available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

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

Liping Zheng ^a, Shuixin Xia ^a, Xiuyang Lu ^b, Zhaoyin Hou ^{a,*}^a Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China^b Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China

ARTICLE INFO

Article history:

Received 23 March 2015

Accepted 16 May 2015

Published 20 October 2015

Keywords:

Glycerol

Dimethyl carbonate

Transesterification

Glycerol carbonate

Calcium-aluminum hydrocalumite

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 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase in the calcined catalysts was stable, but CaO was lost in recycle experiments and thus brought deactivation.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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,

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_2 [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_2 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_2CO_3 [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_2CO_3) was used because of the for-

* Corresponding author. Tel/Fax: +86-571-88273283; E-mail: zyhou@zju.edu.cn

This work was supported by the National Natural Science Foundation of China (21473155, 21273198, 21073159) and the Zhejiang Provincial Natural Science Foundation (LZ12B03001).

DOI: 10.1016/S1872-2067(15)60915-9 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 10, October 2015

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 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO, and it shows strong basicity in CO_2 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_2 (12.5–75 mmol) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (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_2 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_xAl_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 2θ range of 5°–80° using $\text{Cu K}\alpha$ 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_2 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 N_2 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 CO_2 (CO_2 -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% CO_2 (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 ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, 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, $\text{Al}(\text{OH})_3$ (JCPDS 00-033-0018) was formed in Ca_1Al 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_2Al and Ca_3Al . The platelet in Ca_6Al was smaller and an amorphous solid (in white circle) was formed in Ca_1Al . The peony-shaped crystal in Ca_2Al 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_3Al (Fig. 2(d)) [46].

Fig. 1. XRD patterns of fresh Ca-Al hydrocalumite with different Ca/Al ratios. (1) Ca_1Al ; (2) Ca_2Al ; (3) Ca_3Al ; (4) Ca_4Al ; (5) Ca_6Al .

Fig. 2. SEM images of fresh Ca-Al hydrocalumite. (a) Ca_1Al ; (b, c) Ca_2Al ; (d, e) Ca_3Al ; (f) Ca_6Al .

Figure 3 presents the TG-DSC curves of the hydrocalumite (Ca_2Al). 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 $\text{Ca}_4\text{Al}_2\text{O}_7$ to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 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_2Al).

Fig. 4. XRD patterns of synthesized Ca-Al hydrocalumite (Ca_2Al) (1) and calcined at 400 °C (2), 600 °C (3), 800 °C (4), and 1000 °C (5).

calcination at 400 °C. A broad peak at 25°–35° 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 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ [JCPDS 00-048-1882] [39,50]. These results fitted well the TG-DSC analysis.

Figure 5 shows the typical SEM image of hydrocalumite (Ca_2Al) 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_2 -TPD profiles of Ca_2Al 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_2 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_2 adsorbed on CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. 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 $\mu\text{mol/g}$) when the sample was calcined at 800 °C.

Fig. 5. SEM image of Ca_2Al hydrocalumite calcined at 800 °C for 4 h.

Fig. 6. CO₂-TPD profiles of Ca₂Al hydrocalumite calcined at 400 °C (1), 600 °C (2), 800 °C (3), and 1000 °C (4).

Table 1

Surface area and basicity of hydrocalumite (Ca₂Al) calcined at different temperatures.

<i>t</i> /°C	<i>S</i> _{BET} (m ² /g)	Desorbed CO ₂ ^a (μmol/g)		Basicity density of strong basic sites ^b (μmol/m ²)
		250–600 °C	> 600 °C	
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 CO₂-TPD.

^b Calculated by desorbed CO₂ at > 600 °C/*S*_{BET}.

