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Journal of Molecular Catalysis A: Chemical 246 (2006) 24–32

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil

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Received 31 July 2005; received in revised form 27 September 2005; accepted 8 October 2005

Abstract

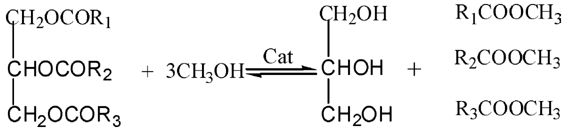
Methyl ester of fatty acids, derived from vegetable oils or animal fats and known as biodiesel, is a promising alternative diesel fuel regarding the limited resources of fossil fuel and the environmental concerns. In this work, an environmentally benign process for the methanolysis of soybean oil to methyl esters using calcined Mg–Al hydrotalcites as solid base catalysts in a heterogeneous manner was developed. When the reaction was carried out at reflux of methanol, with a molar ratio of soybean oil to methanol of 15:1, a reaction time 9 h and a catalyst amount 7.5%, the oil conversion was 67%. The calcined hydrotalcite with an Mg/Al ratio of 3.0 derived from calcination at 773 K was found to be the optimum catalyst that can give the highest basicity and the best catalytic activity for this reaction. The catalysts were characterized with SEM, XRD, IR, DTA-TG and Hammett titration method. The activity of the catalysts for the methanolysis reaction was correlated closely with their basicity as determined by the Hammett method.

Keywords: Methanolysis; Activated Mg–Al hydrotalcite; Solid base catalyst; Calcination; Biodiesel

1. Introduction

The transesterification of vegetable oils or animal fats with methanol in the presence of a catalyst affords the corresponding methyl esters. These esters have significant potential as alternative diesel fuel (better known as biodiesel) both in neat form or blended with conventional diesel fuel. Biodiesel is characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with little or no modifications. Besides, biodiesel is a promising non-toxic and biodegradable renewable fuel, and essentially free of sulphur and aromatics makes it a cleaner burning fuel than petroleum diesel with reduced emissions of SO_x, CO, unburnt hydrocarbons and particulate matter [1–3].

Biodiesel has been produced by transesterification of triglyceride to methyl esters using homogeneous basic catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides, as represented by the following equation [3–5].



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + 3CH_3OH \overset{Cat}{\rightleftharpoons} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R_1COOCH_3 \\ R_2COOCH_3 \\ R_3COOCH_3 \end{array}$$

However, in this conventional method removal of these catalysts was technically difficult and a large amount of waste water was produced to separate and clean the catalyst and the product. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts mainly because of environmental constraints and simplifications in the existing processes. At the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils with methanol [6–10]. For example, Suppes et al. [7] achieved conversion of 78% at 513 K and >95% at 533 K for transesterification of vegetable oils using calcium carbonate rock as catalyst. Besides, Beynese et al. [8] reported the use of EST-4 and EST-10 catalysts to provide conversion of 86 and 53%, respectively at 493 K and 1.5 h reaction time. The both studies above required temperatures in excess of 473 K to achieve higher conversions within the time scales of the experiments. Recently, Kim et al. [10] prepared a solid superbase

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doi:10.1016/j.molcata.2005.10.008

of Na/NaOH/γ-Al_2O_3 that showed almost the same catalytic activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. In most of the experiments using heterogeneous catalysts, the reaction proceeded at a relatively slow rate. Because of the presence of heterogeneous catalysts, the reaction mixture constitutes a three-phase system, oil/methanol/catalyst, which for diffusion reasons inhibits the reaction. Nevertheless, heterogeneous catalysts could improve the synthesis methods for the development of an environmentally benign process and the reduction of production cost.

Hydrotalcites, $Mg_6Al_2(OH)_{16}CO_34H_2O$, have been used as precursors of catalysts and have attracted much attention during the development of new environmentally friendly catalysts [11]. The structure of hydrotalcite resembles that of brucite, $Mg(OH)_2$, where the magnesium cations are octahedrally coordinated by hydroxyl ions, resulting in stacks of edge-shared layers of the octahedral. In the hydrotalcite structure, part of the Mg^{2+} ions are replaced by Al^{3+} ions forming positively charged layers. Charge-balancing anions (usually ${CO_3}^{2-}$) and water molecules are situated in the interlayers between the stacked brucite-like cation layers [11–13]. Calcination at high temperature decomposes the hydrotalcite into interactive, high surface area and well-dispersed mixed Mg–Al oxides which presents basic sites that are associated to structural hydroxyl groups as well as strong Lewis basic sites associated to $O^{2-}M^{n+}$ acid–base pairs [13–15]. Thus, calcined Mg–Al hydrotalcites are able to catalyze a variety of base-catalyzed reaction, such as aldol condensations [16,17], Micheal reaction [18], cyanoethylation of alcohols [19] and nitroaldol reaction [20]. In the present work, calcined Mg–Al hydrotalcites were adopted for methanolysis of soybean oil. Their catalytic efficiency was studied regarding the conversion of soybean oil to methyl esters. The structure properties and the activities of the catalysts were studied with SEM, XRD, IR, DTA-TG analysis and Hammett titration method. Furthermore, a correlation between the basic properties of the catalysts and their catalytic activities towards the methanolysis reaction was discussed, which may give fundamental insight into the catalytic mechanism of the catalyst.

