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Article

Transesterification of glycerol with dimethyl carbonate over Mg-Al hydrotalcites

Liping Zheng^a, Shuixin Xia^a, Zhaotong Hou^b, Mengyuan Zhang^a, Zhaoyin Hou^{a,*}^a Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China^b Jiangsu Changlong Chemical Co., Changzhou 213031, Jiangsu, China

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ABSTRACT

Glycerol carbonate (GC) was synthesized via the catalytic transesterification of glycerol with dimethyl carbonate over a series of Mg-Al hydrotalcites with different Mg/Al ratios (0.5–6) under mild conditions. All catalysts exhibited a high selectivity toward GC. The sample with Mg/Al = 2 exhibited 97.1% of selectivity toward GC and 66.9% of glycerol conversion at 70 °C for 3 h. Characterization results indicated that the activity of calcined Mg-Al hydrotalcites depended mainly on the surface area, pore diameter, and crystallinity.

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1. Introduction

With the rapid consumption of fossil fuels and increasing concerns about greenhouse gas emissions, the use of renewable feedstocks with low CO₂ emissions as alternative energy sources has attracted much attention [1,2]. Among the alternative renewable energy sources reported, the sustainable production of biodiesel from biomass has led many governments to increase production for economic and environmental reasons [3]. However, the growing production of biodiesel through the transesterification of triglycerides with methanol generates a large surplus of glycerol as a major byproduct. In turn, the catalytic conversion of glycerol to valuable products has recently become a hot research topic.

Several products, such as 1,2-propanediol [4–10], dihydroxyacetone [11,12], acrolein [13], hydroxyacetone [14], glycerol carbonate (GC) [15–17] 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, and can yield a wide range of valuable products. GC itself can be used as a solvent in NMR analysis and in organic synthesis. In addition, it has been reported that GC is an important alternative in lithium batteries, cosmetics, surfactants and polymer synthesis [18].

Several routes for obtaining GC from glycerol are known. Phosgenation between glycerol and phosgene [19], direct carbonylation of glycerol with CO₂ [20,21] and the glycerolysis of urea [22,23] have been proposed. However, these methods have disadvantages because of the toxicity and corrosive nature of the feed materials and/or thermodynamic limitations (reversibility of the reaction) toward the formation of GC. The direct reaction between glycerol and CO₂ is an attractive route, but it must be performed at high pressure and the yield of GC is reported to be very low. More recently, Li et al. [24] found that GC could be synthesized from CO₂ and glycerol over

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

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$\text{La}_2\text{O}_3\text{CO}_3\text{-ZnO}$ in acetonitrile with the yield of GC reaching a maximum of 14.3% at 30.3% glycerol conversion.

Transesterification of glycerol with dimethyl carbonate (DMC) is also an attractive way to produce GC under mild conditions [15,17,25]. It was reported that K_2CO_3 [26], CaO [27], and Mg/Al/Zr mixed oxides were effective for this reaction [28], but these catalysts had drawbacks regarding recyclability, reusability, and/or the need for complicated pretreatment. Recently, Pan et al. [25] disclosed that the rate of this reaction depended mainly on the basicity of the catalyst; but elsewhere it was found that the selectivity to GC decreased when a strong base (such as NaOH , KOH , K_2CO_3) was added because of the formation of glycidol [29]. We also found that the pore diameter of the solid base exerted a large influence on the activity and product distribution [25].

Hydrotalcite is a layered double hydroxide (LDH) with general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}]^{x-}\cdot m\text{H}_2\text{O}$ where M^{2+} is a divalent metal such as Mg , Zn , Ni , Co or Cu , M^{3+} is a trivalent metal such as Al , Cr , Fe or Ga [30]. The distance between lamellas in the LDH is usually larger than 0.8 nm. LDH is popularly used as a solid base catalyst. In this work, the transesterification reaction between glycerol and DMC was performed over a series of Mg-Al hydrotalcites with different Mg/Al ratios (0.5–6) under mild conditions, and the activity of these hydrotalcites and their structure was discussed.

