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Ba–ZnO catalysts for soybean oil transesterification

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The transesterification of soybean oil to biodiesel using Ba–ZnO as a solid catalyst was investigated. The Ba–ZnO sample with loading of 2.5 mmol/g Ba on ZnO and being calcined at 873 K for 5 h, was found to be the optimum catalyst, which could exhibit the highest basicity and the best catalytic activity for the reaction. When the transesterification reaction was carried out at reflux of methanol (338 K), with a 12:1 molar ratio of methanol to oil and a catalyst amount of 6 wt.%, the conversion of soybean oil was 95.8%. Furthermore, XRD, XPS, DTA–TG and the Hammett indicator method were employed for the catalyst characterizations, and the relation between the catalytic efficiency and the basicity of the catalysts was also discussed.

KEY WORDS: biodiesel; heterogeneous catalysis; transesterification; loading of Ba on ZnO.

1. Introduction

Recent concerns about the reserves shortage of fossil fuels have excited interest in the production of renewable fuels. Fatty acid methyl esters, produced by the transesterification of vegetable oils or animal fats with methanol and known as biodiesel, have gained considerable attention for their environmental benefits and the fact that they are derived from renewable resources [1]. The advantages of biodiesel include renewability, biodegradability, non-toxicity, low emission profiles, high flashpoint and excellent lubricity. In addition to this, as an alternative fuel, biodiesel is virtually compatible with commercial diesel engines and practically no engine modifications are required [2].

Most biodiesel are currently produced by the transesterification of vegetable oils with methanol using homogeneous mineral acid or alkali catalysts [3–8]. Chemically, the transesterification process is known to be a sequence of three consecutive and reversible reactions where the triglyceride is successively transformed into a diglyceride, then into a monoglyceride and, finally into glycerol and fatty acid methyl esters. Base catalysts, such as NaOH and KOH, are preferred over acid catalysts due to the higher reaction rates and the lower process temperatures, and are therefore generally used for the industrial production of biodiesel. However, in the homogeneous catalyst-based processes, the removal of catalysts from the products entails further treatment of alkaline wastewater, thus leading to multiple process steps. Therefore, environmental concerns about the use of homogeneous base catalysts provide an impetus for the search for more environmentally friendly solid catalysts. Heterogeneous solid base catalysts can be easily separated from the reaction mixture without an extra separation step associated with homogeneous catalysts, and have a less corrosive character, resulting in a cheaper and more environmentally friendly process [9]. In this respect, many heterogeneous base catalysts such as calcined hydrotalcites [10] and Li/CaO [11,12] have been developed to promote the transesterification reaction. Also, experiments in our laboratory show that greater than 90% conversion of soybean oil to biodiesel could be achieved through the soybean oil transesterification catalyzed by Zn/I_2 [13] and KI/Al_2O_3 [14] catalysts.

In the present work, an attempt is made to prepare biodiesel from soybean oil using barium-doped ZnO as a catalyst. The catalysts were prepared by an impregnation method followed by calcination at higher temperatures and then tested the catalytic activities for the transesterification reaction of soybean oil in terms of the conversion to methyl esters. In particular, much attention was paid to the influence of calcination temperatures and doped Ba amounts on the efficiency of the catalysts. Moreover, the dependence of the conversion to methyl esters on the reaction parameters such as the molar ratio of methanol to oil, the catalyst loading and the reaction time was studied. Further, XRD, XPS, DTA–TG and the Hammett indicator method were employed for the catalyst characterizations in an attempt to relate the catalytic activity to the basicity of the catalysts.

2. Experimental

2.1. Materials

Soybean oil was purchased in a local food-store. The fatty acid composition of the soybean oil, as determined

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by gas chromatography (Shimadzu DC-9A) analysis, is given in table 1. The acid value was less than 0.1 mg KOH/g, and the average molecule weight was 874 g/mol, calculated from the saponification index (S.V. = 192.6 mg KOH/g). Zinc oxide used as a support was purchased from Luoyang Chemical Regent Factory (Luoyang, China). All other employed materials were of analytical grade and were used as received without further purification.

