

Preparation of Mg-Al Hydrotalcite by Urea Method and Its Catalytic Activity for Transesterification

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Layered double hydroxides based on the structure $(Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O)$ were synthesized by urea hydrolysis method and characterized by XRD, FTIR, SEM, and EDS. The results revealed that pH played a crucial role in the Mg-Al hydrotalcite precipitation by controlling $[urea]/[NO_3^-]$ molar ratio in reaction solution at 378 K and the optimized $[urea]/[NO_3^-]$ molar ratio was 4.0. The sample calcined at 773 K was used as a solid catalyst for biodiesel synthesis. The catalyst was found to have a high catalytic activity in transesterification of rape oil to methanol with about 94% oil conversion at 338 K for 3 h. The water content of the oil could be kept below 2.0 wt % and free fatty acid content of the oil could be kept below $3.0 \text{ mg KOH} \cdot \text{g[oil]}^{-1}$ in order to get the best conversion. So, the solid catalyst was more tolerant to free fatty acid and water in rape oil than homogeneous basic-catalysts. Moreover, the catalyst could be reused, but catalytic activity decreased on reuse of the catalyst although it remained highly active for the five uses. © 2009 American Institute of Chemical Engineers *AICHE J*, 55: 1229–1235, 2009

Keywords: Mg-Al hydrotalcite, urea hydrolysis, preparation mechanism, crystalline

Introduction

Hydrotalcites, a class of the naturally occurring clay minerals, are layered double hydroxides (LDHs) of magnesium and aluminum ions with the general formula given as $[Mg_{1-x}Al_x(OH)_2]^{x+}(A_{x/n})^{n-} \cdot yH_2O$, where A^{n-} is the compensating anion (CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , organic anions), and y is the content of co-intercalated water. The parent material hydrotalcite of this class is the naturally occurring mineral hydrotalcite, which has the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, and LDHs are consequently also known as hydrotalcites or, more accurately, hydrotalcite-like materials. LDHs have been found to be a wide variety of uses including anion exchangers, adsorbents, catalysts and catalyst supports, and additives to plastics.¹ Mg-Al hydrotalcites have been also used as precursors of catalysts and have attracted

much attention during the development of new environmentally friendly catalysts. Thermal decomposition of these materials by calcination above 723 K results in the formation of basic mixed oxides with high surface areas. They were reported to be potential candidates in the synthesis of a variety of fine chemicals.^{2,3} For example, the calcined Mg-Al hydrotalcite is adopted for alcoholysis of vegetable oil to produce biodiesel which is an alternative fuel for diesel engines. Biofuels are nontoxic, biodegradable and free of sulfur and carcinogenic compounds, as they are obtained from renewable sources.

Generally, LDHs materials are commonly prepared by the constant pH co-precipitation method.⁴ The drawback of the method is that the instantaneous pH value is certainly different in different parts of the slurry no matter how fast the stirring speed is. So it is very difficult to obtain hydrotalcites with high crystallinity.¹ And this method often results in strong agglomeration of primary particles in aggregates with a very large distribution of size. Such morphology leads to

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very low specific surface areas and nearly non porosity. Moreover, once the aggregates are formed they are very stable and resistant to de-cohesion even under powerful ultrasonic treatments.⁴ Urea can form a homogeneous solution with metal nitrates at low temperature leading to its high stability. When the temperature of the solution is raised to 363 K, urea begins to decompose slowly and the pH of the solution increases subsequently. This process can sustain the pH in every part of the solution at a homogeneous level and avoid agglomeration of primary particles. Therefore, high crystalline Mg-Al hydrotalcites are synthesized by this method. Preparation of homogeneous particles of hydrotalcite compounds by the urea method leads to materials with better properties for preparation of catalysts.⁴