2. Experimental

2.1. Preparation of the catalyst

All the hydrotalcites were prepared by co-precipitation method. An aqueous solution (187 ml) containing various Mg/Al ratios of $Mg(NO_3)_2·6H_2O$ and $Al(NO_3)_39·H_2O$ (total metal nitrates, 0.372 mol), was added slowly to a second solution (187 ml) containing NaOH (0.4375 mol) and Na_2CO_3 (0.1125 mol) under vigorous mechanical stirring, maintaining the pH between 8 and 10. The addition took nearly 3 h at room temperature. The mixture was kept at this temperature for 1 h under stirring, after which the product was left for 18 h at 333 K. The resulting white precipitate was filtered, washed to eliminate the alkali metal ions and the nitrate ions until the pH of the washing water was 7. Then the formed hydrotalcite was dried at 353 K for 15 h. In order to obtain the corresponding Mg–Al mixed oxides the samples were calcined in a static air atmosphere at different temperatures for 8 h. For convenience, the catalysts thus obtained with different Mg/Al ratios of 2.0, 2.5, 3.0, 3.5 and 4.0 were designated as 2.0HT, 2.5HT, 3.0HT, 3.5HT and 4.0HT, respectively.

2.2. Characterization methods

Basic strengths of the solid bases (H_-) were determined by using Hammett indicator of 0.5% anhydrous methanol solution. To measure the catalyst basicity the method of Hammett indicator-benzene carboxylic acid (0.02 mol/l anhydrous methanol solution) titration was used [21–23].

The calcined hydrotalcite of 0.5 g was dissolved in 50 ml distilled water, stirred vigorously for 1 h and filtered, then the soluble basicity was titrated by use of 0.02 mol/l anhydrous methanol solution of benzene carboxylic acid.

For SEM analysis a AMRAY-1000B scanning electron microscope was utilized. The accelerating voltage was 20 kV.

The XRD measurements were performed on a Rigaku D/MAX-3B powder X-ray diffractometer using Cu Kα radiation, over a 2θ range of 3–70° with a step size of 0.02° at a scanning speed of 5 °/min. The data were processed with the DiffracPlus software. The phases were identified using the powder diffraction file (PDF) database (JCPDS, International Centre for Diffraction Date).

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

Thermal decomposition of the hydrotalcites was evaluated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) carried out on a Shimadze DT-40 instrument operating under a flow of air at a 10 K/min heating rate up to 1073 K.

2.3. Procedure of soybean oil methanolysis

Commercial edible grade soybean oil was obtained from market and was refined again to reduce free fatty acid and water contents 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 (Shimadze 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, different volume of anhydrous methanol and various amounts of catalyst. The mixture was vigorously stirred and refluxed for the required reaction time. After the methanolysis reaction finished, the mixture was filtered and the residual methanol was separated from the liquid phase via rotary evaporation.

2.4. Analysis methods

The process of soybean oil methanolysis is a sequence of three consecutive and reversible reactions transforming the

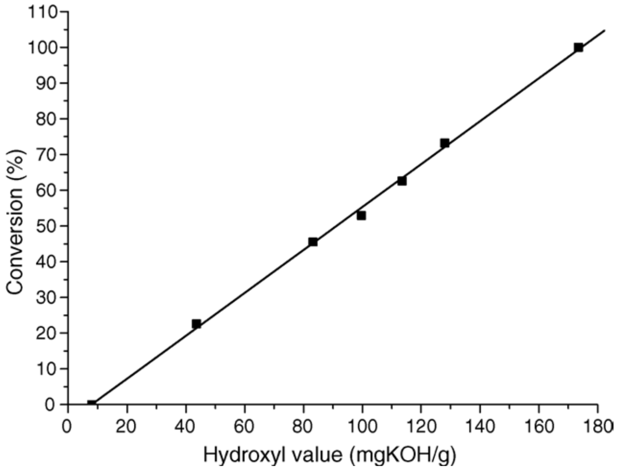

Fig. 1. The relation between hydroxyl value and conversion determined by ^{1}H NMR.

triglyceride into a diglyceride, following into a monoglyceride and, finally into glycerin and the fatty acid methyl esters. The increase of methyl ester amount means the increase of hydroxyl value (H_v) of the liquid phase with the same step because one free alcohol is liberated when one molecular methyl ester is formed in the transesterification reaction. Therefore, when the methanol is removed with bound and free glycerin kept with biodiesel (unbound glycerin would form a free phase), the free alcohols on the glycerin are titrated to essentially determine how much methanol reacted to displace the glycerin and create the free alcohols, and consequently the conversion could be evaluated by titrating free alcohols on bound and free glycerin.

As a means for correlating and crosschecking results with other analytical methods, ^{1}H NMR method was selected. For NMR analysis, the reaction mixture, after methanol was removed completely using a rotary evaporator, 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 magnesium sulfate and then submitted to 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 the methyl ester) and 2.30 ppm (α-carbon CH_2 groups of all fatty acid derivatives) as described by Gelbard et al. [25]. As shown in Fig. 1, it clearly appears that there is a linear correlation between the conversion of soybean oil and the hydroxyl value of the liquid phase. Accordingly, when the hydroxyl value is obtained, the conversion can be confirmed by the simple linear relation. Hydroxyl value of the samples was determined using the conventional method [24].

3. Results and discussion

3.1. Catalyst characterizations

The basic strengths of various mixed Mg–Al oxides derived from Mg–Al hydrotalcites were determined by using Hammett indicator. All samples prepared in our study had the basic strength in the range of 9.3–15.0, which was similar to that of anhydrous Na_2CO_3 measured with the same method.