2. Experimental

2.1. Catalyst preparation

Mg-Al hydrotalcites ($\text{Mg/Al} = 0.5\text{--}6$) were prepared by a conventional coprecipitation method. $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (25–300 mmol) and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (50 mmol) were dissolved in 400 mL water (solution A). Solution B was a mixed aqueous solution of NaOH (0.25 mol/L) and Na_2CO_3 (0.8 mol/L). Solution A and B were simultaneously added to a 2 L beaker under vigorous stirring at room temperature with the pH of the mixture being controlled at 9.4–9.6 during the addition. The resulting suspension was aged at 120 °C for 12 h, filtered and the residue washed thoroughly with distilled water (4 L) until the pH of the filtrate reached 7.0. The precipitate was dried at 110 °C overnight and calcined at 200–600 °C for 4 h. The composition of the Mg-Al hydrotalcites was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

2.2. Characterization

Thermogravimetric differential scanning (TG-DSC) analysis of the prepared samples from RT to 700 °C was carried out on a Netzsch STA409 thermobalance system using a heating rate of 10 °C/min under N_2 . 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). Transmission electron microscope (TEM) images of catalysts were obtained using an accelerating voltage of 200 kV (JEOL-2020 F). 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 pore size distribution was calculated using BJH method. The basicity of the catalyst was determined via temperature programmed desorption of CO_2 ($\text{CO}_2\text{-TPD}$) on an AMI-200 (Zeton Altamira) system. CO_2 in effluent was calibrated using an external standard method [31, 32].

2.3. Catalytic reactions

Controlled amounts of DMC (135 mmol), methanol (7 mL) and glycerol (43.8 mmol) were mixed in a 100 mL round bottomed three-neck jacketed glass reactor fitted with a magnetic stirrer and a reflux condenser. The mixture was first heated under stirring to the desired temperature (30–70 °C) and catalyst (0.45 g) was added to start the reaction. After reaction for 3 h, the solid catalyst was removed by centrifuging the contents and the supernatant liquid was analyzed using a flame ionization detector gas chromatograph (Shimadzu, 14B) equipped with a 30-m capillary column (DB-WAX 52 CB, USA). All products detected in the liquid were verified by a gas chromatography-mass spectrometry system (GC-MS, Agilent 6890) and quantified via an external calibration method. The product selectivity was calculated on a carbon basis.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD result

Figure 1 shows the XRD patterns of freshly precipitated Mg-Al catalysts. All the classical diffraction peaks of the LDH (JCPDS 00-041-1428) could be detected in all samples; hydrotalcite is the main phase in all of the solid catalysts. It was confirmed that mainly perfectly structured hydrotalcite was formed in the samples with $\text{Mg/Al} = 2$ or 4. Other phases, such as $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$ (JCPDS 00-025-0513) in $\text{Mg/Al} = 6$, $\text{Al}(\text{OH})_3$ (JCPDS 00-033-0018) in $\text{Mg/Al} = 1$ and $\text{AlO}(\text{OH})$ (JCPDS 00-049-0113) in $\text{Mg/Al} = 0.5$, appeared in those samples with $\text{Mg/Al} > 4$ or $\text{Mg/Al} < 1$. Figure 1(b) shows the XRD patterns of Mg-Al catalysts calcined at 400 °C. The peaks assigned to the (003), (006), and (012) diffractions of fresh LDH disappeared with concomitant formation of MgO due to the loss of water, carbonate and hydroxide. These results indicate that the formation of a perfect LDH structure should be favored for a Mg/Al ratio of 2–4.

3.1.2. TG-DSC result

Figure 2 shows the TG-DSC curves of the as-synthesized $\text{Mg/Al} = 2$ hydrotalcite. The TG curve indicates three main weight losses at 30–218, 218–311 and 400–700 °C. The first stage is attributed to the removal of adsorbed water, the second stage was due to the loss of bound water or carbonate in the interlayer of the LDH [33], and the last step was attributed to the further removal of hydroxyl groups [34,35].