Biodiesel is synthesized from direct transesterification (alcoholysis) of vegetable oils and animal fat, where the corresponding triglycerides react with a short-chain alcohol, usually methanol in the presence of a catalyst. Although conventional chemical technology using alkaline homogeneous catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides has been applied to biodiesel fuel production, there are several drawbacks to this approach, including difficulties in the recovery of glycerol and potassium and/or sodium salt and the energy-intensive nature of the process. Utilization of basic heterogeneous catalysts for biodiesel production has great potential compared with the homogeneous catalysts.⁵ Many basic solid catalysts were reported to catalyze the transesterification of vegetable oils with methanol, particularly hydrotalcites. Recently, a series of hydrotalcites synthesized using co-precipitation were reported to catalyze the alcoholysis. The Mg-Al hydrotalcite with a Mg/Al molar ratio of 3.0 catalyzed the alcoholysis of glyceryl tributyrate to methanol with 74.8% glyceryl tributyrate conversion at 333 K for 3 h.⁶ For the alcoholysis of soybean oil to methanol, calcined Mg-Al hydrotalcite was found to be an effective catalyst at 333 K where 67% oil conversion was obtained in 9 h.⁵ For alcoholysis of palm oil with methanol, the K-loaded calcined Mg-Al hydrotalcite was an effective basic catalyst giving methyl ester content of 96.9% and yield of 86.6%.⁷ For the alcoholysis of rape oil with methanol, the calcined Mg-Al hydrotalcite with a Mg/Al molar ratio of 3.0 possessed the best catalytic activity with about 90.5% oil conversion.⁸

In the investigation, the process of the formation of Mg-Al hydrotalcite by urea hydrolysis was discussed. The hydrotalcite samples were characterized by XRD, FT-IR, SEM and EDS techniques to study the phase purity, hydroxyl banding, morphology and composition, respectively. The catalytic activities of the calcined hydrotalcite as a catalyst for the alcoholysis of rape oil to methanol were evaluated. In the alcoholysis of rape oil to methanol, calcined Mg-Al hydrotalcite was found to be an effective catalyst at 338 K where about 94% oil conversion was obtained for 3 h.

Experimental

Preparation of the hydrotalcites

All the reagents/reactants used were analytical grade. The urea decomposition method was used to prepare Mg-Al hydrotalcites with a Mg/Al molar ratio of 4.0.

Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in deionized water which added into a three-neck flask. Urea ([urea]/[NO₃⁻] molar ratio of 0.5–6.0) was dissolved in the above solution. The flask was soaked in an oil bath previously heated at 378 K to start the hydrolysis reaction. The pH was measured all along the reaction with an industrial pH electrode for high temperature (Mettler Toledo). The solutions were maintained at 378 K for 10 h under stirring (300 rpm), and then were aged statically at the same temperature for another 18 h. The formed solids were collected by filtration and washed with deionized water and subsequently dried at 373 K for 18 h. Part of the samples ([urea]/[NO₃⁻] molar ratio of 4.0) were calcined at 773 K for 7 h in a muffle furnace for catalytic activity study as a catalyst.

The relative yield of the precipitate (Mg-Al hydrotalcites) was the ratio of practical yield to theoretical yield. The yield was the mass of the precipitate produced after the preparation of Mg-Al hydrotalcites.

Characterization of the hydrotalcites

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-3C ($\lambda = 0.1541\text{\AA}$) with CuK α radiation. FT-IR spectrum was recorded on Perkin-Elmer Spectrum One B instrument using KBr pellet technique. Scanning electron micrograph (SEM) was obtained with a JEOL JSM-6700F instrument and energy Dispersive x-ray spectroscopy (EDS) analysis was performed by a Noran SystemSix instrument. EDS was used to determine elemental composition of the hydrotalcite.

Chemical analysis

The NH₃ was determined by AEROQUAL 500-NH₃ Ammonia Monitor. Acidity (acid value, mgKOH·g⁻¹) was determined by Mettler Toledo 7100Ie Conductivity/Acid-basic Concentration Monitor. Water content was determined by Haino SFY-2100 Microwater meter.

Transesterification reaction

Refined rape oil (acid value 0.5 mg KOH·g[oil]⁻¹; water content 0.2 wt %) and methanol (6:1 molar ratio of methanol to oil) with the calcined Mg-Al hydrotalcite catalyst with Mg/Al molar ratio of 4.0 (1.5%, w/w of oil) were placed into a 500 mL three-angel necked flask equipped with reflux condenser and Teflon stirrer (300 rpm) under atmospheric pressure at 338 K for 3 h. After reaction, the methanol was recovered by a rotary evaporator in vacuum at 318 K. Subsequently, the hydrotalcite catalyst was separated by filtration and the ester layer was separated from the glycerol layer in a separating funnel. The fined ester layer was dried over sodium sulfate and analyzed by gas chromatography on a Perkin-Elmer GC-200 chromatograph with FID detector, equipped with a stainless steel packed column (3 mm × 2 m Silar-9cp). The oven temperature program consisted of: start at 433 K (2 min), ramp at 274.5 K min⁻¹ to 488 K (10 min). Undecanoic acid methyl ester was used as the internal standard.