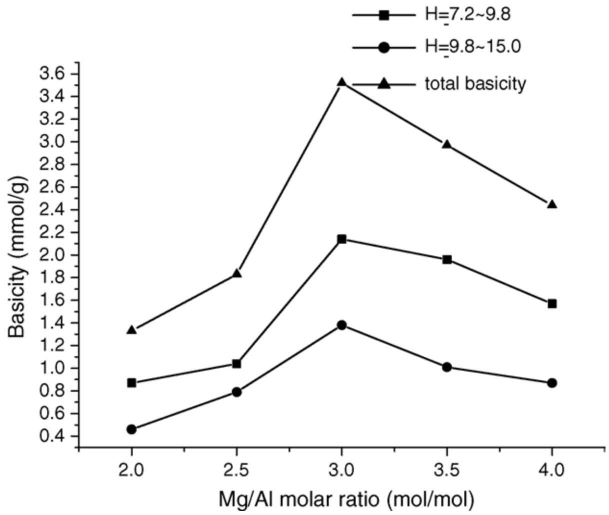

Fig. 2. Basicity of calcined hydrotalcites with different Mg/Al molar ratios.

The basicity of the catalysts with different Mg/Al molar ratios was shown in Fig. 2. As we can observe, the main basic sites with H_- in the range of 7.2–9.8 and the other sites with H_- in the range of 9.8–15.0 were observed, thus suggesting that the calcined hydrotalcites contain different types of surface basic sites. According to Di Cosimo et al. [26] while pure MgO possesses strong basic sites consisting predominantly of O^{2-}, calcined hydrotalcites contain surface basic sites of low (OH^- groups), medium (Mg–O pairs) and strong (O^{2-}) basicities. Our experimental results on the Hammett titration method conform to this viewpoint. It indicates a wide basic site distribution as far as the basicity is concerned.

Furthermore, the total basicity of the catalysts was increased gradually with the Mg/Al molar ratio and came up to the maximum value at the Mg/Al molar ratio of 3.0. But, with further increase in the Mg/Al molar ratio it is observed that the basicity was decreased, which resulted in a drop of the catalytic activity. Qualitatively similar trends were also reported by other researchers [27,28]. Nakatsuka et al. [27] found that the basicity measured by titration with benzoic acid reached a maximum for Mg/Al ratio of about 2.6. Also, Fishel and Davis [28] measured the number of basic sites by TPD of CO_2 and a maximum of the basic site density was observed at Mg/Al ratio of 3.0.

Besides, the basicity of 3.0HT calcined at different temperatures was measured with the same method; the results are illustrated in Fig. 3. From this figure, it can be seen that the maximum basicity, reaching 3.52 mmol/g, is found at a calcination temperature of 737 K, and a low level of basicity is observed below 673 K and above 873 K. The increased basicity could be expected to correlate with an increase of the catalyst activity.

Conventionally, the Hammett indicator measurements are performed using non-polar solvent. However, since methanol was employed as both solvent and reactant, it was proposed appropriate to use methanol in this instance, thus giving a better measure of the catalyst basicity under reaction conditions. Otherwise, it should always be considered that diffusion problems

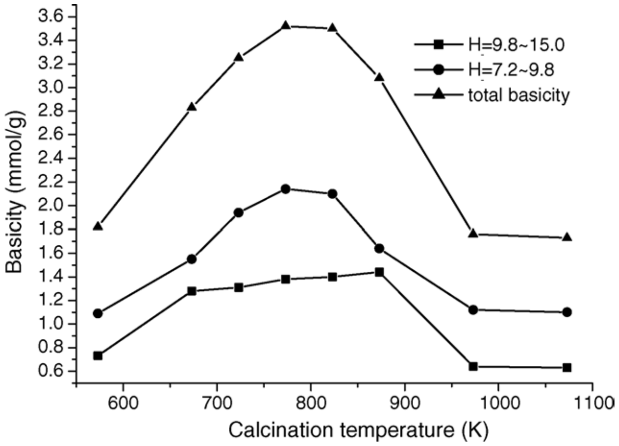

Fig. 3. Basicity of 3.0HT calcined at different temperatures.

of the indicator molecules into the micropores might occur [29]. Nevertheless, the basicities obtained by using Hammett titration, are in good agreement with the catalytic findings that will be discussed later in this paper. Therefore, the Hammett titration method can give qualitative information of the basic properties of the solid catalysts.

Figs. 4 and 5 shows the soluble basicities of the prepared catalysts in water. Obviously, the soluble basicity in water was very small, suggesting that the catalysts were stable. Because the reaction system adopts methanol as one of reactants, and methanol has the similar polarity to water, the stability of the prepared solid bases in water is similar to that in the reaction system. Therefore, the higher soluble basicity shows the weaker stability in the reaction system. It is likely that the catalysts prepared above are proper as catalysts for the reaction.

During calcination the decomposition of hydrotalcites occurs resulting in formation of mixed Mg–Al oxides phases. This fact was confirmed by the XRD patterns of the samples calcined at 773 or 1073 K, which are shown in Fig. 6. The XRD patterns of the mixed oxides exhibit the typical features of a mixed oxide of Mg(Al)O type [30]. For the samples of 2.0HT calcined at 773 K and 3.0HT calcined at 773 K, the characteristic reflections observed clearly at $2\theta \approx 43$ and 63° correspond to a MgO-like phase (periclase) or rather magnesia–alumina solid solution [30], while the peaks of Al_2O_3 phase were very small, indicating that Al^{3+} cations are dispersed in the structure of MgO without formation of spinel species. This can coincide well with the results observed by SEM as the formation of periclase-like Mg–Al–O structure (Fig. 8). Besides, calcination of 3.0HT at 773 K and even 1073 K, resulted in relatively intensive diffraction lines of MgO and less broad peaks, most likely owing to the increased particle size or improved crystallinity, or to both (Fig. 6, curves b and c) [31]. Moreover, with decreasing Al content the diffraction lines became sharper and more intensive, and therefore indicating improved crystallinity (Fig. 6, curves a and b). The larger the crystallites before calcination, the higher the micropore volume after calcination due to increased water and CO_2 evolution [32]. In addition, the characteristic reflections of spinel phase, $MgAl_2O_4$, appeared at $2\theta \approx 19°, 31°, 37°, 59°$ and 65° in the sample of 3.0HT calcined at 1073 K (Fig. 6, curve c). The appearance of the spinel phase may be one of the reasons for the decrease in activity of 3.0HT calcined at higher temperature than 773 K (Fig. 12). Besides, as suggested by other researchers,