3.1.3. Structure and basicity

The textural structure and the basicity of calcined (at 400 °C

Fig. 1. XRD patterns of fresh (a) and calcined (b) Mg-Al hydrotalcites with different Mg/Al ratios. (1) Mg/Al = 0.5; (2) Mg/Al = 1; (3) Mg/Al = 2; (4) Mg/Al = 4; (5) Mg/Al = 6.

for 4 h) Mg/Al hydrotalcites are summarized in Table 1. It can be found that the surface area and average pore diameter of these samples decreased gradually from 216 m²/g and 23.7 nm (Mg/Al = 1) to 127.4 m²/g and 13.1 nm (Mg/Al = 6), respectively. The calculated surface density of basic sites increased from 0.62 to 5.48 μmol/m² when the Mg/Al ratio was increased from 0.5 to 6.

3.1.4. TEM result

Figure 3 shows typical TEM images of samples calcined at 400 °C for 4 h. Some LDH lamellas of various sizes (45–150 nm, see Fig. 3(a)-2, (a)-3) and an Al₂O₃ phase (see Fig. 3(a)-1) could

be observed in the samples with a low content of Mg (Mg/Al = 0.5). The orderliness and size of these solid LDH lamellas noticeably increased in the sample with Mg/Al = 2, and the thickness of these lamellas was 11–12 nm. However, separated MgO particles can be clearly seen in the sample with Mg/Al = 6 (Fig. 3(c)). These images are consistent with the XRD results.

The images of Mg-Al hydrotalcites before and after calcination were further compared in Fig. 4. It was found that the outline of solid LDH lamellas is similar in both samples, while the lattice fingers in a fresh sample (Fig. 4(a)-2) are clearer than that in the calcined sample. These results indicate that the thermal stability of the solid lamellas is relatively high.

3.2. Catalytic activity

3.2.1. The influence of the Mg/Al ratio

Table 2 summarizes the activity of calcined (at 400 °C for 4 h) Mg-Al LDHs with different Mg/Al ratios for the transesterification reaction between glycerol and DMC conducted at 70 °C. The conversions of glycerol increased rapidly from 12.6% to 66.9% when Mg/Al ratio increased from 0.5 to 2, with the selectivity toward GC remaining at 97% above. However, the conversion of glycerol decreased on those samples with higher Mg/Al ratios (> 4). These results indicated that the activity of calcined Mg-Al LDHs depended mainly on basicity, surface area, pore diameter and crystallinity [25]. It is concluded that those catalysts having a mid-range density of basic sites, large pore channels and higher crystallinity are more suitable for this reaction.

3.2.2. Effect of temperature

The conversion of glycerol increased quickly from 9.0% to 66.9% when the reaction temperature was raised from 30 to 70 °C and the selectivity towards GC decreased slightly from 97.9% to 97.1% (see Table 3). The decreased selectivity is attributed to basic sites that increase the decomposition of GC to glycidol (GLYc) at high temperature [29,36]. The results indicate that a higher temperature might cause higher glycerol

Fig. 2. TG-DSC curves of the as-synthesized hydrotalcite with Mg/Al = 2.

Table 1

Structure and basicity of LDHs with different Mg/Al ratios calcined at 400 °C for 4 h.

Mg/Al ratio	S_{BET} / (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Adsorbed CO ₂ * (mmol/g)	Basicity density (μmol/m ²)
0.5	146.1	0.74	18.6	0.09	0.62
1	216.0	0.73	23.7	0.14	0.65
2	158.5	0.44	22.0	0.18	1.10
4	137.0	0.62	14.9	0.25	1.80
6	127.4	0.78	13.1	0.70	5.48

* Calculated from the CO₂-TPD measurements.

Fig. 3. TEM images of the calcined hydrotalcites with different Mg/Al ratios. (a) Mg/Al = 0.5; (b) Mg/Al = 2; (c) Mg/Al = 6.

Fig. 4. TEM images of fresh (a) and calcined (b) hydrotalcite with Mg/Al = 2.

conversion but lower selectivity to GC. We found that it was difficult to raise the reaction temperature above 70 °C because an azeotropic point exists under the reaction conditions used.