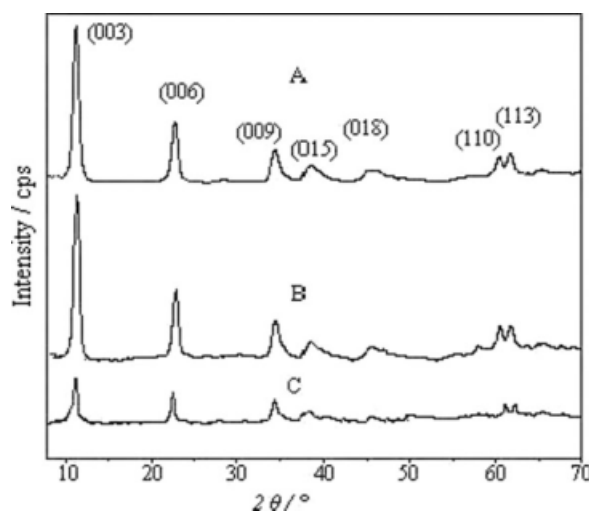


Figure 1. XRD patterns of Mg-Al hydrotalcites with different [urea]/[NO₃⁻] molar ratios.

A: [urea]/[NO₃⁻] = 3.0; B: [urea]/[NO₃⁻] = 4.0; C: [urea]/[NO₃⁻] = 1.0.

Statistical analysis

All the experiments were carried out three times in order to determine the variability of the results and to assess the experimental errors. In this way, the arithmetical averages and the standard deviations (σ) were calculated for all the results.

Results and Discussion

Mg-Al hydrotalcites characterization

The XRD patterns of the Mg-Al hydrotalcites with [urea]/[NO₃⁻] molar ratios of 1.0, 3.0, and 4.0 prepared by the urea method were shown in Figure 1. The XRD patterns of the Mg-Al hydrotalcites were characteristic of hydrotalcite having a layered structure. Although the layered structure with characteristic and symmetric reflections could be obtained when the [urea]/[NO₃⁻] molar ratio was equal to 1.0, the drift of the base line at low 2θ angle indicated that the crystallin-

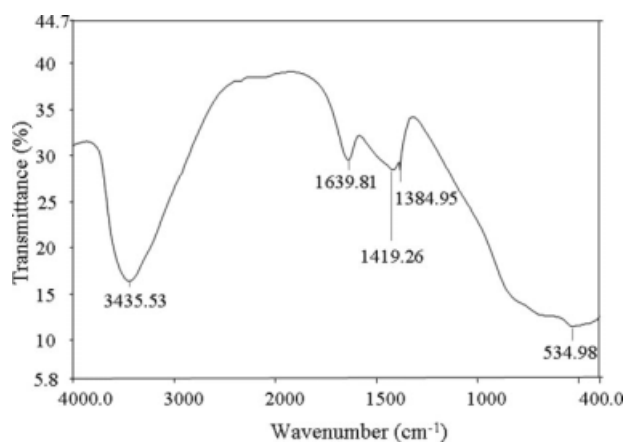


Figure 2. FTIR spectrum of Mg-Al hydrotalcite synthesized by urea method with [urea]/[NO₃⁻] = 4.0.

Table 1. Chemical Composition of Mg-Al Hydrotalcite Sample

	Composition		
	Mg	Al	C
Weight ratio (%)	23.37	9.17	1.88
Molar ratio	9.738	3.396	1.567
Chemical formula	Mg _{6.22} Al _{2.17} (OH) _{16.78} CO ₃ ·4.74H ₂ O		

ity was poor (see Figure 1C). Highly crystalline hydrotalcite was obtained at [urea]/[NO₃⁻] molar ratio of 3.0 and 4.0. There was no significant change in the characteristic reflections between the samples with 3.0 and 4.0 of [urea]/[NO₃⁻] molar ratio (see Figure 1A,B). Further increase of [urea]/[NO₃⁻] molar ratio did not show obvious effects on the crystallinity of the samples. Similar results have been obtained previously by Yang et al.⁹

