# Magnesium Aluminum Spinel as an Acid–Base Catalyst for Transesterification of Diethyl Carbonate with Dimethyl Carbonate

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**Abstract** Mesoporous  $MgAl_2O_4$  spinel (MAO), prepared via one-pot evaporation induced self-assembly strategy, was reported here as an acid–base bifunctionalization catalyst for the reaction for ethyl methyl carbonate from dimethyl carbonate and diethyl carbonate. The physical/ chemical properties of  $MgAl_2O_4$  were characterized by X-ray powder diffraction, N<sub>2</sub> adsorption–desorption, temperature programmed desorption and Fourier transform infrared. The effects to the reaction by adjusting the catalyst amount and reaction time were tested. The transesterification induced by MAO is much faster, and meantime, the thermal stability of MAO is much higher. Moreover, the catalyst can be used directly after filtration without drying and reused for at least five times with only 1.2 % loss in catalytic activity.

**Keywords** Heterogeneous · Acid catalysis · Base catalysis · Ethyl methyl carbonate · Magnesium aluminum spinel

# 1 Introduction

As the simplest asymmetrical carbonate, ethyl methyl carbonate (EMC) is widely used as a co-solvent in a non-aqueous electrolyte to promote the discharge capacity and energy density of the lithium ion cells [1–5]. Various methods have been reported for the synthesis of EMC. One

of the effective processes is the esterification of chloroformate with ethanol in the presence of base catalyst [6]. However, this method is regarded not environmental friendly because of the use of highly toxic regents. Another route is the transesterification of dimethyl carbonate (DMC) with EtOH [7–9]. The disadvantage of this method is that three binary azeotropes (methanol-DMC, ethanol-DMC and ethanol-EMC) are generated during the reaction process, increasing the difficulty of separation.

In addition, EMC can also be synthesized by the transesterification of DMC with diethyl carbonate (DEC) [6, 10–17]. Zhen et al. [11] reported that  $Ti(OBu)_4$  and Bu<sub>2</sub>SnO are active homogeneous catalysts, but it is difficult to separate the catalyst from the reaction mixtures. Lithium diethyl amide and lithiated carbon were found to be able to perform high activity for the reaction [6], however, the high price greatly limits its wide application. MgO, known as a typical solid base, was proved to be the most active one among various metal oxide catalysts examined by Jiang's group [10] and performed well in the transformation of the reactants either in a liquid phase or a vapor phase. The highest yield of 44.2 % was obtained under the moderate conditions. In a work reported by Y. Zhao and coworkers [14], MOF-5,  $[Zn_4O(BDC)_3]$  (BDC = benzene-1,4-dicarboxylate), was found to show higher activity for the reaction of DMC and DEC synthesizing EMC, and the yield of 50.1 % was obtained under moderate conditions: DMC, 1.802 g; DEC, 2.362 g; catalyst, 2 wt%; 100 °C; 3 h. Jia et al. [16] reported that DEC conversion of 47.7 % was achieved with amorphous mesoporous aluminophosphate catalyst. In another work of his group [15], porous carbon-supported MgO (MgO/NC-2) catalyst also shows good activity for the reaction. Recently, Wang et al. [17] discovered that a zeolitic imidazolate framework (ZIF-8)  $[Zn(Melm)_2]$  (Melm = 2-methylimidazole) shows an

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efficient activity on the transesterification of DMC with DEC under the optimum reaction conditions: DMC, 0.1 mol, DEC, 0.1 mol, catalyst, 0.208 g, 100 °C and 3 h. A relatively high EMC yield of 50.7 % was achieved after reacting for 3 h. After filtering, washing with ethanol and drying in oven, ZIF-8 could be reused for at least three times without evident activity loss. However, exploring much more active heterogeneous catalysts is still attractive for the reaction under mild conditions.

MgO-Al<sub>2</sub>O<sub>3</sub>-SBA-15 catalyst, known as a kind of acidbase bifunctional mesoporous material, was proved to perform with a high yield (46 %) of EMC by Chen et al. [13]. Acid-base bifunctional mesoporous materials, which combine specific chemical reactivity of the acid-base materials and the long-term stability of the mesoporous structure, have drawn great interests in their applications. Acid-base bifunctionalization is a concept that explains the roles of acid and base sites in the process of catalytic reaction. As a solid catalyst, acid-base catalysts have shown favorable advantages in many cases, such as enhancing of the reaction velocity, prolonging of the catalyst life and causing fewer disposal problems [13, 18, 19]. Recently in our work, we found that MgAl<sub>2</sub>O<sub>4</sub> spinel prepared by one-pot evaporation induced self-assembly strategy performed an excellent catalytic activity for the reaction of DMC with DEC. The reaction with this catalyst could almost reach equilibrium after 30 min. In addition, as a solid acid-base bifunctional catalyst, MgAl<sub>2</sub>O<sub>4</sub> spinel could be easily regenerated by drying in oven or reused directly after filtration. Although the yield is 1 % lower in our work compared with previous work (ZIF-8), the reaction time of equilibrium is greatly shortened and the catalyst can be reused continuously. The finding may promote its industrial application in the synthesis of EMC.