3.2.3. Recycling of catalysts

Figure 5 presents the performance of recycled catalyst (Mg/Al = 2) for the transesterification reaction between gly-

cerol and DMC at 70 °C. It was found that the conversion of glycerol in the first three recycles remained 66% above, and decreased slightly to 63.1% in the 6th recycle. This decrease might be caused by the loss of catalysts during these experiments because only 0.39 g solid catalyst remained after the sixth recycle.

The XRD patterns of the as-synthesized, calcined, and 6-recycled Mg-Al LDHs (Mg/Al = 2) are compared in Fig. 6. The well-known diffraction peaks in the calcined sample are not well-defined because of the loss of water, carbonate, and hy-

Table 2

Activity of calcined LDHs with different Mg/Al ratios.

Mg/Al ratio	GLY conversion (%)	Selectivity (%)	
		GLYc	GC
—	7.5	2.2	97.8
0.5	12.6	1.6	98.4
1	32.8	2.3	97.7
2	66.9	2.9	97.1
4	57.5	2.7	97.3
6	7.9	2.0	98.0

Reaction conditions: catalyst 0.45 g, glycerol 43.8 mmol, DMC 135 mmol, CH₃OH 7 mL, 70 °C, 3 h.

Table 3

Transesterification of glycerol as a function of temperature.

Reaction temperature (°C)	GLY conversion (%)	Selectivity (%)	
		GLYc	GC
30	9.0	2.1	97.9
50	21.1	2.1	97.9
70	66.9	2.9	97.1

Reaction conditions: catalyst with Mg/Al = 2, 0.45 g, glycerol 43.8 mmol, DMC 135 mmol, CH₃OH 7 mL, 70 °C, 3 h.

Fig. 5. Recycling of catalyst (Mg/Al = 2) in the transesterification of glycerol. Reaction conditions: catalyst with Mg/Al = 2, 0.45 g, glycerol 43.8 mmol, DMC 135 mmol, CH₃OH 7 mL, 70 °C, 3 h.

Fig. 6. XRD patterns of hydrotalcite with Mg/Al = 2. (1) calcined at 400 °C; (2) 6 times recycled; (3) as-synthesized.

dioxide. We found that the expected diffraction peaks of the LDHs appeared in the 6 times recycled sample, and this phenomenon is attributed to the special memory effect of LDH materials [37–39].

4. Conclusions

Mg-Al LDHs (Mg/Al = 0.5–6) could be synthesized by a con-

ventional coprecipitation method. It was confirmed that the crystallinity and uniformity of solid lamellas of LDHs with Mg/Al = 2 are the best. Calcined Mg-Al LDHs (Mg/Al = 2) exhibited high catalytic performance and stability in the transesterification reaction between glycerol and DMC at 70 °C, and the conversion of glycerol reached 66.9%.

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Graphical Abstract

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Transesterification of glycerol with dimethyl carbonate over Mg-Al hydrotalcite

Liping Zheng, Shuixin Xia, Zhaotong Hou, Mengyuan Zhang, Zhaoyin Hou*
Zhejiang University; Jiangsu Changlong Chemical Co.

The transesterification of glycerol with dimethyl carbonate was catalyzed by a series of Mg-Al hydrotalcites with different Mg/Al ratios (0.5–6) under mild conditions. The hydrotalcite with Mg/Al = 2 is the most active catalyst for this reaction.