The FTIR spectrum of the Mg-Al hydrotalcite under a [urea]/[NO₃⁻] molar ratio of 4.0 was shown in Figure 2. The infrared band at about 3435 cm⁻¹ was ascribable to the brucite-like layers (OH⁻ stretching vibration), caused by the interlayer water molecules and hydroxyls groups in the brucite-like layers.¹⁰ The strong band observed in about 1640 cm⁻¹ region (δ -HOH) was due to the H₂O from the interlayer water.^{10,11} The 1384 cm⁻¹ peak corresponded to either carbonate or nitrate group or possibly both.¹² However, nitrate was absent from EDS analysis (see Table 1), leaving us to conclude that the peak corresponds to only carbonate. The peak appearing in the 1420 cm⁻¹ region corresponded with noninterlayer carbonate. The amount of carbonate remaining strongly depended on the Mg content because the basicity of surface oxygen in Mg-containing samples was higher leading to more stable carbonate species.¹³ A SEM micrograph of the Mg-Al hydrotalcite in [urea]/[NO₃⁻] = 4.0 was shown in Figure 3. All the particles were expected hexagonal plate-shaped with narrow size distribution (about 2.5 μ m).

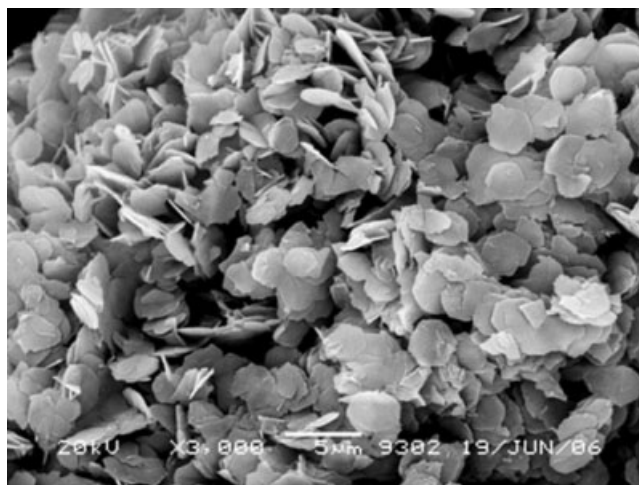


Figure 3. SEM image of Mg-Al hydrotalcite synthesized by urea method with [urea]/[NO₃⁻] = 4.0, 3,000 \times .

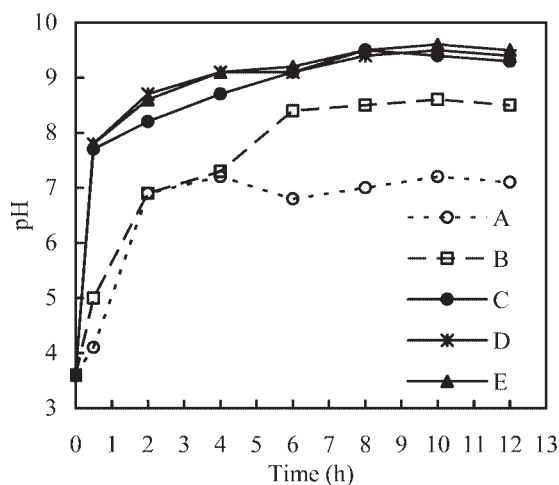


Figure 4. pH in solutions during urea hydrolysis with different $[\text{urea}]/[\text{NO}_3^-]$ molar ratios.

A: $[\text{urea}]/[\text{NO}_3^-] = 0.5$; B: $[\text{urea}]/[\text{NO}_3^-] = 1.0$; C: $[\text{urea}]/[\text{NO}_3^-] = 2.0$; D: $[\text{urea}]/[\text{NO}_3^-] = 3.0$; E: $[\text{urea}]/[\text{NO}_3^-] = 4.0$.