2.2. Catalyst preparation

Ba–ZnO catalysts were prepared by an impregnation method using barium nitrate as a precursor on a commercial zinc oxide. Prior to impregnation, the as-received zinc oxide in powder form was first pretreated at 393 K overnight. Typically, an aqueous solution containing barium nitrate was stirred with appropriate amounts of the ZnO support for 2 h. The resulting slurry was subsequently dried overnight at 393 K. Finally the catalyst precursor material was calcined at desired temperatures (typically 873 K) in air for 5 h before use for the reaction. The loading amounts of barium were calculated on the basis of the starting material amounts. Unless otherwise noted, the barium nitrate was loaded at a dose of 2.5 mmol/g support

2.3. Catalyst characterizations

Powder X-ray diffraction patterns were recorded on a Rigaku D/MAX-3B diffractometer using CuKα radiation (λ = 0.154 nm) at 40 kV and 50 mA over a 2θ range of 10–80°. The XRD phases present in the samples were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standards) database files.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 1600 spectrometer under UHV conditions (base vacuum: $\sim 10^{-8}$ Pa) at room temperature. MgKα (hν = 1253.6 eV) was used as the X-ray source. Binding energies (BE) of elements were referenced to the C 1s energy at 284.6 eV. The XPS spectra reported in the present work were normalized to the value of the most intense transition.

Thermal decomposition of the Ba–ZnO sample was evaluated by thermo-gravimetric analysis (TG) and differential thermal analysis (DTA) carried out in air on a Shimadzu DT-40 instrument, at a 10 K/min heating rate up to 1073 K.

Basic strengths of the samples (H_) were determined by using various Hammett indicators [15]. To measure the basicity of the catalysts, the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used.

Table 1
Fatty acid composition of soybean oil

Acidity index	Composition (wt.%)
Palmitic (C16:0)	12.3
Stearic (C18:0)	5.8
Oleic (C18:1)	26.5
Linoleic (C18:2)	49.4
Linolenic (C18:2)	5.9

2.4. Transesterification procedures

All experiments were performed in a 250 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The transesterification reactions were carried out with 10 g (11.4 mmol, calculated from the average molecular weigh of the soybean oil) of soybean oil, at a catalyst amount of 1–9 wt.% and a methanol/oil molar ratio of 6:1 to 18:1. In order to minimize the mass transfer limitation, each mixture was stirred vigorously at reflux of methanol (338 K) for the required reaction time. Once the reaction was complete, the reaction mixture was filtered and the residual methanol was removed by rotary evaporation at a reduced pressure prior to analysis.

The conversion of soybean oil to fatty acid methyl esters was determined using a ^{1}H-NMR technique (Bruker, DPX-400). Normally, the reaction mixture, after methanol was removed completely, was washed three times with a saturated aqueous NaCl solution for removal of the formed glycerin. The organic phase was separated by decantation, dried with anhydrous sodium sulfate and then submitted to ^{1}H-NMR analysis (Bruker, DPX-400) in $CDCl_3$using TMS as internal standard. The conversion of the soybean oil to a mixture of the methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of methyl esters) and 2.30 ppm (α-carbon CH_2 groups of all fatty acid derivatives) according to the ref. [16].

3. Results and discussion

3.1. Characterization of the catalyst

The powder X-ray diffraction patterns of Ba-doped ZnO samples are depicted in figure 1. The characteristic peaks of the parent ZnO (2θ = 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.8°, 69.1°, 67.9°, 69.1°, 77.0° and 71.4°), were registered in the diffraction patterns of the Ba–ZnO samples with their positions remaining essentially unaffected by the Ba loadings [17], which indicates that the introduction of Ba in the ZnO support cannot cause considerable distortion in the structure of the support though the relative intensity of the ZnO peaks decreased with an increase in the loading of Ba (curve c in figure 1). The decrease in the relative intensity of the characteristic ZnO peaks observed in the 4 mmol/g-loaded sample, may be related to the effect of barium on the ZnO surface expressed in a stronger interaction of barium with the support, because barium has the large cationic radius and thus may 'shade off' the peaks characteristic for the support with a decreased intensity in the samples of higher barium contents. Moreover, the characteristic XRD peaks of $Ba(NO_3)_2$ (2θ = 18.9°, 21.9°, 24.6°, 31.2°, 36.7°, 38.4°, 48.9° and 58.1°) were observed on the sample calcined at 873 K (curves a and c in figure 1), suggesting the existence of undecomposed $Ba(NO_3)_2$ on the catalyst surface. It should be, however, noted that the loaded $Ba(NO_3)_2$ is decomposed completely at the calcination temperature of 1073 K since the characteristic peaks for $Ba(NO_3)_2$ disappeared on the 1073 K-calcined sample (curve b in figure 1). Besides, for all three samples tested, the peaks (2θ = 19.7°, 23.8°, 24.2°, 27.7°, 29.7°, 33.7°, 44.8°, 46.6°, 55.6° and 77.1°) ascribed to $BaCO_3$ phase appeared on the XRD patterns. As reported in the literature [18], the spontaneous decomposition of $BaCO_3$ into BaO and CO_2 at appreciable rates occurs only at temperatures above 1610 K. Thus, it can be postulated that $BaCO_3$ phase is formed by the following successive reactions: first, the loaded $Ba(NO_3)_2$ is decomposed to BaO on the surface of the ZnO support when the sample is calcined at higher temperatures, and then the formed BaO could absorb atmospheric CO_2 with the formation of $BaCO_3$ phase. Such a result was also reported by Kim et al. [19] who mentioned that the heat treatment in air decomposed the Ba nitrate precursor to crystalline $BaCO_3$ on other supports. However, The BaO phase was not detected by XRD in the Ba–ZnO catalysts in the present work, as reported previously by other authors [19]. We think that the trace amounts of BaO phase may have been highly dispersed onto the surface of the ZnO support as a monolayer, which does not allow its registration by XRD. Besides, as we can see from tables 2 and 3, different basic sites with base strengths (H_-) in the range of 7.2–9.8, 9.8–15.0 and 15.0–18.4 were observed, indicating that the Ba–ZnO catalysts contain different types of surface basic sites. By drawing on the results, the formed $BaCO_3$ and probably BaO phase are thus expected to be the main catalytically active sites. Nevertheless, the investigation on further aspects of the catalytically active sites is needed.

