Effect of Preparation Method on the Catalytic Property of Calcined Ca–Al Hydrotalcite for the Synthesis of Ethyl Methyl Carbonate

Xi Zhou* and Chao Zhang

ABSTRACT: Calcined Ca–Al hydrotalcites were prepared by a clean method (CaAl-1) and coprecipitation (CaAl-2), respectively. Effects of preparation methods on the structure and catalytic property of calcined Ca–Al hydrotalcites were investigated. The samples were characterized by X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), thermogravimetric (TG), CO₂-programmed temperature desorption method (CO₂-TPD), low-temperature N₂ adsorption–desorption, and the Hammett indicator method. Compared with CaAl-2, CaAl-1 had a higher specific surface area and surface alkali density, which makes it have relatively higher catalytic activity for transesterification synthesis of ethyl methyl carbonate (EMC). Also, a 50.6% yield of EMC was obtained in the presence of 1.5% CaAl-1 at 100 °C in 1 h. Moreover, the catalytic activity of CaAl-1 showed no remarkable change after five runs.

INTRODUCTION

As an important class of solid base catalysts, calcined hydrotalcite has the advantages of strong alkalinity, high surface alkali content, low cost, and easy separation. It is widely used in alkali-catalyzed reactions such as transesterification of biodiesel and organic carbonates. Compared with the commonly calcined Mg–Al hydrotalcite, the calcined Ca–Al hydrotalcite shows higher alkaline strength. Nowadays, calcined Ca–Al hydrotalcite with a Ca/Al ratio of 2 is more commonly used in the field of catalysis by previous literature works. Zheng et al. prepared calcined Ca–Al hydrotalcite with a Ca/Al ratio of 1–6 by the coprecipitation method and applied it to the reaction of dimethyl carbonate (DMC) and glycerol to synthesize glycerol carbonate through transesterification. Among the catalysts investigated, the calcined Ca–Al hydrotalcite with a Ca/Al ratio of 2 showed the best catalytic performance, with a glycerol conversion of 93% and a selectivity of glycerol carbonate of 98%. Granados-Reyes et al. found that the calcination temperature and time had a significant influence on the structure, composition, and surface alkaline strength of calcined Ca–Al hydrotalcite and further affected its catalytic performance. However, the calcined Ca–Al hydrotalcite solid base catalysts reported in the above literatures are all prepared by the coprecipitation method using metal salt solutions and alkali solutions as raw materials. In the preparation process of the coprecipitation method, about 30 tons of salt-containing (such as NaCl and Na₂SO₄) wastewater is generated for each ton of Ca–Al hydrotalcite produced, which causes serious environmental pollution. Moreover, the specific surface area and surface alkali density of the prepared catalyst are low, and the catalytic performance needs to be further improved.

Herein, calcined Ca–Al hydrotalcite was prepared by a clean method using Ca(OH)₂, Al(OH)₃, and CO₂ as raw materials. The differences in structure, surface alkali strength, and alkali density between the calcined Ca–Al hydrotalcite prepared by the clean method and traditional coprecipitation method were investigated. Synthesis of ethyl methyl carbonate (EMC) via transesterification was used as a probe reaction to explore the effects of preparation methods on the catalytic property of the calcined Ca–Al hydrotalcite.

RESULTS AND DISCUSSION

Catalyst Characterization. HC-1 prepared by the clean method and HC-2 prepared by the coprecipitation method were characterized by X-ray diffraction (XRD). As shown in Figure 1, XRD patterns of HC-1 and HC-2 have characteristic diffraction peaks at 2θ of about 12 and 24°. In addition, the characteristic diffraction peaks of HC-1 at 2θ = 18° belong to unreacted Al(OH)₃. Also, there are characteristic diffraction peaks of HC-1 and HC-2 at 2θ = 29°, indicating that they all contain a small amount of CaCO₃ impurity. By comparison with standard cards and combined with reports in the
literature. HC-1 and HC-2 have typical Ca–Al hydro-talcite structures. Compared with HC-2, the characteristic diffraction peak of HC-1 is sharp and symmetrical, indicating that its crystallinity is relatively high.

Figure 2 shows the XRD patterns of CaAl-1 obtained after roasting HC-1 and CaAl-2 obtained after roasting HC-2 at 600 °C. After calcination, the characteristic diffraction peaks of CaAl-1 and CaAl-2 disappear or weaken at 2θ of about 12 and 24°. Also, strong characteristic diffraction peaks appear at 2θ = 29, 39, and 49°. It shows that the layered structure of Ca–Al hydro-talcite is destroyed after calcination and converted into Ca–Al composite oxide (Ca12Al14O33) and CaO, which is consistent with the results reported in the literature. The diffraction peak of CaAl-1 is higher than that of CaAl-2, indicating that the crystallinity of CaAl-1 is higher.