Mechanism of the formation of Mg-Al hydrotalcites

Urea had a number of advantageous properties that made its use as an agent for precipitation from “homogeneous” solution and had been used in gravimetric analysis to precipitate several meta ions as hydroxides or as insoluble salts when in the presence of a suitable anion.¹⁴ Urea is very weak Brønsted base ($\text{p}K_b = 13.8$), highly soluble in water, and its hydrolyzation is controlled by temperature. During the hydrolysis of urea, hydroxide ions were generated in the homogeneous solution (Eq. 1) and worked as precipitants of the metal nitrates.¹⁵

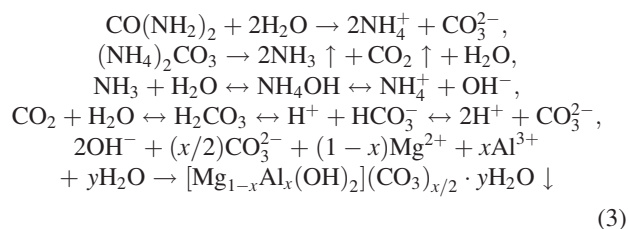


When $[\text{urea}]/[\text{NO}_3^-]$ molar ratio in the reaction solution was below 1.0, the pH of the solution began to rise gradually and reached 7.1 after 4 h, then stayed at about 7.1 (see Figure 4A). No precipitation appeared all the time at 378 K due to the low pH of the solution. In the case of the Mg-Al system, the precipitation of the Mg-Al double hydroxide occurred in the pH range of 7.7–8.5, while the precipitation of $\text{Mg}(\text{OH})_2$ occurred at pH 9.5, and that of $\text{Al}(\text{OH})_3$ at much lower pH 4.0–4.5.¹ Urea was decomposed to form $\text{NH}_3 \cdot \text{H}_2\text{O}$ in aqueous solution when the reaction temperature was more than 363 K, which provided OH^- for reaction.¹⁶ Therefore, the pH of the solution was likely mainly controlled by the amount of urea hydrolysis. The pH was lower (about 7.1) because of lower concentration of urea. Gas evolved from the solution was dissolved into clear $\text{Ca}(\text{OH})_2$ solution. There was precipitation emerging in $\text{Ca}(\text{OH})_2$ solution and no NH_3 was detected by Ammonia Monitor. In the solution (Eq. 2) the following reaction took place:



When $[\text{urea}]/[\text{NO}_3^-]$ molar ratio in the solution was 1.0, the pH of the solution rose and reached 8.4 after 6 h, then maintained

at about pH 8.4 (see Figure 4B). When the pH reached 7.7 after 4.5 h heating, turbidity appeared slowly and gas evolved from the solution, where NH_3 and CO_2 were detected. The relative yield of the precipitate was very lower, about 14.3% ($\sigma = 0.2449$) in a 10 h reaction (see Figure 5). On the other hand, the drift of the base line of the precipitation also indicated that the crystallinity was poor (see Figure 1C). Based on the above description, the precipitation of Mg-Al hydrotalcites occurred according to the following reactions (Eq. 3):



When $[\text{urea}]/[\text{NO}_3^-]$ molar ratio in the solution was above 1.0, the pH of the solution increased rapidly and ascended to about 9.1 after 6 h, then tended to be constant at about 9.6 (see Figure 4C–E) and a mass of gas (NH_3 and CO_2) evolved from the solution. The clear reaction solution turned into slurry when pH increased to about 7.8 after just 0.5 h. The decomposition of $\text{CO}(\text{NH}_2)_2$ maintained the pH of surface of the particles steady, and the dissociation of urea made the pH of the solution increase up to about 9.5. The hydrotalcite particles were obtained at last. In addition, when $[\text{urea}]/[\text{NO}_3^-]$ molar ratio was 4.0, the relative yield of the particles was the highest (see Figure 5). The precipitation compositions with $[\text{urea}]/[\text{NO}_3^-] = 4.0$ were determined by EDS (see Table 1). EDS microanalysis showed Mg, Al and C elements in the sample with a Mg/Al/C molar ratio of about 6/2/1, indicating the removal of the NO_3^- during the growth and assembling of the Mg-Al hydrotalcite crystals. When nitrate was used in the