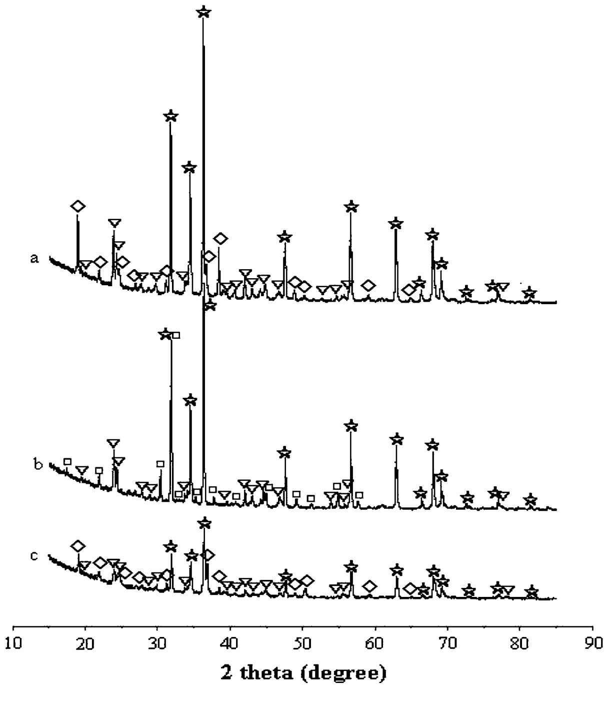

Figure 1. XRD patterns for samples: (a) 2.5 mmol/g Ba–ZnO calcined at 873 K, (b) 2.5 mmol/g Ba–ZnO calcined at 1073 K and (c) 4 mmol/g Ba–ZnO calcined at 873 K. (☆), ZnO; (▽), $BaCO_3$; (◇), $Ba(NO_3)_2$; (□), $BaZnO_2$.

Additionally, as the calcination temperature was raised up to 1073 K, new characteristic diffraction peaks attributed to $BaZnO_2$ perovskite were observed with 2θ of 17.4°, 21.9°, 30.3°, 36.2°, 37.8°, 44.5°, 49.1°, 54.8° and 62.9° (curve b in figure 1). This $BaZnO_2$ phase is probably formed by a solid state reaction between BaO, one of the products of the loaded $Ba(NO_3)_2$ decomposition, and the ZnO support, and hence could be one reason for the lower basicity and catalytic activity of the 1073 K-calcined catalyst, because the surface areas and the basicities of catalysts can be usually decreased once a perovaskite such as $BaZnO_2$ is formed.

XPS is a valuable technique to characterize the composition on the surface of the catalysts. The results of wide XPS survey scans for the ZnO support and a 2.5 mmol/g Ba/ZnO sample showed that the non-loaded ZnO surface solely comprised Zn, O and C, while Ba signal emerged upon loading with Ba, accompanied by an increased O signal (figure not shown). This demonstrates that the Ba element has been supported on the ZnO support.