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Mg-Al水滑石催化甘油与碳酸二甲酯的酯交换反应

郑丽萍^a, 夏水鑫^a, 侯召同^b, 张梦媛^a, 侯昭胤^{a*}

^a浙江大学化学系催化研究所, 浙江杭州310028

^b江苏常隆化工有限公司, 江苏常州213031

摘要: 报道了温和条件下甘油和碳酸二甲酯在一系列不同Mg/Al比(0.5–6)的Mg-Al水滑石催化下合成碳酸甘油酯(GC)的反应。发现, Mg-Al水滑石对该反应具有很高的GC选择性, 其中Mg/Al = 2经400°C处理所得水滑石催化效率最高: 70 °C反应3 h甘油转化率达66.9%时, GC选择性维持在97%以上。表征结果表明, 水滑石样品的比表面积、孔径、结晶度和表面碱性对其催化活性影响很大。
关键词: 甘油; 碳酸甘油酯; 酯交换反应; 镁-铝水滑石

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

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1. 前言

随着化石燃料的急剧消耗及温室气体的过度排放, 寻找一种可再生、安全性能好、可替代石化柴油的新能源正逐步成为当今国际新能源开发的热点^[1,2]. 其中, 生物柴油是一种环保、可再生、使用安全的新型液体燃料, 在欧美等发达国家受到越来越多的关注, 其产量和使用范围正逐年扩大^[3]. 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, 甘油的深度转化和利用已经成为近年来的研究热点.

甘油可以作为一种平台化合物实现向多种衍生物的转化, 例如通过催化氢解甘油可以合成1,2-丙二醇^[4–10]; 通过发酵和催化氧化等步骤可制备二羟基丙酮^[11,12]; 脱水制备丙烯醛^[13]和羟基丙酮^[14]; 经酯交换反

应生成甘油酯等^[15–17]. 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价值. Sonnati等^[18]认为GC可以与醇类、胺类、羧酸、酮类、异氰酸盐等多种物质反应得到一系列具有高附加值的化合物, 而且它可以作为核磁分析、溶酶系统及系列有机合成反应体系的溶剂, 在某些反应中甚至可以替代离子液体^[18]. 此外, GC在锂电池、化妆品工业、表面活性剂及制备高分子聚合材料等领域也具有很广泛的应用前景.

从甘油出发合成碳酸甘油酯已经引起很多学者的关注. 在早期的研究中, Shaikh等^[19]以光气为原料合成GC, 该法具有温度低、转化率高、选择性好等优点, 但使用剧毒的光气, 对环境污染严重, 因此目前已基本被淘汰. 有人曾尝试直接采用CO₂^[20,21]与甘油反应制备GC, 但反应条件苛刻、转化率低. 目前, 比较常见的是以

尿素和甘油为原料合成碳酸甘油酯^[22,23], 该反应具有原料廉价易得等优点, 但在反应过程中需要抽真空以去除生成的 NH_3 , 因此对设备要求较高. Li等^[24]采用 $\text{La}_2\text{O}_2\text{CO}_3\text{-ZnO}$ 复合催化剂, 成功实现了甘油与 CO_2 作用直接合成碳酸甘油酯, 实验用乙腈作为溶剂, 发现经 500°C 处理后, $\text{La/Zn} = 1/4$ 的样品具有最好催化活性, 甘油转化率为30.3%, GC产率达到14.3%. 近年内比较有工业发展潜力的合成路线是以碳酸二甲酯(DMC)为原料与甘油进行酯交换合成GC^[15,17,25], 该方法具有条件温和($50\text{--}70^\circ\text{C}$), 原料低毒而且产物易分离等诸多特点, 具有较好的工业化前景.

Rokicki等^[26]发现, 在 $50\text{--}70^\circ\text{C}$, K_2CO_3 对该反应有一定的催化效果; Ochoa-Gomez等^[27]发现高温焙烧后的CaO也具有较高的催化效率; Malyaadi等^[28]进一步考察了镁铝复合氧化物对该反应的催化性能. 但仍有一些问题需要改进, 比如 K_2CO_3 催化剂不可回收, CaO催化剂易失活, 镁铝复合氧化物预处理条件苛刻等. 最近, Pan等^[25]将一系列碱性催化剂用于该反应中, 发现随着催化剂碱性的增强, 甘油的转化率显著增加; 然而催化剂(如 NaOH , KOH 和 K_2CO_3 等)的碱性过强时, 产物的选择性明显降低, 这主要是由于过强的碱性易导致产物进一步脱除羧基(生成缩水甘油)所致^[29]. 此外, 我们的研究发现, 催化剂的孔道结构对其活性和产物分布具有重要的影响^[25].