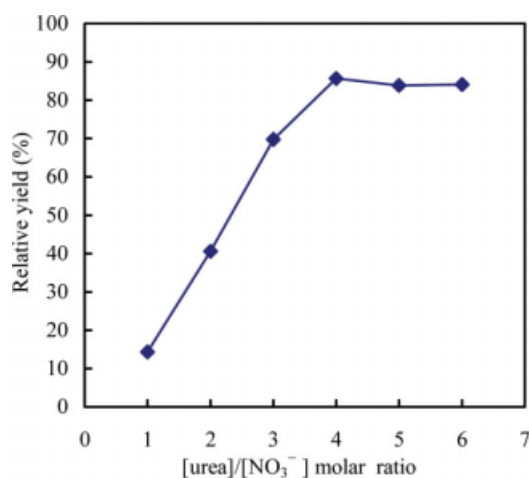
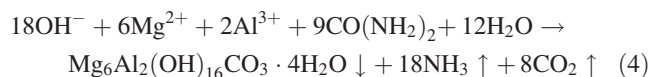


Figure 5. Effect of $[\text{urea}]/[\text{NO}_3^-]$ molar ratio on the precipitation of Mg-Al hydrotalcite for 10 h reaction.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

synthesis by urea method, a large amount of NH_3 was produced from the decomposition of urea at high stated temperature, which would react with NO_3^- . As a result, a large amount of CO_3^{2-} entered the interlayer as main gallery anion.⁹ The type of hydrotalcite $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was formed. The particles could be formed according to the following overall reaction (4):



Formation of crystallites involved two steps, namely stages-nucleation and aging.¹⁷ Precipitation from homogeneous solution using the hydrolysis of urea, which led to a slow increase in pH associated with the formation of ammonia, resulted in well-crystalline Mg-Al hydrotalcites. The nucleating of hydrotalcite was controlled by the hydrolysis of urea. The surface of metal salts solution had low pH at the beginning. The particles sizes were homogeneous due to the existence of a pH gradient. The pH gradient of the solution could be controlled by monitoring $[\text{urea}]/[\text{NO}_3^-]$ molar ratio at highly stated temperature. In the preparation of the hydrotalcite, pH increased from 3.6 of the solution to higher values (see Figure 4), and aluminum hydroxide started to form even at pH 4.0, and could remain and contaminate the hydrotalcite that formed at higher pH (above 7.7). The aluminum ions became $\text{Al}(\text{OH})_4^-$ that dissolved in the solution in the low pH (below 7.7).¹⁸ The nucleation depended on the hydrolysis reaction period and the final pH value. Major uptake of magnesium into hydrotalcite did not occur until the pH plateau reached 7.7. This suggested that hydrotalcite was preferentially formed by the reaction between Mg^{2+} and $\text{Al}(\text{OH})_4^-$, and the Mg^{2+} ions were adsorbed at the surface of the aluminum hydroxide precipitates.¹⁸ After 10 h precipitation reaction, the nucleation stage of Mg-Al hydrotalcites was finished, and then the Mg-Al hydrotalcite particles turned into aging stage. However, the Mg-Al hydrotalcites formation mechanism on aluminum hydroxide has not been clarified at present.

In addition, $[\text{urea}]/[\text{NO}_3^-]$ molar ratio in the reaction solution also affected the yield of the precipitation. The $[\text{urea}]/[\text{NO}_3^-]$ molar ratio was varied in the range of 1.0–6.0 for six different values (1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 of molar ratio). The effect of $[\text{urea}]/[\text{NO}_3^-]$ molar ratio on the relative yield of the precipitate was shown in Figure 5. The relative yield of the precipitate increased with increasing $[\text{urea}]/[\text{NO}_3^-]$ molar ratio in the range of the molar ratios from 1.0 to 4.0, then reached a plateau, where the precipitating process attained the maximum relative yield (about 85.7%, $\sigma = 0.2867$). So, the optimal $[\text{urea}]/[\text{NO}_3^-]$ molar ratio was 4.0 for the Mg-Al hydrotalcite precipitation reaction after 10 h.

Catalytic activity of Mg-Al hydrotalcite

In the work reported here, the activity of the solid base catalyst (calcined Mg-Al hydrotalcite prepared in $[\text{urea}]/[\text{NO}_3^-]$ molar ratio of 4.0) was investigated to determine its suitability for producing biodiesel. The alcoholysis of rape