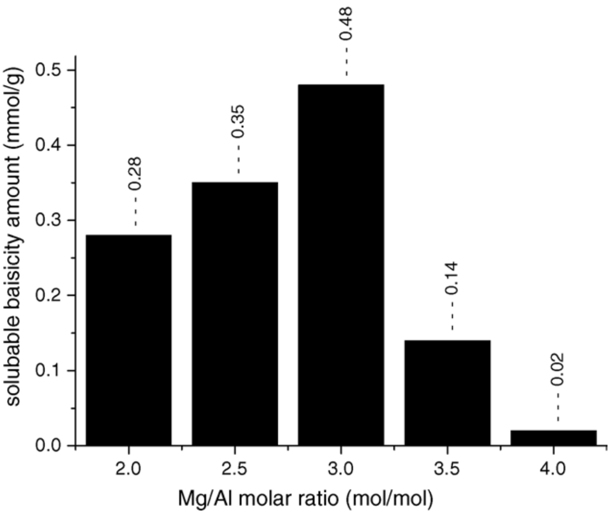

Fig. 4. Soluble basicity of 3.0HT with different Mg/Al molar ratios.

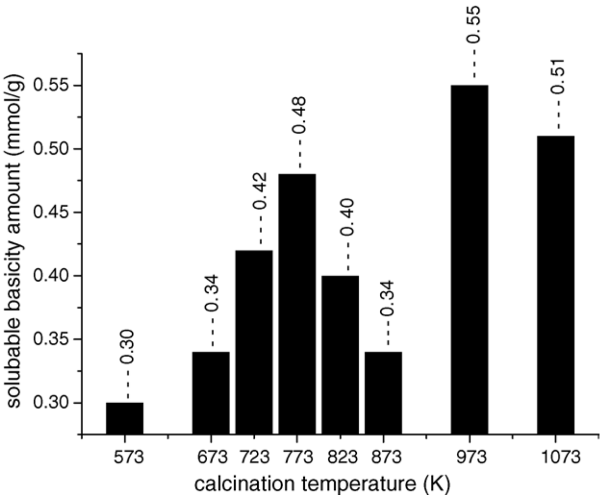

Fig. 5. Soluble basicity of 3.0HT calcined at different temperatures.

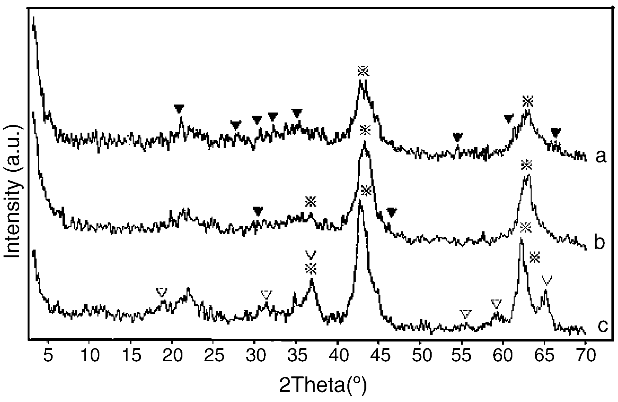

Fig. 6. XRD patterns for samples: (a) 2.0HT calcined at 773 K, (b) 3.0HT calcined at 773 K and (c) 3.0HT calcined at 1073 K. ▼, Al_2O_3; ▽, $MgAl_2O_4$; ※, MgO.

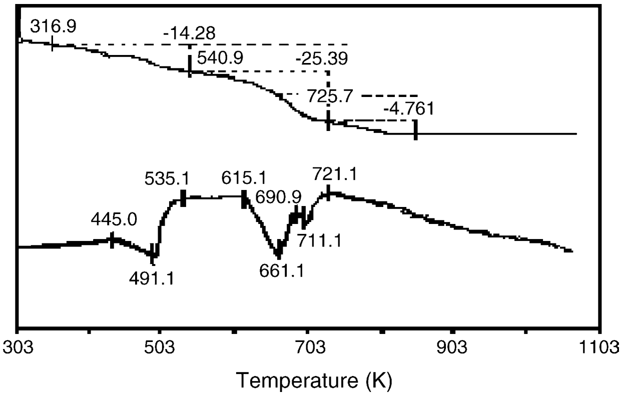

Fig. 7. DTA-TG curves of 3.0HT as synthesized.

the dehydroxylation, which began well before the formation of the spinel phase, probably resulted in a decrease of activity and the basic sites are essentially the hydroxyl groups rather than O^{2-} species [33]. Indeed, as shown in the IR spectra (Fig. 9), some hydroxyl groups are still present after calcination.