The thermogravimetric (TG) characterization results of HC-1 and HC-2 are shown in Figure 3. The TG curve of HC-1 mainly consisted of three stages, which are similar to the results reported in the literature. The first stage of 90–230 °C was due to the loss of recrystallized water (0.4% weight loss ratio), the second stage of 230–430 °C was attributed to the removal of an intercalated hydroxyl group and carbonate ion (8.8% weight loss ratio), and the third stage of 650–830 °C might be due to the decomposition of CaCO3. The TG curve of HC-2 also included three stages. The first stage of 90–250 °C was due to the loss of recrystallized water (14.0% weight loss ratio), the second stage of 250–550 °C was attributed to the removal of the intercalated hydroxyl group and carbonate ion (13.5% weight loss ratio), and the third stage of 650–770 °C might be due to the decomposition of CaCO3. The results show that both HC-1 and HC-2 contain three TG stages within 900 °C, but the TG rates of each stage are significantly different, indicating that there are differences in their compositions and structures.

The surface alkali strength and alkali density of solid base catalysts have significant effects on their catalytic activity and selectivity. Therefore, CO2-programmed temperature desorption method (CO2-TPD) was used to characterize the surface alkalinity strength and alkali density of calcined Ca–Al hydro-talcite. As shown in Figure 4, CaAl-1 has CO2 desorption peaks in the ranges of 50–190, 190–300, and 650–800 °C, respectively. There is a CO2 desorption peak in the range of 650–800 °C, indicating that it has a strong base center. CaAl-2 has CO2 desorption peaks in the ranges of 50–150, 150–270, 470–510, and 650–770 °C, respectively. The total surface alkali density of CaAl-1 is higher than that of CaAl-2.

The Ca/Al molar ratio of CaAl-1 and CaAl-2 was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the results are shown in Table 1. There is a difference in the molar ratio of Ca/Al between CaAl-1 and CaAl-2 when the Ca/Al molar ratio of the raw material is 2. The CaAl-1 molar ratio of CaAl-1 is similar to that of the raw material. However, the Ca/Al molar ratio of CaAl-2 is higher than that of the raw material. This may be because part of the aluminum is dissolved in the strong alkaline reaction system for the coprecipitation method. In addition, the surface Ca/Al molar ratio of CaAl-1 and CaAl-2 was evaluated by X-ray photoelectron spectroscopy (XPS). The results showed that the surface Ca/Al molar ratios of CaAl-1 and CaAl-2 were slightly lower than their Ca/Al molar ratios in bulk.

The specific surface area, pore diameter, and pore volume of the calcined Ca–Al hydro-talcite were characterized by low-temperature N2 adsorption–desorption. According to the results in Table 1, Brunauer–Emmett–Teller (BET) specific
surface areas \( (S_{\text{BET}}) \) of CaAl-1 and CaAl-2 are 17.2 and 5.7 m²/g, respectively. The former is about three times as much as the latter. Compared with CaAl-2, the average pore diameter of CaAl-1 is relatively small, but the pore volume is relatively high. The surface alkali strength and density of solid base catalysts have a significant effect on their catalytic activity and selectivity.\(^{15-19}\) The surface alkali strength of CaAl-1 and CaAl-2 are both in the range of 13.4–15.0 (\( \text{H}_2 \)) by the Hammett indicator method. However, the surface alkali density of CaAl-1 is higher than that of CaAl-2, which is consistent with the results by \( \text{CO}_2 \)-TPD. The reason may be that the \( S_{\text{BET}} \) of the former is higher than that of the latter.

**Effect of Preparation Method on the Catalytic Property.** As a kind of important asymmetric carbonate, ethyl methyl carbonate (EMC) can be utilized as a cosolvent in a nonaqueous electrolyte to improve the energy density and discharge capacity of the lithium-ion cells. EMC can be prepared by the transesterification of dimethyl carbonate (DMC) with diethyl carbonate (DEC) over a catalyst.\(^{20-22}\) Herein, the effect of the preparation method on the catalytic synthesis of EMC by calcined Ca–Al hydrotalcite was investigated under the conditions of 1:1 ratio of DMC to DEC, 1.5% catalyst amount (based on the total mass of reactant), 100 °C, and 1 h.