The O1s core level spectrum of non-modified and modified ZnO samples is presented in figure 2A. As shown in this figure, the O1s spectra of ZnO exhibit a peak centered at 530.8 eV, which is mainly assigned to the oxygen atoms coordinated with Zn atoms, consistent with values reported in the literature [20]. However, there is a shoulder in high binding energy side on the O1s signal for the ZnO support, which is probably due to the surface hydroxyl groups of the ZnO. In the case of Ba-doped ZnO samples, the O1s peak observed at 531.4 eV (curves a, b and c in figure 2A) with a slight shift in the value of the binding energy as compared to that of the pure ZnO sample, is ascribed partially to $BaCO_3$ [21] and/or $Ba(NO_3)_2$ [21,22] present on the catalyst surface, in agreement with the XRD results. It is noteworthy that the O1s peak for the catalyst could not be properly fitted to a single component since it became somewhat broader with the Ba loading on the ZnO.

The Zn 2p XPS narrow scan spectra is shown in figure 2B. As evident in this figure, when the Ba was loaded on the support, the peak positions of both Zn

Table 2
Catalytic activities and basicities of 2.5 mmol/g Ba–ZnO samples calcined at different temperatures

Calcination temperature (K)	Basicity (mmol/g)			Total basicity (mmol/g)	Conversion (%)
	H_ = 7.2–9.8	H_ = 9.8–15.0	H_ = 15.0–18.4		
673	0	0	0	0	0
773	1.15	2.39	0.51	4.14	20.8
873	4.83	5.77	3.94	14.54	95.2
973	3.32	4.44	2.95	11.90	87.9
1073	2.85	3.65	2.62	9.12	85.5

Table 3
Catalytic activities and basicities of 873 K-calcined Ba/ZnO samples with different Ba loading amounts

Loading amount (mmol/g)	Basicity (mmol/g)			Total basicity (mmol/g)	Conversion (%)
	H_ = 7.2–9.8	H_ = 9.8–15.0	H_ = 15.0–18.4		
1.0	0.84	2.65	1.36	4.85	48.6
1.5	1.19	3.52	1.77	6.48	53.5
2.0	1.21	3.76	3.61	8.58	89
2.5	4.83	5.77	3.94	14.54	95.2
3.0	3.84	3.89	3.65	11.38	89.5
3.5	3.03	3.4	3.09	9.52	85.5
4.0	2.38	2.78	2.2	7.36	81.7

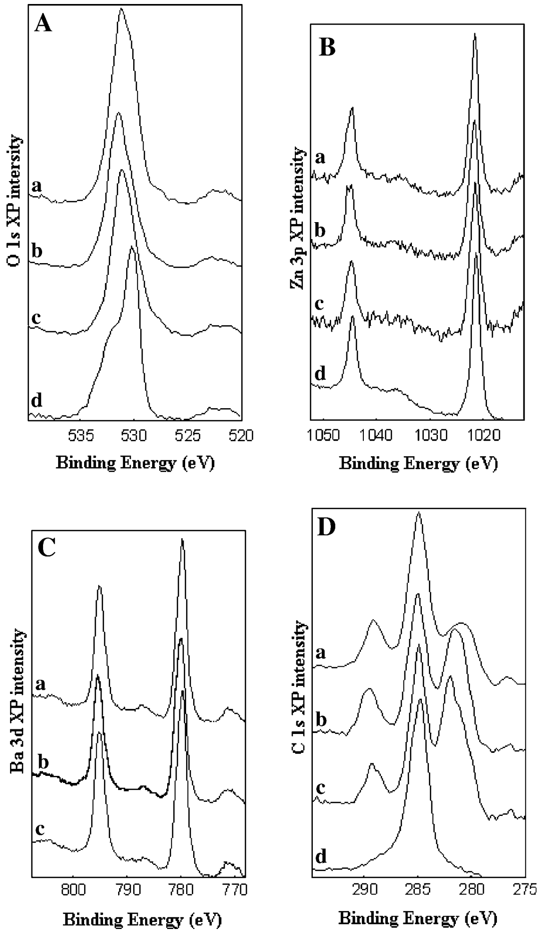

Figure 2. XPS spectra patterns for samples: (a) 2.5 mmol/g Ba–ZnO calcined at 873 K; (b) 2.5 mmol/g Ba–ZnO calcined at 1073 K; (c) 4 mmol/g Ba–ZnO calcined at 873 K and (d) ZnO.

$2p_{3/2}$ (1021.0 eV) and Zn $2p_{1/2}$ (1044.8 eV) from the Ba-doped ZnO surface were shifted by 0.4 and 0.8 eV toward the lower binding energy compared to those of Zn $2p_{3/2}$ (1021.4 eV) and Zn $2p_{1/2}$ (1045.6 eV) peaks of pure ZnO. Theses shifts in the binding energies presumably indicate a change in chemical binding states due to the interactions of zinc oxide and guest compounds. The associated Ba 3d spectra of Ba-doped ZnO samples are shown in figure 2C. The Ba 3d spectra exhibit XPS peaks at 779.8 and 795.3 eV attributed to Ba $3d_{5/2}$ and Ba$3d_{3/2}$, with a peak separation of 15.5 eV, indicative of the presence of BaO [23] and/or $BaCO_3$ [21] on the catalyst surface. The fact that Ba 3d spectra for the catalysts can be deconvoluted into two distinct components is understandable because it is characteristic of the catalyst to possess different Ba atoms.