The thermal behaviour of 3.0HT with $CO_3{}^{2-}$ as the compensating anion is shown in Fig. 7. It can be seen that the DTA curve resembled the hydrotalcite pattern as reported in the literature [16–18]. As shown in Fig. 7, the first endothermic DTA peak in the range of 445–535 K, which was accompanied by a mass loss of 14.28%, corresponded to the elimination of interlayer water and the surface weakly held water without collapse of the hydrotalcite structure. The second and third endothermic peaks, overlapping mass loss steps at around 661 and 761 K, respectively (total mass loss of approximately 25.4%), were attributed to the combination of the decomposition of interlayer carbonate anion present in the brucite layer (with CO_2 evolution) and the ever deeper dehydroxylation of vicinal OH groups in the hydrotalcite (with H_2O evolution). As a result, the Mg–Al mixed oxides were formed with lots of dislocations-ideal for a potential catalyst [34]. Due to dehydroxylation and interlayer carbonate decomposition, water and carbon dioxide are released, giving rise to an increased mesopore volume (compared to that of the as-synthesized sample) and formation of micropores, which results in high catalytic activity. Besides, a very broad endothermic band in the temperature of above 780 K, overlapping partly a small mass loss of about 4.8% in the region between 780 and 870 K, was also observed in the DTA profile. This may be attributed mainly to the heat absorbed during the formation of spinel ($MgAl_2O_4$) phase or/and the structural rearrangement. The XRD analysis of 3.0HT calcined at 1073 K in air for 8 h confirmed the formation of $MgAl_2O_4$ (Fig. 6).

In order to determine the morphology and particle size distribution of the Mg–Al hydrotalcites we have selected different representative samples which where studied by SEM. It can be observed clearly from SEM image of uncalcined hydrotalcite in Fig. 8 that the air-dried 3.0HT formed well-developed, thin flat crystals with obvious edges indicating the layered structure (Fig. 8a). Moreover, the flat crystals, were not the same size (with particle sizes in range of 1–120 μm) by the SEM observation at high magnification and probably consisted of Mg–Al hydrotalcite crystals. Such flat structure was still observed with decreasing the size after calcination at 773 K (Fig. 8b) and further reducing the size after calcination at 1073 K (Fig. 8c). In other words, when the mixed oxides were formed, the flat structure still largely retained, with the varying sizes depending on calcination temperature. This is probably because Mg–Al hydrotalcite consists of $Mg(OH)_2$ brucite sheets, in which Al^{3+} substitutes for the Mg^{2+} sites, and is transformed to periclase-like Mg–Al–O solid solutions by calcination at high temperature. Thus, the morphology due to the brucite sheets was kept after calcination at 773 K and still remained in the resulting periclase-like Mg–Al–O structure and even in the structure after the calcination at 1073 K. This is in agreement with the results reported previously [35], which show that upon heating Mg–Al hydrotalcites, water and CO_2 are released by a cratering mechanism rather than by exfoliation, and that the crystal morphology is preserved. In general, the activation of hydrotalcites via thermal treatment is considered to involve the replacement of interlayer carbonate by hydroxyl groups without a drastic effect on the original ordered stacked structure of the aggregates.

The IR spectra of the catalysts prepared under different conditions are presented in Fig. 9. For all the samples an intense broad band at approximately 3450 cm^{-1} may be ascribed to the ν_{OH} stretching vibration of the hydroxyl groups attached to Al and Mg [30]. Moreover, for 3.0HT samples the intensity of ν_{OH} mode decreased with increasing calcination temperature (Fig. 9, curves e, f, g and h), indicating the start of layer dehydroxylation. The minor absorption peak at about 1635 cm^{-1} could be assigned to δ_{OH} bending vibration of H_2O molecule in the interlayer space or absorbed from air [30]. Besides, the bands at around 500 and 700 cm^{-1} corresponds to the translation and deformation modes of the hydroxyl groups influenced mainly by Al cations, whereas that at around 620 cm^{-1} is interpreted as being the Mg–OH translation modes [32].

After calcination of Mg–Al hydrotalcite, a weaker and broader IR absorption at about 1507–1419 cm^{-1} attributed to carbonates were observed, except for samples of 3.0HT calcined at 673 K and 3.5HT calcined at 773 K (Fig. 10). The readsorption of gaseous CO_2 (coming from the ambient atmosphere) on the basic sites of the Mg–Al oxides or no totally decomposed carbonates at this temperature could explain the still remaining carbonates on the calcined hydrotalcites [30]. Thus the prepared catalysts stored in air partly lose their catalytic activity (date not shown) due to the carbonation process with CO_2 from the ambient atmosphere and therefore must reactivated before use.

3.2. Influence of catalyst preparation conditions on the conversion of soybean oil

We tested the catalytic activity of hydrotalcite as synthesized and the calcined hydrotalcite samples in the methanolysis of soybean oil. In the absence of calcination, the hydrotalcite with carbonate as the compensating anion displays no particular catalytic activity in the reaction. But after calcination the hydrotalcites are then in the form of mixed oxides, and exhibit a significant activity.

In order to determine the influence of the Mg/Al molar ratio of calcined hydrotalcites on their catalytic activity, hydrotal-