水滑石类化合物(LDH)的半经验分子式可写作 $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{A}^{n-}_{x/n}\cdot m\text{H}_2\text{O}$, M^{2+} 是二价金属, 如 Mg , Zn , Ni , Co , Cu 等, 而 M^{3+} 是三价金属如 Al , Cr , Fe , Ga 等^[30]. 通常经典的水滑石都可以作为一种固体碱, 并且水滑石层板间隔的距离可以达到 0.8 nm 以上, 因此, 碱性 Mg-Al 水滑石对甘油与碳酸二甲酯的酯交换反应可能具有较高的活性和目的产物选择性.

本文采用共沉淀法制备了一系列不同 Mg/Al 比的水滑石, 并用于催化甘油和DMC的酯交换反应, 探讨了反应活性与催化剂结构之间的关系.

2. 实验部分

2.1. 催化剂的制备

将 $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($25\text{--}300\text{ mmol}$)和 $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (50 mmol)溶解于 400 mL 去离子水中, 于 25°C 将上述水溶液和含有 Na_2CO_3 (0.25 mol/L)+ NaOH (0.8 mol/L)的混合溶液并流滴定, 用雷磁pH复合电极在线监测混合液的pH值, 并控制其在 $9.4\text{--}9.6$ 范围内. 滴定结束后继续搅拌

0.5 h 使体系混合均匀, 然后静置过夜. 在 120°C 下陈化 12 h 后, 过滤出白色固体, 并用大量去离子水(4 L)洗涤以去除 Na^+ , 同时用精密pH试纸监测确保最后的水洗滤液为中性. 最后于 110°C 干燥过夜. 使用前在 $200\text{--}600^\circ\text{C}$ 下焙烧 4 h , 升温速率 2°C/min , 然后直接用于反应或保存在干燥器中备用. 所制水滑石样品中的 Mg/Al 比采用电感耦合等离子体(ICP-AES)测定.

2.2. 催化剂的表征

未焙烧样品中的水分和碳酸根的脱除过程采用Netzsch STA409型综合热分析仪检测, 测定范围从室温至 700°C , N_2 气氛, 升温速率 10°C/min . X-射线衍射(XRD)测试在日本理学公司的Rigaku D/MAX-2500 PC型X射线衍射仪上进行, $\text{Cu K}\alpha$ 辐射($\lambda = 0.15406\text{ nm}$), 扫描范围 $2\theta = 5^\circ\text{--}80^\circ$. 催化剂的形貌采用JEOL 2020型透射电子显微镜(TEM)观测, 加速电压 200 kV . 样品的孔结构采用美国麦克公司的TriStar II型自动吸附分析仪, 在 -196°C 进行 N_2 物理吸附测得, 样品测定前先在 150°C 高真空($< 2.66\text{ Pa}$)下脱气 10 h , 样品孔径利用BJH方法算得. 样品的碱性采用 CO_2 程序升温脱附法($\text{CO}_2\text{-TPD}$)测量, 在美国Zeton Altamira公司的AMI-200型自动吸附仪上进行, 以高纯Ar为载体, 先将样品(0.3 g)在高纯Ar (30 mL/min)中于 450°C 预处理 0.5 h , 然后冷却至 50°C , 通入 $20\%\text{ CO}_2\text{-}80\%\text{ Ar}$ 混合气直至样品吸附 CO_2 饱和, 继续用高纯Ar气吹扫 5 h 以除去物理吸附的 CO_2 , 以 10°C/min 程序升温至 550°C , 尾气中脱附的 CO_2 用四极质谱仪(OmniStarTM, GSD301, Switzerland)检测, 脱附出来的 CO_2 采用标准气体标定的结果对比进行计算^[31,32].