Figure 2D shows C1s peaks for the catalysts. It can be seen that a sharp peak of hydrocarbon was depicted at 285.0 eV (curves a–d in figure 2D) in the C1s spectra, as usual. The hydrocarbon species is believed to be the contamination from the adventitious hydrocarbon, which present in the ambient or in the in-situ cell of the XPS spectrophotometer could not be avoided. Besides, a peak of C1s at 289.8 eV (curves a–c in figure 2D) corresponding to the $BaCO_3$ phase, was recorded in the Ba–ZnO sample [21], showing that $Ba(NO_3)_2$ is decomposed and converted to BaO, and then the BaO reacts with CO_2 (coming from the air) and is finally converted to $BaCO_3$ at higher calcination temperatures. Furthermore, a strong C1s signal in the Ba–ZnO sample was observed at around 282 eV. It is difficult to assign this signal; but we think that it may be tentatively due to

BaC compounds, which appeared probably because of the post-treatment process of the catalysts.

XPS measurements show the existence of a chemically distinct barium species on the surface of the catalysts. As a result, Ba is most likely present in the form of small $BaCO_3$ and probable BaO phases dispersed on the ZnO support, which is responsible for the activity of the catalysts. After 1073 K calcination the $BaZnO_2$ phase in the spinel structure is formed by a solid state reaction between the Ba species and the ZnO support with the depletion of the BaO phase, perhaps leading to a decease in the basicity and in the surface area.

The DTA–TG profile of the Ba–ZnO sample is reported in figure 3 and shows DTA peaks with the associated mass loss in the temperature range 303–1083 K. The sample for the thermal analysis was dried at 373 K for 24 h prior to analysis. As shown in figure 4, there are no peaks due to the elimination of the surface loosely held water in the thermal analysis profiles, suggesting that the surface physisorbed water is removed during the course of dryness. Besides, two endothermic DTA peaks around 847.1 and 989.2 K, overlapping a concomitant mass loss of 10.7%, may be tentatively attributed to the combination of the thermal decomposition of the $Ba(NO_3)_2$, the removal of the deeper held water and the solid-state interaction between the guest compound with the support.

3.2. Catalytic activities of the catalyst

The basicity of Ba–ZnO samples and their catalytic performance data are presented in table 2 as a function of calcination temperatures. The transesterification reaction was carried out at reflux of methanol, with a 12:1 molar ratio of methanol to oil and a catalyst amount of 6 wt.%. From the obtained results, it is shown that the calcination temperature affects significantly the basicity and the catalytic activity of the catalysts. With the rise of calcination temperature from 673 to 873 K, the basicity of the catalysts was gradually increased, and mostly owing to this, leading to an improvement of the corresponding conversion to methyl esters. However, when the calcination temperature was higher than 873 K, the basicity of Ba–ZnO catalysts reduced, paralleled by a decrease in the soybean oil conversion. Most probably, this decrease in catalytic activities is due to the formed $BaZnO_2$ phase at higher calcination temperatures, according to the XRD results described earlier. The formation of $BaZnO_2$ can result in a decrease not only in basicities but also in surface areas of the catalysts. However, it has been reported by Meher that the basicity rather than the surface area has much influence on the catalytic activity of solid base catalysts towards the transesterification [12]. Although the basic sites in various Ba/ZnO samples calcined at different temperatures are of equal strength (15.0 > H_ > 18.4), the observed basicity of catalysts calcined at 873 K is the highest, and thereby, resulting in the maximum conversion. Interestingly, it is observed from table 2 that the catalytic activity for the reaction could be correlated with the basicity as measured by the Hammett titration method, thus indicating that the number of basic sites has a significant impact on the catalytic activity. Since $Ba(NO_3)_2$ is inactive for this reaction, the activity variation of catalysts calcined at different temperatures should be attributed to the different $Ba(NO_3)_2$ decomposition extents and the different states of barium on the ZnO support.