3.2. Catalytic reactions

3.2.1. Transesterification of glycerol over Ca₂Al calcined at different temperatures

Figure 7 shows the activity of Ca₂Al 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 Ca₂Al prepared at different calcination temperatures. Reaction conditions: calcined Ca₂Al 0.15 g, glycerol 45 mmol, DMC 45 mmol, 70 °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_xAl with different Ca/Al ratios

Table 2 summarizes the activity of calcined (at 800 °C for 4 h) Ca_xAl 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 Ca₁₂Al₁₄O₃₃ 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(C₃H₇O₃)(OCO₂CH₃) during the reaction [51]. On the basis of these results, we conclude that Ca₁₂Al₁₄O₃₃ 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 (Ca₂Al, 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
Ca ₁ Al	51	96	4
Ca ₂ Al	75	98	2
Ca ₃ Al	69	93	7
Ca ₄ Al	67	94	6
Ca ₆ Al	66	91	9

Reaction conditions: catalyst (Ca_xAl 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	Glycerol conversion (%)	GC selectivity (%)	Glycidol selectivity (%)
1	75	98	2
2	84	97	3
3	93	97	3
4	68	98	2

Reaction conditions: catalyst (Ca₂Al 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_2Al). 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_2Al) 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 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 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^{2+} 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 ($\text{Ca}/\text{Al} = 2\text{--}6$) 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

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_2Al -800. Characterization disclosed that $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ was stable, but the CaO crystalline phase disappeared during recycle experiments and the leaching of CaO brought deactivation.

References

- [1] Pagliaro M, Ciriminna R, Kimura H, Rossi M, Della Pina C. *Angew Chem Int Ed*, 2007, 46: 4434
- [2] Zhou C H, Beltramini J N, Fan Y X, Lu G Q. *Chem Soc Rev*, 2008, 37: 527
- [3] Bozell J J, Petersen G R. *Green Chem*, 2010, 12: 539
- [4] Ide M S, Davis R J. *Acc Chem Res*, 2014, 47: 825
- [5] Maris E P, Ketchie W C, Murayama M, Davis R J. *J Catal*, 2007, 251: 281
- [6] Vasiliadou E S, Eggenhuisen T M, Munnik P, de Jongh P E, de Jong K P, Lemonidou A A. *Appl Catal B*, 2014, 145: 108
- [7] Nakagawa Y, Tomishige K. *Catal Sci Technol*, 2011, 1: 179
- [8] Wang S, Liu H C. *Catal Lett*, 2007, 117: 62
- [9] Maris E P, Davis R J. *J Catal*, 2007, 249: 328
- [10] Huang Z W, Cui F, Kang H X, Chen J, Zhang X Z, Xia C G. *Chem Mater*, 2008, 20: 5090
- [11] Zope B N, Hibbitts D D, Neurock M, Davis R J. *Science*, 2010, 330: 74
- [12] Nie R F, Liang D, Shen L, Gao J, Chen P, Hou Z Y. *Appl Catal B*, 2012, 127: 212
- [13] Liu S S, Sun K Q, Xu B Q. *ACS Catal*, 2014, 4: 2226
- [14] Katryniok B, Paul S, Dumeignil F. *ACS Catal*, 2013, 3: 1819
- [15] Chai S H, Wang H P, Liang Y, Xu B Q. *J Catal*, 2007, 250: 342
- [16] Chai S H, Wang H P, Liang Y, Xu B Q. *Green Chem*, 2007, 9: 1130
- [17] Takagaki A, Iwatani K, Nishimura S, Ebitani K. *Green Chem*, 2010, 12: 578
- [18] Liu P, Derchi M, Hensen E J M. *Appl Catal A*, 2013, 467: 124
- [19] Liu P, Derchi M, Hensen E J M. *Appl Catal B*, 2014, 144: 135
- [20] Sonnat M O, Amigoni S, Taffin de Givenchy E P, Darmanin T, Choulet O, Guittard F. *Green Chem*, 2013, 15: 283
- [21] Shaikh A A G, Sivaram S. *Chem Rev*, 1996, 96: 951
- [22] Vieville C, Yoo J W, Pelet S, Mouloungui Z. *Catal Lett*, 1998, 56: 245
- [23] Aresta M, Dibenedetto A, Nocito F, Pastore C. *J Mol Catal A*, 2006, 257: 149
- [24] Hammond C, Lopez-Sanchez J A, Ab Rahim M H, Dimitratos N, Jenkins R L, Carley A F, He Q, Kiely C J, Knight D W, Hutchings G J. *Dalton Trans*, 2011, 40: 3927
- [25] Wang L G, Ma Y B, Wang Y, Liu S M, Deng Y Q. *Catal Commun*, 2011, 12: 1458
- [26] Kim D W, Park K A, Kim M J, Kang D H, Yang J G, Park D W. *Appl Catal A*, 2014, 473: 31
- [27] Zhang J, He D H. *React Kinet, Mech Catal*, 2014, 113: 375
- [28] Jagadeeswarai K, Kumar C R, Prasad P S S, Lorient S, Lingaiah N. *Appl Catal A*, 2014, 469: 165
- [29] Li H G, Gao D Z, Gao P, Wang F, Zhao N, Xiao F K, Wei W, Sun Y H. *Catal Sci Technol*, 2013, 3: 2801
- [30] Zhang J, He D H. *J Colloid Interf Sci*, 2014, 419: 31
- [31] Rokicki G, Rakoczy P, Parzuchowski P, Sobiecki M. *Green Chem*, 2005, 7: 529
- [32] Ochoa-Gomez J R, Gomez-Jimenez-Aberasturi O, Maestro-Madurga B, Pesquera-Rodriguez A, Ramirez-Lopez C, Lorenzo-Ibarreta L, Torrecilla-Soria J, Villaran-Velasco M C. *Appl Catal A*, 2009, 366: 315

