

### Article

# Transesterification of glycerol with dimethyl carbonate over calcined Ca-Al hydrocalumite



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#### 1. Introduction

### Biodiesel is an important renewable biofuel which can be produced from animal fat and vegetable oil via transesterification. The application of biodiesel can help reduce the dependence on fossil energy. Glycerol is a byproduct in the production of biodiesel, and the rapidly rising production of biodiesel leads to a large surplus of glycerol. The catalytic conversion of glycerol to valuable products has become a hot research topic [1–4]. Several products, such as propanediols [5–10], dihydroxyacetone [11–13], acrolein [14–16], and glycerol carbonate (GC) [17–19], can be synthesized from glycerol. Among these products, GC is one of the most attractive derivatives of glycerol because of its high reactivity with alcohols, amines, carboxylic acids, ketones, and isocyanates, which can yield a wide range of valuable products [20]. GC itself can be used as a solvent in NMR analysis and organic synthesis [20]. In addition,

#### ABSTRACT

A series of Ca-Al hydrocalumite with different Ca/Al ratios (1–6) were synthesized and used in the transesterification of glycerol with dimethyl carbonate (DMC) to glycerol carbonate (GC) under mild conditions. The calcined Ca-Al hydrocalumites were active with a selectivity toward GC that reached 97% at 93% conversion of glycerol over the sample with Ca/Al = 2 at 70 °C, 3 h, and DMC/glycerol = 3. The glycerol conversion depended mainly on the proportion of strong basic sites in the calcined Ca-Al catalysts. The Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> phase in the calcined catalysts was stable, but CaO was lost in recycle experiments and thus brought deactivation.

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> it has been reported that GC is an important alternative solvent in lithium batteries, cosmetics, surfactants, and polymer synthesis [20]. Several routes, such as phosgenation between glycerol and phosgene [21], direct carboxylation of glycerol with CO<sub>2</sub> [22,23], and the glycerolysis of urea [24–28], have been proposed for the production of GC from glycerol. Among these, the direct reaction between glycerol and CO<sub>2</sub> is an attractive route, but it must be performed at high pressure and the yield of GC is low [29,30].

> Transesterification of glycerol with dimethyl carbonate (DMC) is also an attractive way to produce GC under mild conditions [17,18]. It was reported that K<sub>2</sub>CO<sub>3</sub> [31], CaO [32], K-zeolite derived from coal fly ash [33], Mg/Zr/Sr [34] and Mg/Al/Zr [35] mixed oxides were effective for this reaction. The rate of this reaction depended on the basicity of the catalyst [36], but the selectivity of GC decreased when a strong base (such as NaOH, KOH, and K<sub>2</sub>CO<sub>3</sub>) was used because of the for-

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mation of glycidol [37]. More recently, Liu et al. [19] disclosed that the activity of transition metal doped hydrotalcites (HT-M) for the transesterification between glycerol and DMC depended on the surface density of basic sites.

Hydrocalumite is a layered double hydroxide (LDH) with a well ordered Ca-Al distribution in the hydroxide layers, while the anions and water are highly ordered in the interlayer spaces [38,39]. The calcined hydrocalumite-like compound mainly contains Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and CaO, and it shows strong basicity in CO<sub>2</sub> adsorption [40] and in the production of biodiesel via transesterification [41,42]. In this work, a series of Ca-Al hydrocalumite with different Ca/Al ratios (1–6) were synthesized and used in the transesterification of glycerol with DMC to GC under mild conditions. The activity and structure of the calcined hydrocalumite were discussed.

#### 2. Experimental

#### 2.1. Catalyst preparation

Ca-Al hydrocalumite (Ca/Al = 1-6) was prepared by a conventional coprecipitation method. CaCl<sub>2</sub> (12.5-75 mmol) and AlCl<sub>3</sub>·6H<sub>2</sub>O (12.5 mmol) were dissolved in 75 mL deionized water (solution A) [43]. Solution B was an aqueous solution of 2 mol/L NaOH. Solutions A and B were simultaneously added to a 250 mL three-necked flask under a purified N<sub>2</sub> flow at 30 °C with the pH of the mixture controlled at 11 during the addition [44]. The resulting suspension was filtered and washed thoroughly with deionized water until the pH of the filtrate reached about 7.0. The precipitate was dried at 110 °C overnight and calcined at 400–1000 °C for 4 h under a purified  $N_2$ flow. The composition of the Ca-Al hydrocalumites was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The obtained Ca-Al hydrocalumite was denoted as Ca<sub>x</sub>Al-y, in which x represented the molar ratio of Ca/Al and y denoted the calcination temperature.

#### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 diffractometer with a  $2\theta$  range of 5°–80° using Cu  $K_{\alpha}$  radiation ( $\lambda$  = 0.15406 nm). Thermogravimetric differential scanning (TG-DSC) analysis of the samples from room temperature to 800 °C was carried out on a Netzsch STA409 thermobalance system using a heating rate of 10 °C/min under N<sub>2</sub> nitrogen flow. Scanning electron microscopic (SEM) images were obtained on a Leo Evo Series SEM (VP 1430, Germany). Samples were coated with gold to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. The N2 adsorption-desorption isotherm was measured at -196 °C using a TriStar II analyzer after pretreatment of the sample at 150 °C for 10 h. The basicity of the catalyst was determined by temperature-programmed desorption of CO2 (CO2-TPD). In this experiment, the sample was first treated in Ar at 600 °C for 30 min, cooled to 50 °C and exposed to 20% CO2 (50 mL/min, Ar in balance) for 30 min. It was then purged with Ar for 1 h at 100 °C and heated linearly at 15 °C/min to 800 °C in 50

mL/min Ar.  $CO_2$  (*m*/*e* = 44) in the effluent was recorded continuously as a function of temperature.

#### 2.3. Catalytic reaction

Measured amounts of DMC (45 mmol) and glycerol (45 mmol) were mixed in a 10 mL round bottomed glass reactor fitted with a magnetic stirrer and a reflux condenser. The mixture was first heated under stirring to 70 °C, and the catalyst (0.15 g) was added to start the reaction. After reacting for 3 h, the solid catalyst was removed by centrifugation, and the supernatant liquid was analyzed using a gas chromatograph (Shimadzu, 14B) equipped with a 30-m capillary column (DB-WAX 52 CB, USA) and a flame ionization detector. All products detected in the liquid were identified by a gas chromatography-mass spectrometry system (GC-MS, Agilent 6890) and quantified by an external calibration method. The product selectivity was calculated on a carbon basis.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

Figure 1 shows the XRD patterns of the Ca-Al samples. All the diffraction peaks of the (002), (004), (010), and (006) planes of hydrocalumite (Ca<sub>4</sub>Al<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>·10H<sub>2</sub>O, JCPDS 00-031-0245) [44,45] were detected. This result indicates that a hydrocalumite-like compound formed and a high degree of crystallinity was detected in all those samples with Ca/Al = 2–6. On the other hand, Al(OH)<sub>3</sub> (JCPDS 00-033-0018) was formed in Ca<sub>1</sub>Al due to the high content of Al [40].

Figure 2 shows typical SEM images of the Ca-Al hydrocalumites. Solid Ca-Al lamellas were formed in all samples. A clear image of separated lamellas was detected in Ca<sub>2</sub>Al and Ca<sub>3</sub>Al. The platelet in Ca<sub>6</sub>Al was smaller and an amorphous solid (in white circle) was formed in Ca<sub>1</sub>Al. The peony-shaped crystal in Ca<sub>2</sub>Al showed the rough outline of hydrocalumite. The high resolution image of this sample is shown in Fig. 2(c). We can also see some "rosette" particles in Ca<sub>3</sub>Al (Fig. 2(d)) [46].



**Fig. 1.** XRD patterns of fresh Ca-Al hydrocalumite with different Ca/Al ratios. (1) Ca<sub>1</sub>Al; (2) Ca<sub>2</sub>Al; (3) Ca<sub>3</sub>Al; (4) Ca<sub>4</sub>Al; (5) Ca<sub>6</sub>Al.



Fig. 2. SEM images of fresh Ca-Al hydrocalumite. (a) Ca<sub>1</sub>Al; (b, c) Ca<sub>2</sub>Al; (d, e) Ca<sub>3</sub>Al; (f) Ca<sub>6</sub>Al.

Figure 3 presents the TG-DSC curves of the hydrocalumite (Ca<sub>2</sub>Al). The TG curve indicated that there were four stages of weight losses at 50–152, 265–329, 420-494, and 600–750 °C. The first stage was attributed to the removal of adsorbed water, the second stage was due to the loss of bound water or chloride in the interlayer of the hydrocalumite [47], and the third and the fourth stage was attributed to the further removal of hydroxyl groups. At the same time, an exothermic peak was detected at 786 °C without obvious weight loss, which was attributed to the decomposition of layered Ca<sub>4</sub>Al<sub>2</sub>O<sub>7</sub> to Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and CaO [48,49].