According to the results in Table 2, the EMC yield was 41.9% using CaAl-2 as the catalyst. Under the same reaction conditions, EMC yield increased to 50.6% by replacing CaAl-2 with CaAl-1, which was close to its equilibrium yield.\(^{20-22}\) According to the characterization results (Table 1), \( S_{\text{BET}} \) and surface alkali density of CaAl-1 are higher than those of CaAl-2. This may be the reason for the relatively high catalytic activity of CaAl-1. Compared with mesoporous MgAl\(_2\)O\(_4\), MOF-5, and ZIF-8 reported in the recent literature,\(^{20-22}\) the turnover frequency (TOF) value of CaAl-1 is much higher than that of those solid catalysts with similar EMC yields. It also indicated that CaAl-1 shows excellent catalytic activity for the synthesis of EMC by transesterification.

**Effect of Calcination Temperature on the Catalytic Property.** As shown in Figure 5, calcination temperature has a significant effect on the catalytic synthesis of EMC by calcined Ca–Al hydrotalcite prepared by the clean method. The yield of EMC decreased to 19.7% with a continuous increase in the calcination temperature from 400 to 600 °C. According to the literature reports,\(^{15-18}\) the pore structure of calcined Ca–Al hydrotalcite will collapse and the \( S_{\text{BET}} \) will decrease when the calcination temperature is too high. The results showed that the \( S_{\text{BET}} \) of calcined Ca–Al hydrotalcite decreased to 6.1 m²/g, while the calcination temperature increased to 800 °C. This may be one of the reasons for the decrease in catalytic activity of calcined Ca–Al hydrotalcite.

**Effect of Catalyst Amount on the Yield of EMC.** The effect of catalyst amount on the synthesis of EMC by transesterification of DMC and DEC was investigated, and the result is shown in Figure 6. The yield of EMC increased from 29.5 to 50.6% with increasing calcination temperature from 400 to 600 °C. However, the EMC yield showed no observable change with an increasing catalyst amount, 100 °C, and 1 h.

**Table 1. Effect of the Preparation Method on the Composition and Structure of Calcined Ca–Al Hydrotalcite**

| entry | catalyst | \( \text{Ca}/\text{Al} \) molar ratio | \( \text{Cu}^{2+} \) amount (\%) | \( \text{Fe}^{2+} \) amount (\%) | \( \text{Na}^{+} \) amount (\%) | TOF (h\(^{-1}\)) | ref |
|-------|----------|--------------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------|-----|
| 1     | CaAl-1   | 1.98                                 | 1.91                          | 17.2                          | 5.9                           | 0.059        | this work |
| 2     | CaAl-2   | 2.09                                 | 2.02                          | 5.7                           | 15.5                          | 0.048        | this work |
| 3     | MgAl\(_2\)O\(_4\) | 4.8                                  | 0.5                           | 49.0                          | 212                           | 1.65         | ref |
| 4     | MOF-5    | 2                                    | 3                             | 50.1                          | 87                            | 21           | ref |
| 5     | ZIF-8    | 1                                    | 3                             | 50.7                          | 176                           | 22           | ref |

*Detected by ICP-OES. \(^{4}\)Evaluated by XPS.*

**Figure 5.** Effect of calcination temperature on the catalytic property of the catalyst. Reaction conditions: 0.1 mol DMC, 0.1 mol DEC, 1.5% catalyst amount, 100 °C, and 1 h.

**Figure 6.** Effect of CaAl-1 amount on the yield of EMC. Reaction conditions: 0.1 mol DMC, 0.1 mol DEC, 100 °C, and 1 h.
Effect of Reaction Time on the Yield of EMC. Effect of reaction time on the yield of EMC was investigated under the conditions of the DMC/DEC molar ratio of 1:1, the CaAl-1 dosage of 1.5%, and 100 °C. As shown in Figure 7, the yield of EMC reached 39.1% and the TOF value reached 537 h⁻¹ within 0.5 h, which also indicated that CaAl-1 has excellent catalytic activity for the synthesis of EMC. When the reaction time was extended from 0.5 to 1 h, the yield of EMC increased to 50.6%. Further prolonging the reaction time had no viewable effect on the yield of EMC, indicating that the reaction reached equilibrium within about 1 h.

Reusability Test. The reusability of CaAl-1 for the synthesis of EMC was also investigated in the presence of 1.5% CaAl-1 at 100 °C within 1 h, and the results are shown in Figure 8. The ECM yield showed no remarkable change after CaAl-1 was used five times. In addition, the characterization results showed that the specific surface area and surface alkali density of CaAl-1 did not change significantly after using it five times. The above results indicated that CaAl-1 shows well reusability for the synthesis of EMC.