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

Graphical Abstract

Chin. J. Catal., 2015, 36: 1759–1765 doi: 10.1016/S1872-2067(15)60915-9

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

Liping Zheng, Shuixin Xia, Xiuyang Lu, Zhaoyin Hou*
Zhejiang University

Calcined Ca-Al hydrocalumites are active and selective for the transesterification of glycerol with dimethyl carbonate, and the yield of glycerol carbonate reached 92% at 70 °C and 3 h.

- [33] Algoufi Y T, Hameed B H. *Fuel Process Technol*, 2014, 126: 5
- [34] Parameswaram G, Srinivas M, Hari Babu B, Sai Prasad P S, Lingaiah N. *Catal Sci Technol*, 2013, 3: 3242
- [35] Malyaadri M, Jagadeeswaraiah K, Prasad P S S, Lingaiah N. *Appl Catal A*, 2011, 401: 153
- [36] Zheng L P, Xia S X, Hou Z T, Zhang M Y, Hou Z Y. *Chin J Catal* (郑丽萍, 夏水鑫, 侯召同, 张梦媛, 侯昭胤. 催化学报), 2014, 35: 310
- [37] Pan S Y, Zheng L P, Nie R F, Xia S X, Chen P, Hou Z Y. *Chin J Catal* (潘赛勇, 郑丽萍, 聂仁峰, 夏水鑫, 陈平, 侯昭胤. 催化学报), 2012, 33: 1772
- [38] Pfeiffer H, Ávalos-Rendón T, Lima E, Valente J S. *J Environ Eng*, 2011, 137: 1058
- [39] Cavani F, Trifirò F, Vaccari A. *Catal Today*, 1991, 11: 173
- [40] Chang P H, Lee T J, Chang Y P, Chen S Y. *ChemSusChem*, 2013, 6: 1076
- [41] Gao L J, Teng G Y, Xiao G M, Wei R P. *Biomass Bioenergy*, 2010, 34: 1283
- [42] Kuwahara Y, Tsuji K, Ohmichi T, Kamegawa T, Mori K, Yamashita H. *Catal Sci Technol*, 2012, 2: 1842
- [43] Zhou J Z, Xu Z P, Qiao S Z, Liu J Y, Liu Q, Xu Y F, Zhang J, Qian G R. *Appl Clay Sci*, 2011, 54: 196
- [44] Wang Q, Gao Y S, Zhang Z, Duan L H, Umar A, O'Hare D. *Sci Adv Mater*, 2013, 5: 411
- [45] Zhang P, Qian G R, Shi H S, Ruan X X, Yang J, Frost R L. *J Colloid Interf Sci*, 2012, 365: 110
- [46] Lv T F, Ma W, Xin G, Wang R, Xu J, Liu D M, Liu F J, Pan D C. *J Hazard Mater*, 2012, 237-238: 121
- [47] Zhang J, Xu Y F, Qian G R, Xu Z P, Chen C, Liu Q. *J Phy Chem C*, 2010, 114: 10768
- [48] Alvarez M G, Segarra A M, Contreras S, Sueiras J E, Medina F, Figureueras F. *Chem Eng J*, 2010, 161: 340
- [49] Yuan Z L, Wang L N, Wang J H, Xia S X, Chen P, Hou Z Y, Zheng X M. *Appl Catal B*, 2011, 101: 431
- [50] Martavaltzi C S, Lemonidou A A. *Ind Eng Chem Res*, 2008, 47: 9537
- [51] Simanjuntak F S H, Kim T K, Lee S D, Ahn B S, Kim H S, Lee H. *Appl Catal A*, 2011, 401: 220