2.3. 催化剂的评价

甘油酯交换反应在带有回流冷凝管、磁力搅拌器和温度计的 100 mL 的三颈烧瓶中进行. 反应体系内加入 0.45 g Mg-Al 水滑石(以 400°C 焙烧后的质量为标准), 43.8 mmol 甘油, 135 mmol DMC , 7 mL 甲醇, 在 $30\text{--}70^\circ\text{C}$ 反应 3 h 后, 取反应液于离心管中, 离心分离后取上清液用于气相色谱(Shimadzu, 14B)分析, 采用毛细管色谱柱(DB-WAX 52 CB USA)分离. 所有的产物采用色-质联用仪(GC-MS, Agilent 6890)进行鉴定, 外标法定量. 产物的选择性根据碳原子数计算.

3. 结果与讨论

3.1. 催化剂表征结果

3.1.1. XRD结果

图1为沉淀法所制 Mg-Al 样品的XRD谱. 从图1(a)可

以看出,所有样品均有明显的水滑石晶体的衍射峰(JCPDS 00-041-1428),表明所制样品主要晶相为水滑石晶体.当 $\text{Mg}/\text{Al}=2$ 和4时,所制的催化剂中只含有水滑石晶体,而当 $\text{Mg}/\text{Al}>4$ 或 $\text{Mg}/\text{Al}<1$ 时,所制的样品中出现其他的物相.例如在 $\text{Mg}/\text{Al}=6$ 的样品中出现了 $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ 杂相(JCPDS 00-025-0513); $\text{Mg}/\text{Al}=1$ 时样品中出现了 $\text{Al}(\text{OH})_3$ (JCPDS 00-033-0018)晶相; $\text{Mg}/\text{Al}=0.5$ 的样品中还出现 $\text{AlO}(\text{OH})$ (JCPDS 00-049-0113).由图1(b)可见,400 °C焙烧后,水滑石(003), (006), (012)晶面的特征衍射峰消失,说明随着层板间的结晶水、碳酸根及氢氧根的脱除,水滑石的有序堆积被破坏.当 $\text{Mg}/\text{Al}=0.5$ 时样品中出现了微弱 $\text{AlO}_{1.06}(\text{OH})_{0.94}$ (JCPDS 01-074-6248)衍射峰,进一步增大 Mg/Al 比时,还检测到 MgO 的衍射峰.这表明保持完美的 $\text{Mg}-\text{Al}$ 水滑石晶体需要适合的 Mg/Al 配比.可以看出,当 $\text{Mg}/\text{Al}=2$ 和4时样品中都形成了比较理想的水滑石晶体,其中 $\text{Mg}/\text{Al}=2$ 时样品的结晶度最好.而当 Mg/Al 比超出2–4时所制样品的XRD衍射峰强度均有所减弱.当 $\text{Mg}/\text{Al}=6$ 时可以明显看到所有晶面的衍射峰均变宽,说明 Mg 含量增多时晶体的颗粒变细.另外,随着 Mg/Al 比的增加,样品衍射峰位置均向小角度方向移动,表明水滑石结构晶间距离增大.这与制备水滑石的原料中镁铝的配比有很大关系,因为 Mg^{2+} 体积比 Al^{3+} 的大,从而导致晶间距离的改变.

3.1.2. TG-DSC结果

图2为新鲜制备 $\text{Mg}/\text{Al}=2$ 水滑石样品的TG-DSC曲线.可以看到,样品经历了三个失重阶段,主要发生在30–218, 218–311和400–700 °C.第一阶段可以归属于样品外表面物理吸附水的挥发,第二阶段是水滑石层板间结晶水和碳酸盐的脱除^[33],最后的失重阶段主要是归属于样品表面羟基的脱除^[34,35].

3.1.3. 催化剂结构及碱性

表1为不同 Mg/Al 比的水滑石经400 °C焙烧4 h处理后的结构性质及碱性分析结果.可以看出,随着 Mg/Al 比从1增至6时,样品的比表面积和平均孔径分别从216 m^2/g 和23.7 nm逐渐减小至127.4 m^2/g 和13.1 nm.还可以发现,随着 Mg/Al 比从0.5增至6时,催化剂的碱密度由0.62 $\mu\text{mol}/\text{m}^2$ 逐渐增至5.48 $\mu\text{mol}/\text{m}^2$.