CONCLUSIONS
The preparation method has a significant effect on the structure and catalytic property of calcined Ca−Al hydrotalcite solid base for EMC synthesis. Compared with CaAl-2 prepared by the traditional coprecipitation method, CaAl-1 prepared by the clean method has a higher specific surface area and surface alkali density, which makes it have relatively higher catalytic activity for transesterification synthesis of EMC. Also, a 50.6% EMC yield was obtained with 351 h⁻¹ TOF value using CaAl-1 as the catalyst. The result provides an alternative method for the preparation of highly efficient calcined hydrotalcite solid base catalysts.

EXPERIMENTAL SECTION
Preparation of Catalysts. Preparation of calcined Ca−Al hydrotalcite by the clean method is as follows. First, Ca(OH)₂ (0.08 mol, 5.9 g) and Al(OH)₃ (0.04 mol, 3.1 g) were added into a reactor containing 200 mL of water. Second, we increased the temperature to 80 °C in an atmosphere of CO₂, turned on mechanical stirring (rotation speed 220 rpm) and stirred for 2 h, and crystallized in a hydrothermal reactor at 90 °C for 19 h. After filtration, drying, and grinding, Ca−Al hydrotalcite was obtained, labeled as HC-1. At last, calcined Ca−Al hydrotalcite was obtained after roasting at 600 °C for 4 h in the air, labeled as CaAl-1.

Preparation of calcined Ca−Al hydrotalcite by the coprecipitation method followed a typical procedure. First, CaCl₂ (0.08 mol, 9.3 g) was added to 80 mL of water to dissolve into salt solution I. NaOH (0.06 mol, 2.5 g), NaAlO₂ (0.04 mol, 5.2 g), and Na₃CO₃ (0.02 mol, 2.1 g) were added to 80 mL of water to dissolve into salt solution II. Second, solution I and solution II were simultaneously dropped into a reactor containing 40 mL of water by a peristaltic pump (driving speed 2300 μL/min), keeping the reaction temperature at 80 °C and stirring continuously. After the solution was dropped, it was stirred for 1 h and then crystallized in a hydrothermal reactor at 90 °C for 19 h. After filtration, drying, and grinding, Ca−Al hydrotalcite was obtained, labeled as HC-2. At last, it was calcined in a muffle furnace at 600 °C for 4 h in air, labeled as CaAl-2.

Characterization of Catalysts. The crystal structure of the catalyst was characterized by X-ray diffraction (XRD). Continuous scanning with Cu Kα ray, scanning range 2θ = 10°−90°, scanning speed 0.03°/s, tube voltage 40 kV, tube current 45 mA. The specific surface area, pore size, and pore volume of the catalyst were determined using the low-temperature N₂ adsorption−desorption method. The bulk composition of catalysts was determined by ICP-OES after the sample was dissolved in HNO₃. The surface composition of catalysts was evaluated by XPS. The specific surface area was calculated using the BET method. Also, the pore size and pore volume were calculated using the Barrett−Joyner−Halenda (BJH) method. Thermogravimetric characterization of the samples from room temperature to 900 °C was performed by a Hoven HCT-1 thermobalance system using a heating rate of 10 °C/min. The surface alkali strength and alkali content of the catalyst were tested according to the CO₂-programmed temperature desorption method (CO₂-TPD) using Ar as the carrier gas. The Hammett indicator method was also used to detect the surface alkali strength and density of the catalyst using Nile blue A (pKₐ = 10.1), tropaeolin O (pKₐ = 11), thiazole yellow G (pKₐ = 13.4), and 2,4-dinitroaniline (pKₐ = 15.0) as indicators.

Synthesis of Ethyl Methyl Carbonate. The typical procedure for the synthesis of ethyl methyl carbonate is as follows. Dimethyl carbonate (9.00 g), diethyl carbonate (11.80 g), and the catalyst (0.312 g) were added to a 50 mL three-necked, round-bottom flask with a stirrer and a refluxing device. Also, the reaction was continued for 1 h at 100 °C.
under continuous stirring. After the reaction was completed, the reaction mixture was quickly cooled to room temperature, and the catalyst was separated by centrifugation. The reaction solution was quantitatively analyzed by GC (Scion 456) equipped with an FID detector and a capillary column (HP-5, 30 m × 320 μm × 0.25 μm).

■ AUTHORIZED INFORMATION

Corresponding Author
Xi Zhou — Department of Food and Chemical Engineering, Shaoyang University, Shaoyang 422000, Hunan, P. R. China; @ orcid.org/0000-0002-6736-7160; Email: z_zhouxi@163.com

Author
Chao Zhang — Department of Food and Chemical Engineering, Shaoyang University, Shaoyang 422000, Hunan, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c06269

Notes
The authors declare no competing financial interest.

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