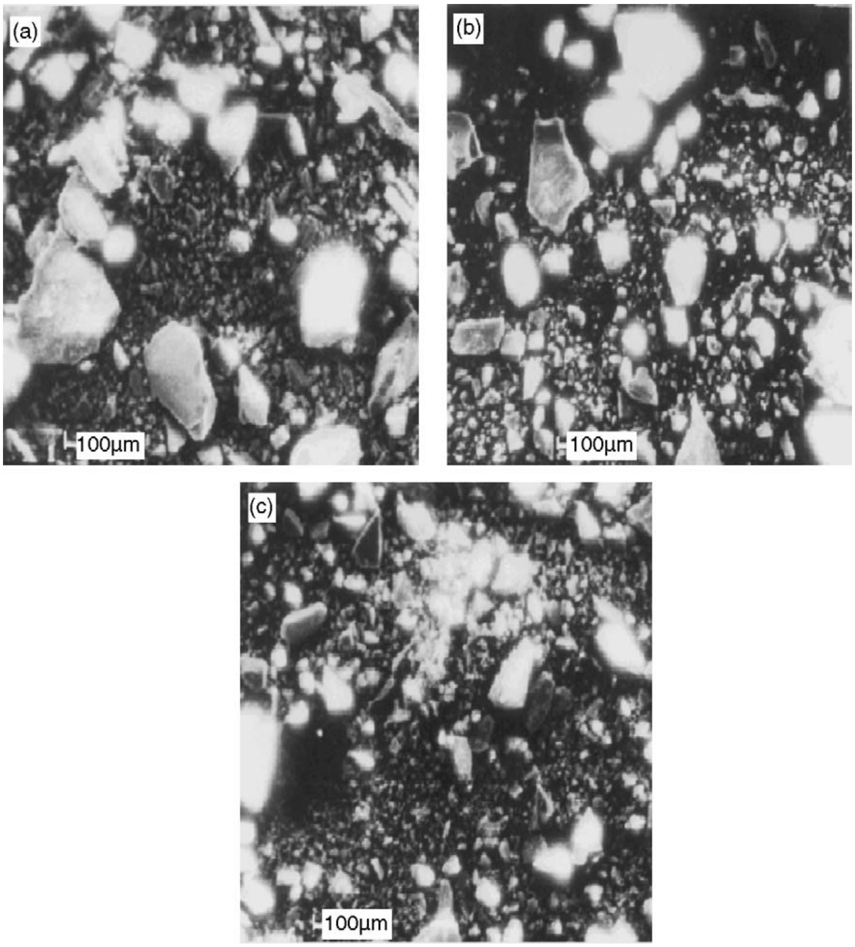

Fig. 8. SEM images of samples: (a) 3.0HT air-dried, (b) 3.0HT calcined at 773 K and (c) 3.0HT calcined at 873 K.

cites with different Mg/Al molar ratios were prepared and used to catalyze the methanolysis reaction after being calcined at 773 K for 8 h. The experimental results are illustrated in Fig. 10, which indicates that the catalytic activity was improved with the increase in Mg content when the Mg/Al molar ratio was below 3.0, but when the Mg/Al molar ratio was above 3.0, the catalytic activity dropped. Clearly, such a tendency could be correlated well to that for the variation of the catalyst basicity with various Mg/Al ratios. As expected, a catalyst with a 3:1 molar ratio of Mg to Al, which had the highest basicity as mentioned above, showed the highest activity.

It is known that all the Al^{3+} cations occupy the octahedral sites in hydrotalcites before calcination and the structure rearranges at high temperature, i.e. Al^{3+} cations transfer from octahedral to tetrahedral sites, substituting Mg^{2+} cations isomorphously in the mixed oxides [36]. The positive charge generated by this isomorphous substitution could be compensated by the formation of two types of defects: cationic vacancies and/or inclusion of intersticial oxygens in the structure. The amount of tetrahedral aluminium decrease with increasing the Mg/Al ratio in the hydrotalcite calcined at high temperature, and at least a part of the tetrahedral aluminium is located at tetrahedral positions in MgO lattice. This structure could give rise to the formation of clusters of Mg–Al inverse spinel type. The Al^{3+} located at the tetrahedral or octahedral sites produces the defect of Mg^{2+} or Al^{3+} in the framework in order to compensate the positive charge generated. The O^{2-} ions adjacent to the Mg^{2+} or Al^{3+} defects become coordinatively unsaturated and could provide strong basic sites. On the other hand, Since Al is more electronegative than Mg, an increase in Al should increase the average electronegativity of the catalyst, and thus, a decrease in the average electronic density of the unsaturated framework oxygens could be expected, with the corresponding effect on their basicity and catalytic activity [26,30,37]. As a result, the basicity and catalytic activity increased with elevating of Mg/Al molar ratio. However, when the Mg/Al molar ratio exceeds 3.0, the catalytic activity decreases. It may be due to the formation of new weaker basic sites and thus decrease of strong basic site amount.

The influence of calcination temperature on the catalyst activity is displayed in Fig. 11. From the results obtained, it is shown that calcination temperature affected significantly the catalytic activity. With the rise of calcination temperature from 573 to 773 K, the conversion of soybean oil increased gradually and came up to the maxima of 66% when the calcination temperature was 773 K, which could be correlated well with the increase of the catalyst basicity with the increase of calcination temperature between 573 and 773 K (Fig. 4). However, when the calcination