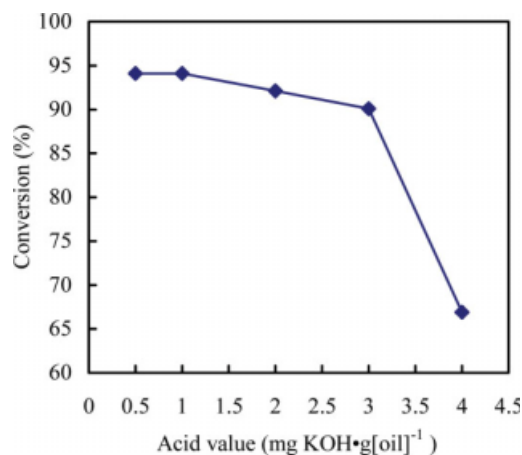


Figure 6. Effect of free fatty acid in rape oil on the catalyst activity.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

oil to methanol was carried out with the catalyst. The catalyst showed a highly catalytic activity and gave about 94% ($\sigma = 0.2055$) oil conversion (mass conversion of rape oil). Its activity was higher than that of the catalyst (about 90.5% oil conversion) synthesized by co-precipitation method in our previous works.⁸

In the alcoholysis catalyzed by homogeneous basic-catalysts such as NaOH or KOH, the vegetable oil should have an acid value less than 1.0 mg KOH·g[oil]⁻¹, namely free fatty acid content less than 0.5%, and all materials should be substantially anhydrous in order to get the best conversion.^{19–21} As the high level of free fatty acid and water content could result in soap formation, which consumed the catalyst and reduced catalyst efficiency.²⁰ The presence of water had a greater negative effect than that of the free fatty acid. So, the water content should be kept below 0.06 wt %, much lower than the allowable free fatty acid content.²¹ Because of the important effect of water and free fatty acid on the alcoholysis catalyzed by homogeneous basic-catalysts, their effects on the oil conversion by the solid catalyst were studied.

Refined rape oil found to be 0.5 mg KOH·g[oil]⁻¹ acid value was adjusted with oleic acid from 0.5 mg KOH·g[oil]⁻¹ to 1.0, 2.0, 3.0, and 4.0 mg KOH·g[oil]⁻¹ of acid value. Under the same reacting conditions, the effect of acid value in the rape oil on oil conversion catalyzed by the solid catalyst was shown in Figure 6. As can be seen, the oil conversion declined with increase in acid value of the oil. The acid value of less than 3.0 mg KOH·g[oil]⁻¹ resulted in oil conversion above 90.1% ($\sigma = 0.2055$) after 3 h reaction. Up to an acid value 3.0 mg KOH·g[oil]⁻¹, the oil conversion decreased rapidly. With acid value 4.0, the oil conversion was much lower and only attained 66.9% ($\sigma = 0.2082$) for 3 h reaction. So, successful catalytic transesterification was obtained at acid value less than 3.0 mg KOH·g[oil]⁻¹ in the oil. It was higher than the value recommended (<1.0 mg KOH·g[oil]⁻¹, catalyzed by homogeneous basic-catalysts) reported in the literature.²¹

Water content was an important factor in the alcoholysis of vegetable oils. Figure 7 showed a direct comparison of the oil conversion of methanol to the oil with various water contents. Several tests at higher water contents were carried out to study the effect of water on the oil conversion. Rape oil containing 0.2 wt % water was diluted with water from 0.2 wt % to 1.0, 2.0, 3.0, and 4.0 wt %. It was seen that the conversion decreased with increase in water content. There was no significant difference between the conversions under the 2.0 wt % water content, the oil conversion above 92.7% ($\sigma = 0.1247$) for 3 h reaction. So as high as 2.0 wt % water content in rape oil did not greatly affect the conversion. Up to 2.0 wt % water content, the alcoholysis reaction could still be catalyzed by the catalyst, but the conversion was much lower and decreased to 79.8% ($\sigma = 0.2014$) at water content of 3.0 wt % and 69.8% ($\sigma = 0.1547$) at water content of 4.0 wt % for 3 h reaction. The above results showed that rape oil used in the alcoholysis by the solid catalyst could contain a high water content (≤ 2.0 wt %) and free fatty acid (≤ 3.0 mg KOH·g[oil]⁻¹). Hence, the catalyst was more tolerant to free fatty acid and water in the oil than homogeneous base catalysts.