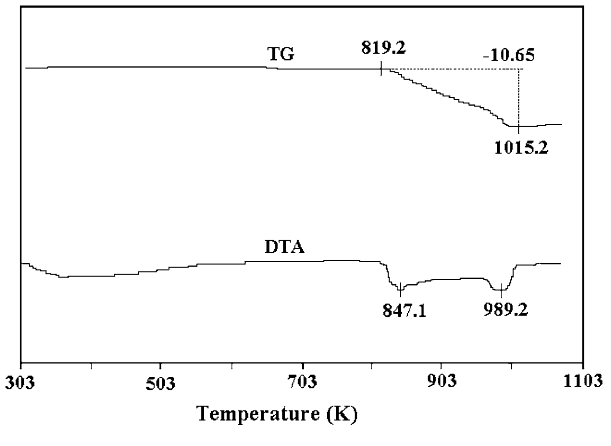

Figure 3. DTA–TG trace of the Ba–ZnO sample.

The effect of Ba loading amount on the basicity and the catalytic activity of catalysts was studied. For comparison, the transesterification was performed under the same reaction conditions as mentioned above. As can be observed from table 3, with the increase of Ba loading from 1.0 to 2.5 mmol/g, both the basicity of the catalysts and the corresponding oil conversion increased obviously and the best conversion together with the highest basicity were reached at the loading of 2.5 mmol/g Ba on the ZnO. However, the increase in the Ba loading amount over 2.5 mmol/g led to a drop of the basicity of catalysts, and the conversion of soybean oil was therefore decreased. This is most likely due to the coverage of surfaces basic sites by the excess Ba compounds. The same relationship between the catalytic activity and the active component loading amount was also observed for other supported catalysts if a monolayer of active component was covered on the support [24]. By drawing on the results, the optimum loading amount of Ba is 2.5 mmol/g. Besides, it should be noted that the observed activity of the Ba-doped ZnO catalysts in the reaction, as shown in table 3, is also related to the amount of basic sites, further demonstrating that the activity of the catalysts is dependent on their basicity. The basic sites are relevant to the decomposition amount of $Ba(NO_3)_2$, instead of the total loading amount of $Ba(NO_3)_2$. At a lower loading amount of $Ba(NO_3)_2$, the active base sites are more dispersed on the ZnO surface and the strong adsorption of reactants may occur at unreactive surface sites. However, the higher Ba loadings may result in agglomeration of active phases

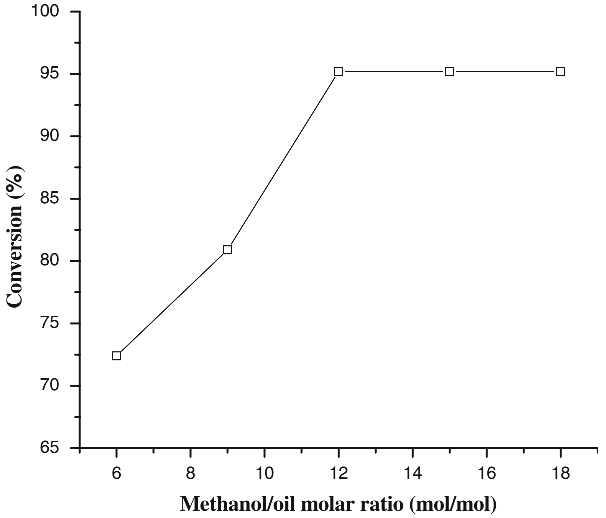

Figure 4. Conversions of soybean oil as a function of methanol/oil molar ratio. Reaction conditions: catalyst amount 6 wt.%, reaction time 1 h, reaction temperature 338 K.

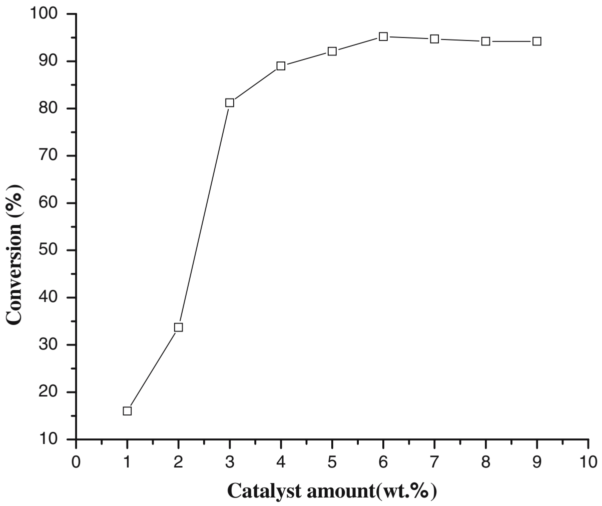

Figure 5. Conversions of soybean oil as a function of catalyst amount. Reaction conditions: methanol/oil molar ratio 12:1, reaction time 1 h, reaction temperature 338 K.

and hence lower the surface area of active components and lower the catalytic activity [20].