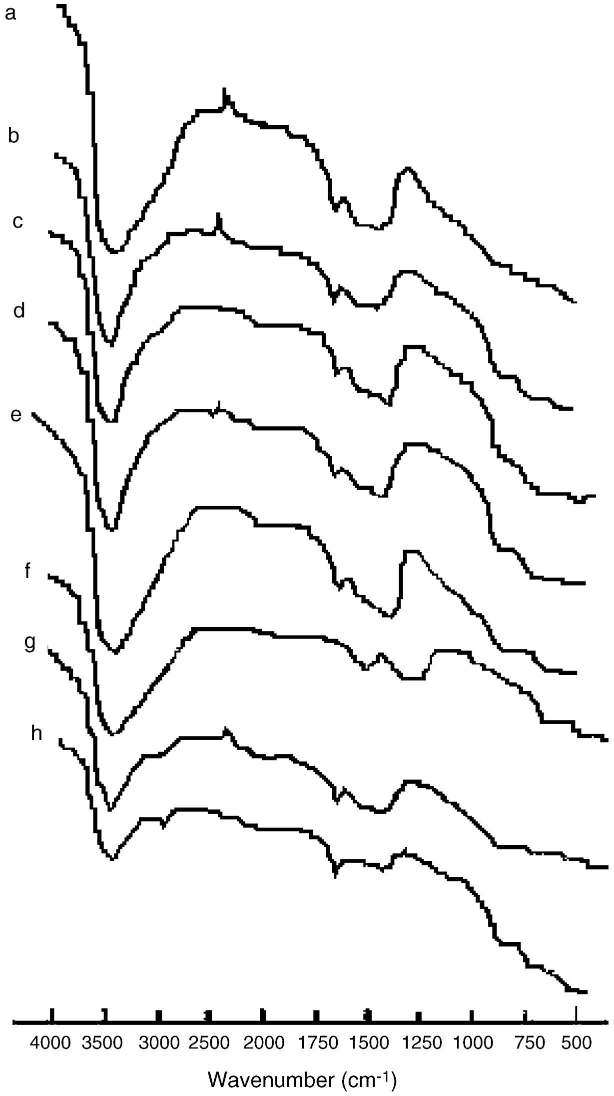

Fig. 9. IR spectra of samples: (a) 2.0HT calcined at 773 K, (b) 2.5HT calcined at 773 K, (c) 3.5HT calcined at 773 K, (d) 4.0HT calcined at 773 K, (e) 3.0HT calcined at 673 K, (f) 3.0HT calcined at 773 K, (g) 3.0HT calcined at 873 K and (h) 3.0HT calcined at 973 K.

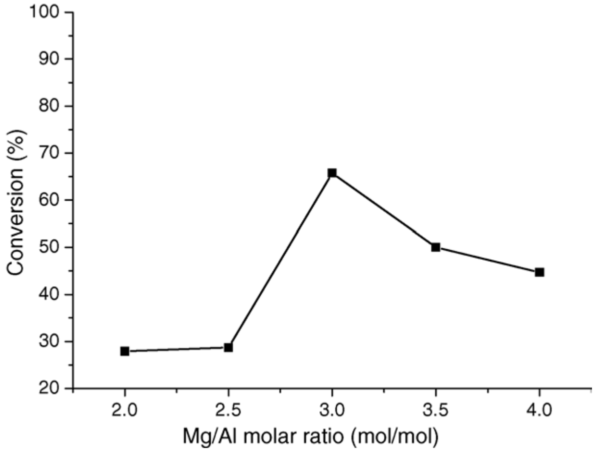

Fig. 10. Influence of Mg/Al molar ratio of calcined hydrotalcites on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5%, reaction time 9 h and methanol reflux temperature.

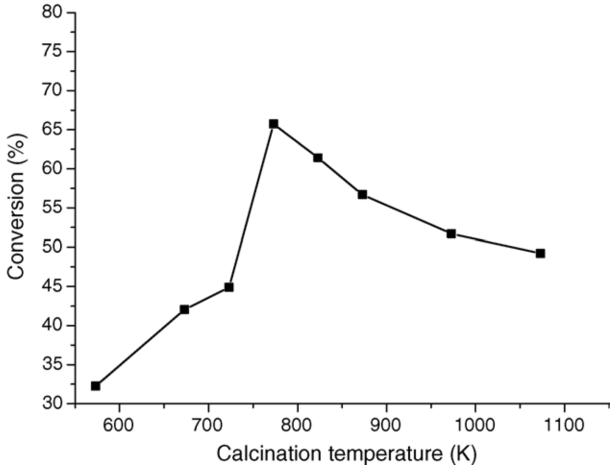

Fig. 11. Influence of calcination temperature on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5%, reaction time 9 h and methanol reflux temperature.

temperature was higher than 773 K, resulting in lower basicity and corresponding to the formation of the spinel phase, the conversion dropped considerably. When being calcined at 773 K, the catalyst exhibited the highest basicity and, for this reason the highest activity in the process of soybean oil methanolysis, giving a maximum conversion of 66%.

The temperature of 773 K is probably the optimum temperature for calcination of 3.0HT. Under this temperature, Al^{3+} substitutes isomorphously Mg^{2+} at the highest level, and Mg^{2+} coordinates with O^{2-} as most as possible. However, the basicity of coordination of Mg^{2+} with O^{2-} is higher than that of Al^{3+} with O^{2-} [26,38]. Consequently, it has the most active centres and highest catalytic activity when 3.0HT calcined at 773 K. But when the hydrotalcite is calcined above 773 K, the bulk $MgAl_2O_4$ spinel phase is formed, and due to this, the catalytic activity decrease. Such effect of calcination temperature on the catalytic activity has already been reported in the literature for the aldol condensation reaction [38].

3.3. *Influence of variation of reaction parameters on the soybean oil methanolysis*

On account of the highest activity of 3.0HT calcined at 737 K in the methanolysis reaction, the influences of various reaction conditions were studied to optimize the reaction procedure.

Stoichiometrically, the methanolysis of soybean oil requires three moles of methanol for each mole of oil. However, in practice, 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. It is observed that lower molar ratio required longer reaction period. Fig. 12 reflects the effect of methanol/oil molar ratio on the conversion. As shown in this figure, by increasing the methanol amount, the conversion was increased considerably. The conversion reached the maximum value when the methanol/oil molar ratio was very close to 15:1. Beyond the molar ratio of 15:1, the excessively added methanol had no significant effect on the conversion. Therefore, we could conclude that to elevate the