Figure 4 shows the XRD patterns of Ca-Al hydrocalumite calcined at different temperatures for 4 h. The peaks assigned to the (002), (004), and (006) planes of hydrocalumite disappeared with the loss of water, chloride, and hydroxide after



Fig. 3. TG-DSC curves of the hydrocalumite (Ca<sub>2</sub>Al).



Fig. 4. XRD patterns of synthesized Ca-Al hydrocalumite (Ca<sub>2</sub>Al) (1) and calcined at 400  $^{\circ}$ C (2), 600  $^{\circ}$ C (3), 800  $^{\circ}$ C (4), and 1000  $^{\circ}$ C (5).

calcination at 400 °C. A broad peak at  $25^{\circ}$ - $35^{\circ}$  in the sample calcined at 600 °C was attributed to the formation of amorphous CaO due to the partial collapse of layered structure. Calcination above 800 °C led to the generation of mayenite Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> (JCPDS 00-048-1882) [39,50]. These results fitted well the TG-DSC analysis.

Figure 5 shows the typical SEM image of hydrocalumite (Ca<sub>2</sub>Al) calcined at 800 °C for 4 h. It is obvious that the layered structure was broken and the lamellas had accumulated as one hard stone.

Figure 6 presents the CO<sub>2</sub>-TPD profiles of Ca<sub>2</sub>Al hydrocalumite calcined at different temperatures. The desorption profiles were deconvoluted to incorporate two kinds of basic sites. The first (250 to 600 °C) was ascribed to the desorption of CO<sub>2</sub> adsorbed on the surface of LDH lamella and Lewis basic sites of Ca in the LDH framework [49,50]. The proportion of these basic sites was higher in the samples calcined at 400 and 600 °C. The second peak (desorbed above 600 °C) was attributed to the desorption of CO<sub>2</sub> adsorbed on CaO and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. The proportion of these basic sites was calculated and summarized in Table 1. The calculated amount of total basic sites decreased along with the surface area when the calcination temperature was increased from 400 to 1000 °C. But it is interesting to note that the proportion of strong basic sites reached a maximum value (56.9 µmol/g) when the sample was calcined at 800 °C.



Fig. 5. SEM image of Ca<sub>2</sub>Al hydrocalumite calcined at 800 °C for 4 h.



Fig. 6.  $CO_2$ -TPD profiles of Ca<sub>2</sub>Al hydrocalumite calcined at 400 °C (1), 600 °C (2), 800 °C (3), and 1000 °C (4).

#### Table 1

Surface area and basicity of hydrocalumite (Ca<sub>2</sub>Al) calcined at different temperatures.

+ /0C	$S_{\text{BET}}$	Desorbed CO <sub>2</sub> <sup>a</sup> (µmol/g)		Basicity density of strong		
ίζ	(m²/g)	250-600 °C	> 600 °C	basic sites <sup>b</sup> (µmol/m <sup>2</sup> )		
400	13.7	155.4	20.7	1.5		
600	6.4	53.8	24.0	3.7		
800	5.5	28.4	56.9	10.3		
1000	1.6	0.6	13.1	8.2		
A Determined by CO TADD						

<sup>a</sup> Determined by CO<sub>2</sub>-TPD.

<sup>b</sup> Calculated by desorbed CO<sub>2</sub> at > 600 °C/S<sub>BET</sub>.

#### 3.2. Catalytic reactions

# 3.2.1. Transesterification of glycerol over Ca<sub>2</sub>Al calcined at different temperatures

Figure 7 shows the activity of Ca<sub>2</sub>Al hydrocalumite calcined at different temperatures for the transesterification reaction between glycerol and DMC at 70 °C. The conversion of glycerol increased steadily from 27% to 75% when the calcination temperature rose from 400 to 800 °C, and the selectivity of GC was higher than 97%. The conversion of glycerol and selectivity of GC over the hydrocalumite calcined at 1000 °C decreased to



Fig. 7. Transesterification of glycerol over Ca<sub>2</sub>Al prepared at different calcination temperatures. Reaction conditions: calcined Ca<sub>2</sub>Al 0.15 g, glycerol 45 mmol, DMC 45 mmol, 70  $^{\circ}$ C, 3 h.

63% and 92%, respectively. These results indicated that calcined Ca-Al hydrocalumites were effective catalysts for the transesterification reaction between glycerol and DMC, and strong basic sites were more active. The conversion of glycerol depended mainly on the proportion of strong basic sites (Table 1).