3.1.4. TEM结果

图3为经400 °C焙烧4 h后水滑石样品的TEM照片.可以看出, $\text{Mg}/\text{Al}=0.5$ 时样品中出现明显的水滑石片,但大小不一,从45–150 nm不等,而且还有部分单独的氧

化铝相(图3 (a)-1),与XRD结果吻合; $\text{Mg}/\text{Al}=2$ 时,样品为结晶较好的水滑石片,且颗粒较为均匀,厚度为11–12 nm.当 $\text{Mg}/\text{Al}=6$ 时,样品中除了水滑石片以外,还可以明显看到 MgO 颗粒,这与XRD结果一致.

图4比较了 $\text{Mg}/\text{Al}=2$ 的水滑石样品在焙烧前后的形貌.可以看出,焙烧前后的样品均保留了水滑石的主要层板骨架结构,但未焙烧样品的形貌更加规整,可明显看出水滑石层板间的晶格条纹;而焙烧后,这样的条纹则没有那么清晰.然而,焙烧前后水滑石晶片的形貌改变不大,说明其具有良好的热稳定性.

3.2. 反应活性评价

3.2.1. 不同 Mg/Al 比的水滑石样品对酯交换反应的催化活性

表2是400 °C焙烧所制不同 Mg/Al 比的水滑石上甘油酯交换反应活性.由表可见,当催化剂中 Mg/Al 从0.5增至2时,甘油的转化率从12.6%逐渐增加到66.9%,GC选择性均在97%以上.这主要是由于随着 Mg/Al 的增加,催化剂中水滑石的结晶度提高、比表面积较高,同时其碱性增加所致.进一步提高 Mg/Al 时,甘油的转化率却逐渐下降,初步推测这与催化剂的结构有关.XRD结果显示,当 $\text{Mg}/\text{Al}>4$ 时,其结晶度开始变差、晶体颗粒变小、比表面积尤其是平均孔径显著减小,因而甘油的转化率降低.可见,催化剂的活性可能与其孔径分布和结晶度之间的关系紧密.所以,我们认为这个反应可能对催化剂的孔结构有较高的要求,碱性适中、结晶度好、孔径大的催化剂的活性较高.

3.2.2. 温度对酯交换反应活性的影响

由表3可见,随着反应温度的升高,甘油转化率快速增加,至70 °C时GC选择性略有降低.研究表明^[29,36],温度较高时,碱将催化GC分解成为副产物缩水甘油(GLYc),因此温度过高不利于产物选择性的提高.此外发现,在本文所采用的原料组成条件下,70 °C时已经达到其共沸点,因此70 °C反应比较合适.

3.2.3. 催化剂的重复使用性能

由图5可见,水滑石样品重复使用3次后其催化性能基本不变(甘油转化率维持在66%以上),至第6次时,甘油转化率稍有下降至63.1%.这可能是因为催化剂在转移洗涤时有所损失所致.实验最初使用催化剂0.45 g,而在使用6次回收后为0.39 g.

图6为6次重复使用后的催化剂、焙烧后的新鲜催化剂和水滑石前驱体的XRD谱.可以看出,焙烧后的新鲜催化剂中除了微弱的 MgO 衍射峰以外,水滑石前驱体的

衍射峰已经很不明显. 但可喜的是, 6次循环使用后的样品却部分恢复了经典水滑石的层状结构. 这主要应归因于水滑石特殊的“形状记忆功能”^[37–39].

4. 结论

采用共沉淀法制备了不同Mg/Al比的水滑石. 结果

表明, 当Mg/Al = 2时可得到结晶度高、颗粒均匀的水滑石前驱体, 再经焙烧后所得样品在甘油与DMC的酯交换反应中具有较高的活性和稳定性. 其中, 经400 °C处理过的Mg/Al = 2水滑石上甘油的转化率达66.9% (3 h), GC选择性达97.1%. 另外, 该催化剂具有特殊的结构“还原”现象, 是一种高活性、高选择性, 且可重复使用的催化剂.