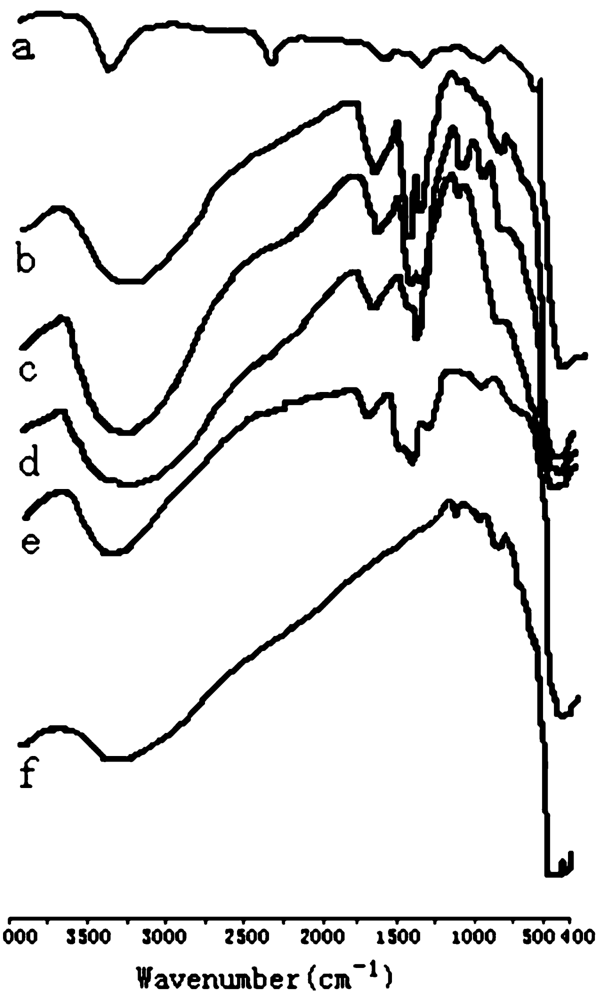

Figure 3. FTIR spectra of samples:(a) ZnO; (b) KF/ZnO without calcination; (c) KF/ZnO calcined at 673 K; (d) KF/ZnO calcined at 773 K; (e) KF/ZnO calcined at 873 K; (f) KF/ZnO calcined at 973 K.

Taking all the information mentioned above into account, we can finally conclude that KF species derived

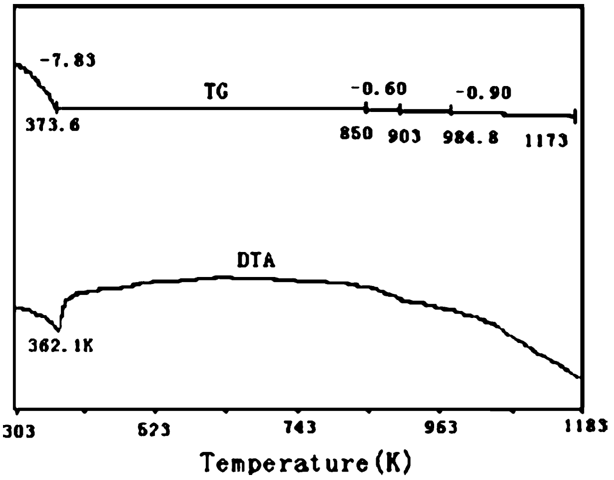

Figure 4. DTA-TG profiles of KF/ZnO sample.

at high calcination temperature and the surface hydroxyl groups were probably the main catalytically active sites.

3.7. *Influence of reaction condition on the transesterification*

The influence of various reaction variables on the conversion of soybean oil was examined. Among the variables, the most important factors are the methanol/oil molar ratio and catalyst amount. Because the reaction is reversible, an increase in the amount of one of the reactants will result in higher yields. Also, small change in the catalyst amount has great increasing effect on the conversion.

The stoichiometric molar ratio of methanol to soybean oil was 3:1. But when the mass transfer was limited due to problems of mixing, the mass transfer rate seemed to be much slower than the reaction rate, so the methanol/oil molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion and produce more methyl esters as product. Figure 5 shows the effect of methanol/oil molar ratio on the conversion. As shown in this figure, by increasing the amount of loading methanol, the conversion was increased considerably. When the methanol/oil molar ratio was very close to 10:1, the conversion reached the maximum value of 87%. However, beyond the molar ratio of 10:1, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of methanol/oil to produce methyl ester is approximately 10:1.