3.3. Transesterification of soybean oil with methanol

Transesterification reactions catalyzed by heterogeneous catalysts are known for their slow reaction rates [25,26]. Due to the presence of heterogeneous solid catalysts, the reaction mixture initially constitutes a three-phase system, oil–methanol-catalyst, which for diffusion reasons inhibits the reaction. Stoichiometrically, 3 mol of methanol are required for each mole of triglyceride. The conversion of soybean oil could be elevated by introducing an excess amount of methanol to shift the equilibrium to the methyl esters side, as suggested by other researchers who used heterogeneous base catalysts to study the transesterification reaction [27,28]. Industrially, the excess methanol can be recovered and reused after its purification. Figure 4 graphically illustrates the change of the conversion under the employed reaction conditions as a function of methanol/oil molar ratio. As shown in this graph, the conversion to methyl esters increased from 72.3% to 95.2% when the molar ratio of methanol/oil was increased from 6:1 to 12:1. The maximum conversion was obtained at a molar ratio of about 12:1. Beyond the molar ratio of 12:1, the conversion more or less remained the same. Thus, a 12:1 molar ratio of methanol to soybean oil is sufficient for the soybean oil transesterification under the reaction conditions.

The influence of the catalyst amount was examined in the present work. The catalyst amount was varied in the range between 1.0% and 9.0% referred to the starting oil weight. The obtained results, reported in figure 5, indicate that the transesterification reaction is obviously affected by the catalyst applied. By increasing the catalyst amount from 1 to 6 wt.%, the conversion to methyl esters was increased gradually and came up to its maximum of 95.2%. However, as the catalyst amount was raised higher than 6 wt.%, a decrease in the conversion was observed, which is possibly due to the rise of mixing problem of reactants, products and solid catalyst. Accordingly, the transesterification reaction was further studied with 6 wt.% of the catalyst for optimization of reaction time.

A plot of the conversion of soybean oil versus the reaction time is shown in figure 6. As can be seen, the conversion was improved steadily in the reaction time range between 15 and 60 min, and thereafter remained almost constant of about 95% representative of near completion of the reaction. Thus, the maximum conversion is achieved after 1 h of reaction time.

In order to study the stability of Ba–ZnO catalyst, it was separated by filtration, and then was initially washed with cyclohexane to remove any non-polar compounds such as methyl ester present on the surface. Further, the catalyst was washed by methanol to remove the polar compounds such as glycerol. Finally, the catalyst was heated at 398 K overnight and further used for the next transesterification. The transesterification reaction was carried out with the same reaction conditions as before. It was shown that the reaction catalyzed by the recovered catalyst provided a 43.2% conversion, which was lower than the conversion over the original catalyst. The recovered catalyst was characterized for its basic strength and its basicity. The results show a decline could be observed in the basic strength ($H\_$) from 15.0–18.4 to 9.8–15.0 and in the basicity from 15.3 to 9.7 mmol/g, respectively, and mostly due to this, leading to a drop of the catalytic activity of the spent catalyst. The reduced basic strength and basicity observed here

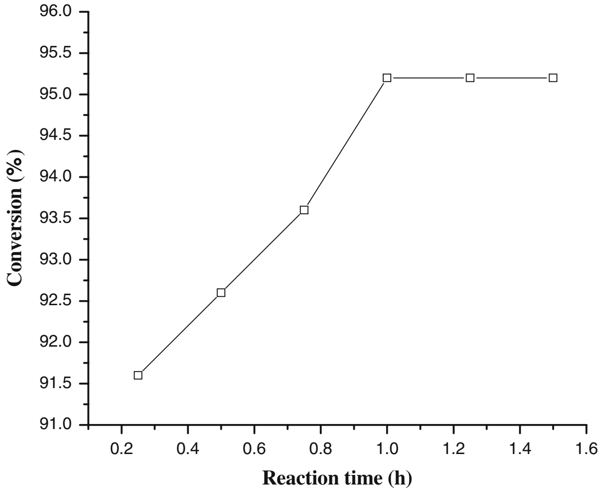

Figure 6. Conversions of soybean oil as a function of reaction time. Reaction conditions: methanol/oil molar ratio 12:1, catalyst amount 6 wt.%, reaction temperature 338 K.

could be, probably, owing to the leaching of Ba species such as BaO from the support catalysts.

However, the spent Ba–ZnO catalyst can be regenerated by impregnating it in an aqueous solution of $Ba(NO_3)_2$ as described in the experimental section. The obtained result shows that the regenerated catalyst could give a high conversion of 93.7% under the same reaction conditions as in the case of fresh catalysts, thus implying that the used catalyst could be regenerated by this method.