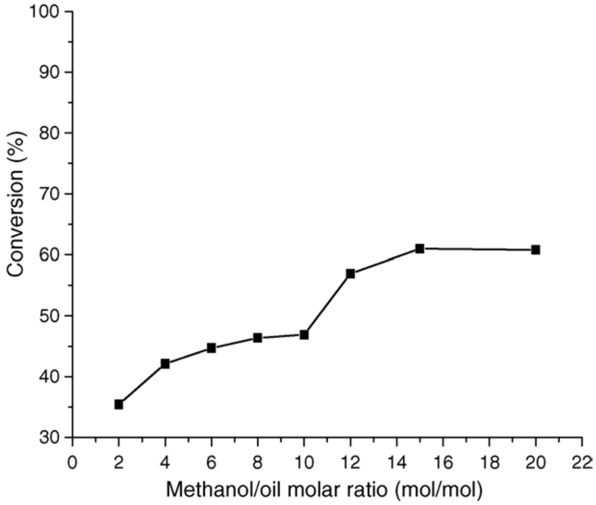

Fig. 12. Influence of methanol/oil molar ratio on the conversion. Reaction conditions: catalyst amount 6.3%, reaction time 7 h and methanol reflux temperature.

conversion an excess methanol feed was effective to a certain extent.

The effect of the catalyst amount was investigated. The catalyst amount is varied in the range of 1.0–9.0%. These percentages are weight fractions of the oil supplied for this reaction. The reaction profiles of Fig. 13 indicate that the conversion of soybean oil was increased first with the increase of catalyst amount from 1.0 to 7.5%. However, with further increase in the catalyst amount the conversion was decreased, which was possibly due to the rise of mixing problem of reactants, products and solid catalyst. At 7.5% catalyst amount, high conversion of up to 66% was obtained.

The rate of methanolysis reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Commonly, the methanolysis is conducted close to the boiling point of methanol at atmospheric pressure. In Fig. 14, the conversion versus reaction time is presented. It can be seen that the conversion increased steadily with reaction time and then reached a plateau value representative of a nearly equilibrium conversion. A nearly maximum conversion of 65% is obtained after 9 h reaction time.

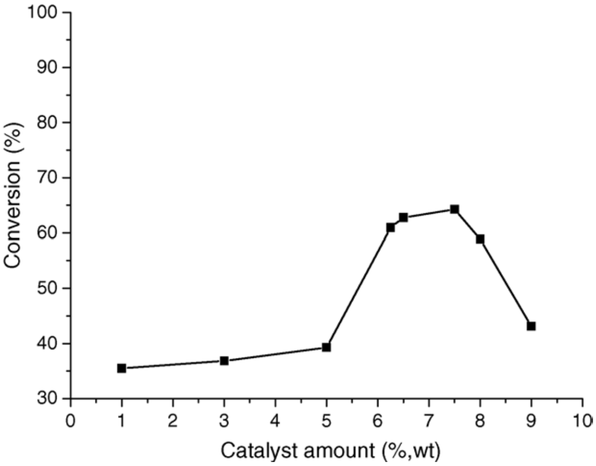

Fig. 13. Influence of catalyst amount on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, reaction time 7 h and methanol reflux temperature.

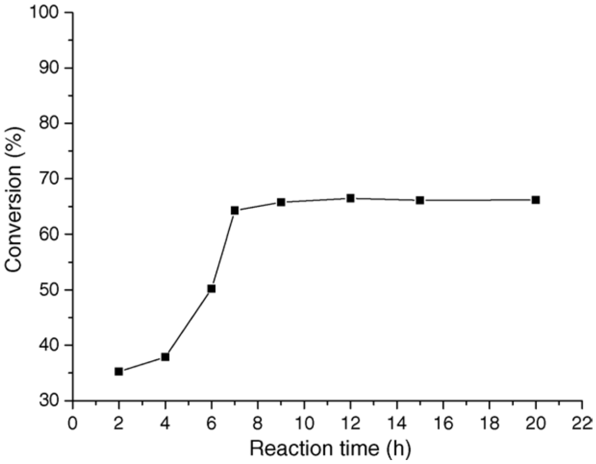

Fig. 14. Influence of reaction time on the conversion. Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 7.5% and methanol reflux temperature.

The effect of mixing was also investigated. Basically, since methanol and soybean oil are immiscible, the reactants initially form a three-phase system, oil/methanol/catalyst. Accordingly, the methanolysis reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. Generally, the faster stirring speed causes better contact among the reactants and solid catalyst, resulting in the increase of reaction rate. Thus, the methanolysis reaction was carried out at two randomly chosen stirring speeds (100 and 600 rpm). At lower stirring speed, the oil conversion reached only 34.8% after 9 h of reaction, whereas at 600 rpm the oil conversion reached 65.8% at the same reaction conditions. This results showed that an efficient mixing of the reagents was essential to reach a high conversion of the oil.

4. Conclusions

For the transesterification of soybean oil with methanol, calcined Mg–Al hydrotalcite was found effective as catalyst. When the reaction was carried out at reflux of methanol, with a molar ratio of soybean oil to methanol of 15:1, a reaction time 9 h, and a catalyst amount 7.5%, the conversion of soybean oil was 67% over 3.0HT. The catalytic activities of the calcined hydrotalcites show a striking correlation with their corresponding basic properties towards soybean oil transesterification. The prepared catalyst were characterized with Hammett indicator-benzene carboxylic acid titration, SEM, DTA-TG, IR and XRD, showing that the strong Bronsted basic site (hydroxyl groups) in double layers and the presence of coordinatively unsaturated O^{2-} ion acting as Lewis basic sites in calcined hydrotalcites may be responsible for their catalytic activities.

Even though the reported conversions are low and thus are not of practical value, the use of this heterogeneous catalyst is advantageous because of its easy separation from the product. Now, in our laboratory, different ways of improving the conversion are under investigation. Either through studies at higher temperatures and pressures or the use of modified hydrotalcite leading to higher basicity, it would be expected to improve the conversions greater than 90% that are of commercial interest.

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