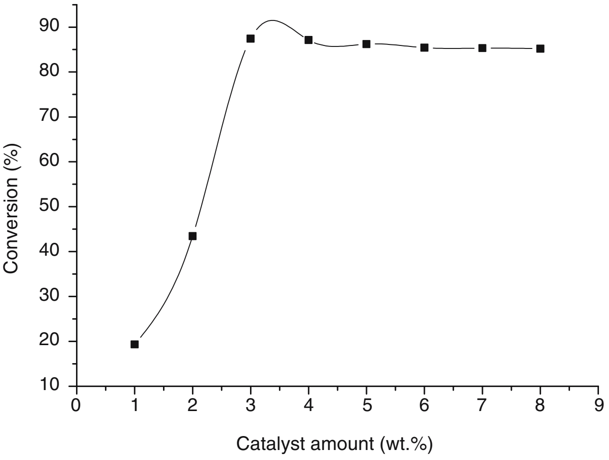

Figure 6. Influence of catalyst amount on the conversion. Reaction conditions: methanol/oil molar ratio 10:1, reaction time 9 h, methanol reflux temperature.

The effect of catalyst loading was studied at 10:1 molar ratio of methanol to soybean oil with KF/ZnO catalyst at reflux of methanol for 9 h. The reaction profile of figure 6 showed that the transesterification reaction is strongly dependent upon the catalyst applied. Without addition of a catalyst, the transesterification procedure did not occurred, and the presence of KF/ZnO really increased the reaction rate as shown in figure 6. When increasing the amount of loading catalyst from 1% to 3%, the conversion to methyl esters was increased from 18% to 87%. But, the conversion did not distinctly benefit from increasing the catalyst amount beyond 3 wt.%.

Figure 7 graphically illustrates the change of the conversion under these conditions as a function of reaction time. As can be seen from the graph, the conversion increased in the reaction time range between 1 and 9 h and thereafter kept nearly the constant indicative of a nearly equilibrium conversion. On the basis of these results, the optimum reaction time for the synthesis of biodiesel is considered to be around 9 h at reflux of methanol.

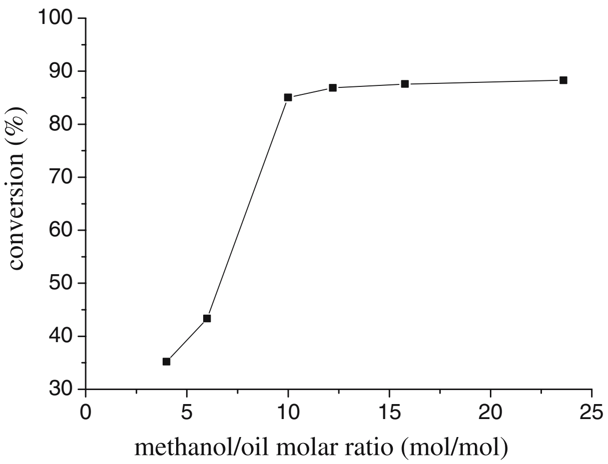

Figure 5. Influence of methanol/oil molar ratios on the conversion. Reaction conditions: catalyst amount 3%, reaction time 9 h, methanol reflux temperature.

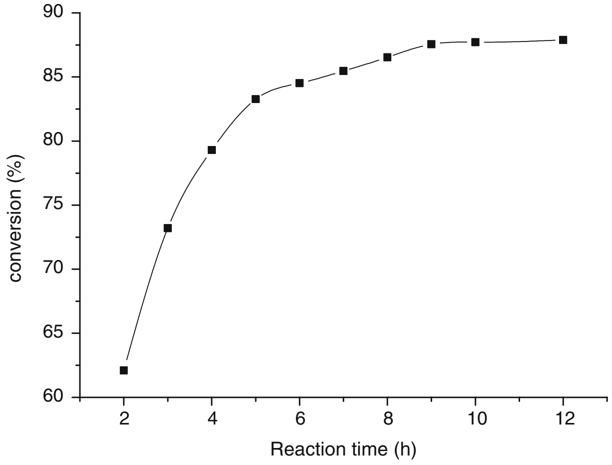

Figure 7. Influence of reaction time on the conversion. Reaction conditions: methanol/oil molar ratio 10:1, catalyst amount 3%, methanol reflux temperature.

4. Conclusions

The KF loaded on ZnO is an active and promising heterogeneous catalyst for the production of biodiesel from soybean oil. Both the active KF species formed by the reaction of KF and ZnO and surface hydroxyls, originated the strong basic sites of the catalyst. The catalyst with 15 wt.% KF loaded on ZnO and after calcined at 873 K for 5 h was found to be the optimum catalyst which can give the highest basicity and the best catalytic activity for the transesterification reaction. When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to soybean oil of 10:1, a reaction time 9 h, and a catalyst amount 3%, the conversion of soybean oil was 87% over the catalyst. The catalytic activities showed a correlation with their corresponding basic properties towards soybean oil transesterification.