4. Conclusions

The Ba-doped ZnO prepared by an impregnation method followed by calcination at higher temperatures, appears to be an active catalyst in soybean oil transesterifications. The catalyst loaded 2.5 mmol/g Ba on zinc oxide and after being calcined at 873 K for 5 h, it was found to be the optimum catalyst, which could give the maximum basicity and the best catalytic activity. The optimized reaction conditions for the transesterification were 6 wt.% Ba–ZnO catalyst, a molar ratio of methanol to oil of 12:1 and a reaction time 1 h, which resulted in a 95.2% conversion of soybean oil at reflux of methanol (338 K). Furthermore, the prepared catalyst was characterized with XRD, XPS, DTA–TG and the Hammett indicator method. The obtained results show that the basicity of the catalysts is a chief factor which determines their catalytic activity in the transesterification reaction. Although the catalyst show a good initial activity for the reaction, a decrease in catalytic activity was observed when the spent catalyst was reused

References

[1] F. Ma and M.A. Hanna, Bioresour. Technol. 70 (1999) 1.
[2] B.K. Barnwal and M.P. Sharma, Renew. Sust. Energy Rev. 9 (2005) 363.
[3] E. Crabbe, C.N. Hipolito, G. Kobayashi, K. Sonomoto and A. Ishizaki, Process Biochem. 37 (2001) 65.
[4] M. Canakci and J.V. Gerpen, ASAE Trans. 42 (1999) 1203.
[5] M.D. Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nastasi and E. Santacesarua, J. Mol. Catal. A 239 (2005) 111.
[6] G. Antolín, F.V. Tinaut, Y. Briceño and V. Castanñ, Bioresour. Technol. 83 (2002) 111.
[7] J.M. Encinar, J.F. González and J.J. Rodríguez, Energy Fuel 16 (2002) 443.
[8] S.L. Dmytryshyn, A.K. Dalai and S.T. Chaudhari, Bioresour. Technol. 92 (2004) 55.
[9] R. Stern, G. Hillion, J.J. Rouxel, US Patent 6, 147,196 (2000).
[10] M.D. Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser and E. Santacesaria, Ind. Eng. Chem. Res. 45 (2006) 3009.
[11] R.S. Watkins, A.F. Lee and K. Wilson, Green Chem. 6 (2004) 335.
[12] L.C. Meher, M.G. Kulkarni, A.K. Dalai and S.N. Nain, Eur. J. Lipid Sci. Technol. 108 (2006) 389.
[13] H. Li and W. Xie, Catal. Lett. 107 (2006) 25.
[14] W. Xie and H. Li, J. Mol. Catal. A 255 (2006) 1.
[15] J. Take, N. Kikuchi and Y. Yoneda, J. Catal. 21 (1971) 164.
[16] G. Gelbard, O. Brès and R.M. Vargas, J. Am. Oil Chem. Soc. 72 (1995) 1239.
[17] W.Q. Zhou, X.Q. Zhao, Y.J. Wang and J.Y. Zhang, Appl. Catal. A. 260 (2004) 19.
[18] J.P. Breen, M. Marella, C. Pistarino and J.R.H. Ross, Catal. Lett. 80(3–4) (2002) 123.
[19] D.H. Kim, Y.H. Chin, J.H. Kwak, J. Szanyi and C.H.F. Peden, Catal. Lett. 105 (2005) 259.
[20] E. Agostinelli, C. Battistoni, D. Fiorani, G. Mattogno and M. Nogues, J. Phys. Chem. Solids 50 (1989) 269.
[21] A.B. Christie, J. Lee, I. Sutherland and J.M. Walls, Appl. Surf. Sci. 15 (1983) 224.
[22] R.P. Vasquez, J. Electron Spectrosc. Relat. Phemon. 56 (1991) 217.
[23] NIST Standard Reference Database 20, Version 3.4 (Web Version), http://www.srdata.nist.gov/xps/.
[24] D.E. Jiang, G.C. Pan, B.Y. Zhao, G.P. Ran, Y.C. Xie and E. Min, Appl. Catal. A 201 (2000) 169.
[25] S. Gryglewicz, Bioresour. Technol. 70 (1999) 249.
[26] S. Furuta, H. Matsulashi and K. Arata, Catal. Commun. 5 (2004) 721.
[27] W. Xie, H. Peng and L. Cheng, Appl. Catal. A 300 (2006) 67.
[28] J.V. Gerpen, Fuel Process. Technol. 86 (2005) 197.
[29] 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.