# 3.2.2. Transesterification of glycerol over Ca<sub>x</sub>Al with different Ca/Al ratios

Table 2 summarizes the activity of calcined (at 800 °C for 4 h) Ca<sub>x</sub>Al hydrocalumites with different Ca/Al ratios for the transesterification reaction between glycerol and DMC at 70 °C. The conversion of glycerol increased from 51% to 75% when the Ca/Al ratio increased from 1 to 2. The selectivity to GC remained higher than 96%. However, the conversion of glycerol and the selectivity of GC decreased slowly on the samples with higher Ca/Al ratios (> 3). The characterization disclosed that Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and CaO were formed in the calcined (at 800 °C for 4 h) Ca/Al hydrocalumites. Although CaO can catalyze this reaction, the selectivity of the desired product was low (62%). At the same time, CaO can combine with glycerol and DMC as Ca(C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>)(OCO<sub>2</sub>CH<sub>3</sub>) during the reaction [51]. On the basis of these results, we conclude that Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> derived from calcined Ca/Al hydrocalumite is more selective to GC.

# 3.2.3. Influence of DMC/glycerol molar ratio on the conversion of glycerol

Table 3 summarizes the activity of calcined hydrocalumite (Ca<sub>2</sub>Al, at 800 °C for 4 h) for the transesterification reaction between glycerol and DMC at 70 °C with different feed composition (DMC/glycerol ratio). The conversion of glycerol reached 93% when the DMC/glycerol molar ratio was 3. Further increase in the amount of DMC in the feed did not promote the conversion of glycerol because the intersolubility of DMC and glycerol is low.

#### Table 2

Activity of calcined hydrocalumite with different Ca/Al ratios.

Catalyst	Glycerol conversion (%)	GC selectivity (%)	Glycidol selectivity (%)
Pure CaO	60	62	38
Ca1Al	51	96	4
Ca <sub>2</sub> Al	75	98	2
Ca₃Al	69	93	7
Ca <sub>4</sub> Al	67	94	6
Ca <sub>6</sub> Al	66	91	9

Reaction conditions: catalyst (Ca<sub>x</sub>Al hydrocalumite calcined at 800 °C for 4 h) 0.15 g, glycerol 45 mmol, DMC 45 mmol, 70 °C, 3 h.

#### Table 3

Transesterification of glycerol as a function of DMC/glycerol molar ratio.

DMC/ Glycerol conversion GC selectivity Glycidol se	lectivity
glycerol (%) (%) (%)	)
1 75 98 2	
2 84 97 3	
3 93 97 3	
4 68 98 2	

Reaction conditions: catalyst (Ca<sub>2</sub>Al hydrocalumite calcined at 800 °C for 4 h) 0.15 g, glycerol 45 mmol, 70 °C, 3 h.



**Fig. 8.** Performance of the recycled catalyst (Ca<sub>2</sub>AI). Reaction conditions: glycerol 45 mmol, DMC 90 mmol, 70 °C, 3 h.

#### 3.2.4. Recycling of the catalyst

Figure 8 presents the performance of a recycled catalyst (Ca<sub>2</sub>Al) for the transesterification reaction between glycerol and DMC at 70 °C. The reused catalyst was collected and dried in vacuum for several hours. The conversion of glycerol decreased from 84% to 38% as the recycle number increased. XRD analysis of the 6-time recycled catalyst disclosed that the crystalline structure of Ca12Al14O33 in the recycled catalyst was similar to that of the fresh calcined sample, but the CaO crystalline phase had disappeared (Fig. 9). ICP analysis also confirmed that the content of Ca<sup>2+</sup> decreased from 12.2 mmol/g (in fresh catalyst) to 9.64 mmol/g (in the 6-times recycled catalyst). These results indicated that the deactivation of the calcined Ca-Al hydrocalumite was due to the leaching of Ca and the loss of catalyst during the recycle experiment (the weight of the catalyst decreased from the initial 0.150 to 0.075 g after 6 recycles).

### 4. Conclusions

Ca-Al hydrocalumite (Ca/Al = 2–6) with high crystallinity was synthesized by a conventional coprecipitation method in  $N_2$  atmosphere. Calcined Ca-Al hydrocalumite was an effective catalyst for the transesterification of glycerol with DMC and



Fig. 9. XRD patterns of fresh calcined (1) and 6-times recycled (2) catalyst ( $Ca_2Al$ ).

gave a high selectivity towards GC under mild conditions. The highest conversion of glycerol at 70 °C reached 93% with 97% selectivity to GC over the calcined hydrocalumite Ca<sub>2</sub>Al-800. Characterization disclosed that Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> was stable, but the CaO crystalline phase disappeared during recycle experiments and the leaching of CaO brought deactivation.

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