Another important issue concerning the use of the solid catalyst was its reusability and stability under reaction conditions. To gain insight into this issue, we performed seven runs using of the catalyst after filtration, and then washing with methanol for removing the ester and glycerol attaching the catalyst. The results were shown in Figure 8. It was found that the catalyst became deactivated after each run. However, the catalyst could be recycled without obvious loss in activity and could be kept over 91% oil conversion in the five recycle experiments for 3 h reaction. After five uses, the activity of the catalyst decreased sharply, giving a 78.7% ($\sigma = 0.1642$) oil conversion in the 6th recycle and 69.7% ($\sigma = 0.2153$) in the 7th recycle. The reusability and stability of the catalyst synthesized by urea were higher than those of the catalyst synthesized by co-precipitation in our previous works.⁸ In our previous researches, it was found that the catalyst synthesized by co-precipitation could only be recycled

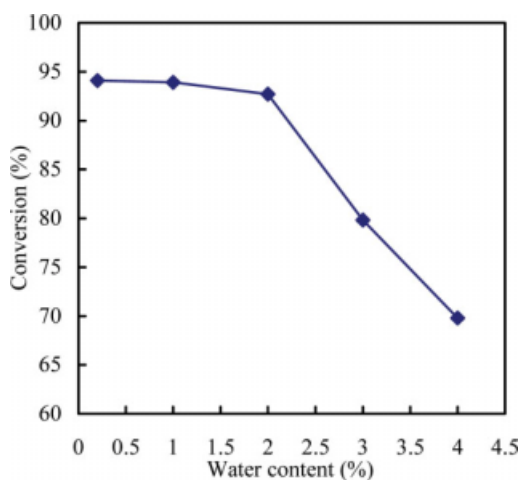


Figure 7. Effect of water content in rape oil on the catalyst activity.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

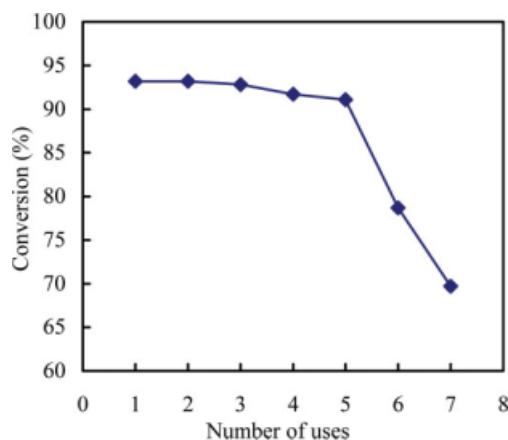


Figure 8. Effect of the number of uses on the catalyst activity.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

without appreciable loss in activity and kept over 88.0% oil conversion in the three recycle experiments.⁸ So, the catalyst in the present work had high reusability and stability in the process.

Activated Mg-Al hydrotalcite synthesized by urea hydrolysis had a higher activity than the corresponding sample synthesized by co-precipitation method in our previous works⁸ and the similar results were also reported by other researchers.^{22,23} One reason for the enhanced activity in the urea hydrolysis sample as a catalyst for the transesterification reaction may be that the catalyst showed better crystallinity in the XRD and SEM data.^{16,23,24} High crystallinity prevented the formation of a poorly lamellar structure of calcined Mg-Al hydrotalcite and the loss of the lamellar structure was the main cause of the catalyst deactivation.²⁴ However, the mechanism for a higher activity of the catalyst prepared by urea hydrolysis compared with those synthesized by co-precipitation method was amphibolous.²² So, further work is in progress to understand the mechanism of the reaction over the Mg-Al hydrotalcite catalyst and check if the basicity of the catalyst has any role to play.

Conclusion

A layered double Mg-Al hydrotalcite with high crystallinity was synthesized by a homogenous precipitation method utilizing urea hydrolysis. The urea method was an efficient pH control method by adjusting [urea]/[NO₃⁻] molar ratio in the solution for the synthesis of hydrotalcite at 378 K. When [urea]/[NO₃⁻] molar ratio in the preparation solution was 1.0 or above 1.0 at 378 K, hydrotalcite particles were obtained and the optimal [urea]/[NO₃⁻] molar ratio for the precipitation reaction was 4.0. Taking all the information obtained from the calcined Mg-Al hydrotalcite as a catalyst into account, we can finally conclude that the catalyst have high activity in transesterification of rape oil to methanol and the rape oil used in alcoholysis could have a high water content (≤ 2.0 wt %) and free fatty acid (≤ 3.0 mg KOH·g[oil]⁻¹). In addition, the catalyst could be reused with the retention of its high catalytic activity in the five uses.

Acknowledgments

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