The easy preparation, comparatively low cost of KF/ZnO as well as the easy removal of a heterogeneous catalyst underline the advantage of KF/ZnO as catalyst comparing to the homogeneous bases KOH, sodium methoxide and other heterogeneous catalysts.

References

[1] F. Ma and M.A. Hanna, Biores. Technol. 70 (1999) 1.
[2] A.S. Ramadhas, S. Jayaraj and C. Muraleedharan, Fuel 84 (2005) 335.
[3] S.K. Karmee and A. Chadha, Biores. Technol. 96 (2005) 1425.
[4] G. Antolín, F.V. Tinaut, Y. Briceño and V. Castanñ, Biores. Technol. 83 (2002) 111.
[5] J.M. Encinar, J.F. González and J.J. Rodríguez, Energy Fuel 16 (2002) 443.
[6] S.L. Dmytryshyn, A.K. Dalai and S.T. Chaudhari, Biores. Technol. 92 (2004) 55.
[7] G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mankidy and M.J. Goff, Appl. Catal. A: Gen. 257 (2004) 213.
[8] G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Mason and J.A. Heppert, J. Am. Oil Chem. Soc. 78 (2001) 139.
[9] E. Leclercq, A. Finiels and C. Moreau, J. Am. Oil Chem. Soc. 78 (2001) 1161.
[10] C.R. Beynese, H. Hinnekens, and J. Martens, US Patent 5,508,457(1996).
[11] H.J. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, J.S. Lee and K.Y. Lee, Catal. Today 93–95 (2004) 315.
[12] R.S. Watkins, A.F. Lee and K. Wilson, Green Chem. 6 (2004) 335.
[13] J.M. Clacens, D. Genuit, L. Delmotte, A. Gercia-ruiz, G. Bergeret, R. Montiel, J. Lopez and F. Figueres, J. Catal. 221 (2004) 483.
[14] H. Kabashima, H. Tsuji, S. Nakata, Y. Tanaka and H. Hattori, Appl. Catal. A: Gen. 194–195 (2000) 227.
[15] J. Yamawaki, T. Kawata and A.T. Hanafusa, Bull. Chem. Soc. Jpn. 56 (1983) 1885.
[16] P. Laszlo and P. Pennetreau, Tetrahedron Lett. 26 (1985) 2645.
[17] J.H. Clark, D.G. Cork and M.S. Robertson, Chem. Lett. (1983) 1145.
[18] F. Texier-Boullet, D. Villemin, M. Ricard, H. Moison and A. Foucaud, Tetrahedron 41 (1985) 1259.
[19] A.S. Radhakrishna, S.K. Suri, K.R.K. Prasad Rao, K. Sivaprakash and B.B. Singh, Synth. Commun. 20 (1990) 345.
[20] L. Forni, Catal. Rev. 8 (1974) 65.
[21] J. Zhou, Y. Chun, Y. Wang and Q. Xu, Catal. Today 51 (1999) 103.
[22] H. Gorzawski and W.F. Hoelderich, J. Mol. Catal. A: Chem. 144 (1999) 181.
[23] B.C. Gates and T.K. Cheung, Top. Catal. 6 (1998) 41.
[24] C. Paquot and A. Hautfenne, *Standard Methods for the Analysis of Oils, Fats and Derivatives, International Union of Pure and Applied Chemistry* 7 ed.(Blackwell Scientific Publications Ltd., California, 1987) p. 122.
[25] G. Gelbard, O. Brès and R.M. Vargas, J. Am. Oil Chem. Soc. 72 (1995) 1239.
[26] T. Ando, S.J. Brown, J.H. Cark, P.G. Cork, T. Hanfusa, J. Ichihara, J.M. Miller and M.S. Robertson, J. Chem. Soc. Perkin. Trans. 2 (1986) 1133.
[27] T. Ando, J.H. Clark, D.G. Cork, T. Hanafusa, J. Khihara and T. Kimura, Tetrahedron Lett. 28 (1987) 1421.
[28] Y. Wang, W.Y. Huang, Z. Wu, Y. Chun and J.H. Zhu, Meter. Lett. 46 (2000) 198.
[29] D. Jiang, B. Zhao, Y. Xie, G. Pan, G. Ran and E. Min, App. Catal. A: Gen. 219 (2001) 69.
[30] L.M. Weinstock, J.M. Stevenson, S.A. Tomellin, S.-H. Pan, T. Utne, R.B. Jobson and D.F. Reinhold, Tetrahedron Lett. 27 (1986) 3845.