Ca-Al催化剂上甘油与碳酸二甲酯酯交换合成碳酸甘油酯

郑丽萍^a, 夏水鑫^a, 吕秀阳^b, 侯昭胤^{a,*}

^a浙江大学化学系, 浙江省应用化学重点实验室, 浙江杭州310028

^b浙江大学化学工程与生物工程系, 浙江杭州310027

摘要: 生物柴油是一种环保、可再生、使用安全、可替代石化柴油的新型液体燃料, 其产量和使用范围正逐年扩大。然而生物柴油生产过程中的主要副产物甘油严重过剩, 因此甘油资源化转化和利用已经成为近年研究热点。甘油可以作为一种平台化合物实现向多种高附加值化学品的转化, 例如通过催化氢解合成1,2-丙二醇, 通过发酵和催化氧化制备二羟基丙酮, 通过脱水制备丙烯醛和羟基丙酮, 通过酯交换反应生成甘油酯等。其中, 以甘油为原料合成的碳酸甘油酯(GC)具有很好的工业应用前景。以碳酸二甲酯(DMC)为原料与甘油进行酯交换合成GC是近年内比较有工业发展潜力的合成路线。前期研究发现, 固体碱对该反应具有很好的催化活性, 而且随着催化剂碱性增强, 甘油转化率明显增加, 然而当催化剂(如NaOH, KOH和K₂CO₃等)碱性过强时, 产物选择性明显降低。水滑石类化合物是一种常见的碱性温和的固体催化剂, 而且其碱性与结构可以调节, 因此我们选择了一种常见水滑石——水铝钙石作为本研究的重点。

本文通过共沉淀法制备了一系列不同Ca/Al比(1–6)的Ca-Al水滑石,并以此作为前驱体制备了新型的固体碱催化剂. XRD结果表明,当Ca/Al比为1–6时,所有样品都出现了明显的水滑石特征衍射峰,但当铝含量过高时会出现氢氧化铝杂相. SEM结果发现,当Ca/Al = 2–4时,样品中水滑石的结晶度高,有较完整的水滑石晶片, Ca/Al = 6的样品中水滑石晶片较小, Ca/Al = 1的样品中有明显的无定形氧化铝杂相. TG-DSC结果表明, Ca/Al = 2的样品除了几个与水滑石相关的特征失重峰以外,在786 °C还检测到明显的热吸收峰,说明此时钙铝石已经发生分解,生成了单独的 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 晶相和氧化钙,这与SEM结果一致. 这些水滑石经焙烧后用于温和条件下催化甘油与DMC酯交换生成GC的反应,发现上述催化剂对该反应具有很高的催化活性和目的产物选择性. 当DMC与甘油的摩尔比为3时, 70 °C反应3 h后,甘油转化率达到93%, GC选择性高于97%. 表征结果显示,甘油转化率主要取决于焙烧后Ca-Al催化剂中强碱性中心数量. 其中经800 °C焙烧后Ca/Al = 2的样品中强碱性中心数量最多,因而表现出最高的催化活性. 焙烧后催化剂中形成的 $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ 晶相在多次重复使用后仍可以稳定存在,但是表面CaO易流失,可能会降低催化剂的重复使用活性.

关键词: 甘油; 碳酸二甲酯; 酯交换; 碳酸甘油酯; 钙铝水滑石

收稿日期: 2015-03-23. 接受日期: 2015-05-16. 出版日期: 2015-10-20.

*通讯联系人. 电话/传真: (0571)88273283; 电子信箱: zyhou@zju.edu.cn

基金来源: 国家自然科学基金(21473155, 21273198, 21073159); 浙江省自然科学基金(LZ12B03001).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).