## 2 Experiment

#### 2.1 Chemical Reagents

Dimethyl carbonate (DMC >99 %) and diethyl carbonate (DEC >99 %) were purchased from Tianjin Guangfu Fine Chemical Research Institute. (EO)20(PO)70(EO)20 triblock copolymer (Pluronic P123) was purchased from Sigma-Aldrich. All other chemicals were analytically pure and purchased from Tianjin Kemiou Chemical Reagent Conference. All reagents were used without further purification.

## 2.2 Preparation of the Catalyst

Mesoporous MgAl<sub>2</sub>O<sub>4</sub> composite metal oxides with different Mg/Al mole ratios were synthesized via a volatile process as reported previously [20]. Typically, approximately 1.0 g (EO)20(PO)70(EO)20 triblock copolymer (Pluronic P123) was dissolved in 20 mL absolute ethanol under stirring. Then, 1.6 mL of 67 wt% nitric acid, accompanied by 1.02 g aluminum isopropoxide  $(C_9H_{21}AlO_3)$  and 1.28 g magnesium nitrate hexahydrate were added (total amount of Mg and Al is 10 mmol) into the above mixtures. After stirring for at least 5 h at room temperature, the homogeneous sol was incubated in a drying oven under 60 °C for 48 h to allow the solvent evaporation. A white solid material (denoted as MAO-x, where x is the mole ratio of Mg to Al according to the mixture added in catalyst preparation process) was obtained after calcination at 700 °C for 6 h in air. In order to investigate the synergistic effect of Mg and Al, the mesoporous alumina without Mg was facilely fabricated by the same method as that of MgAl<sub>2</sub>O<sub>4</sub>.

For comparison, pure commercial MgO powder was used after further treatment at 500 °C for 5 h in air.

## 2.3 Catalyst Characterization

The phase purity of the samples was determined by XRD with a Bruker D8 advance X-ray diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 0.15418$  nm) in the 2 $\theta$  range from 10 to 70°. N<sub>2</sub> adsorption-desorption isotherms were measured with a Quadrasorb-SI apparatus at -196 °C. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated from the desorption branch using the Barett-Joyner-Halenda theory. Temperature programmed desorption (TPD) was carried out using CO<sub>2</sub> or ammonia gas as probe molecules [16]. Typically, 50 mg portion of each sample was calcined at 800 °C for 1 h, and then cooled to 50 °C. Carbon dioxide (99.9 %, 20 mL min<sup>-1</sup>) or ammonia gas (99.9 %, 20 mL min<sup>-1</sup>) was injected into the stream, and the system was maintained at 50 °C for 30 min. After reaching saturation, the system was purged with flowing Ar for 1 h at 50 °C, the sample was heated at a rate of 10 °C min<sup>-1</sup> in Ar (40 mL min<sup>-1</sup>), and the concentration change of the desorbed CO2 was monitored using an online thermal conductivity detector.

## 2.4 Catalytic Reaction

Transesterification of DEC with DMC was carried out as follows: 4.5 g (0.05 mol) of DMC, 5.9 g (0.05 mol) of DEC, and 5 wt% (based on the total mass of the reactants) of catalyst were charged in a 100 ml one-neck flask, equipped with a reflux condenser. Then the mixture was heated up to 103 °C. The reaction products were analyzed by a gas chromatography (GC-2014C) equipped with an OV-17 capillary column and FID. In the experiment of investigating the reusability of catalyst, catalyst was



Fig. 1 XRD patterns of different catalysts: a MgO, b MAO-1, c MAO-1.5, d MAO-2, e MAO-3. 289  $\times$  202 mm (300  $\times$  300 DPI)

separated by filtration, dried in oven at 80  $^{\circ}$ C for 5 h, and reused for the next time.

#### **3** Results and Discussion

## 3.1 Characterizations

The XRD patterns of different catalysts are shown in Fig. 1. It is noticeable that sample MAO-2 exhibited typical diffraction lines ascribed to MgAl<sub>2</sub>O<sub>4</sub> spinel (JCPDS 21-1152) in the wide-angle XRD pattern [21, 22]. In order to demonstrate the changes of the lattice after calcining the mixture of C<sub>9</sub>H<sub>21</sub>AlO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> wide-angle XRD pattern of pure MgO is also shown in Fig. 1. In addition, the phaenomena that the intensities of diffraction peaks gradually become weaker and the location of the main diffraction peak moves towards lower two theta degree with the increase of Mg was observed. The same results were obtained in previous literatures [18, 23]. However, when the mole ratio of Mg/Al is three, peaks of MgO and MgAl<sub>2</sub>O<sub>4</sub> prove the coexistence of both phases in MAO-3, indicating that Mg was over added. All these facts prove that the new phase of MgAl<sub>2</sub>O<sub>4</sub> was fabricated in the process of calcination at 700 °C for 5 h in air.

As is known, MgO is one of the most common solid base catalysts, and  $Al_2O_3$  is a common-used solid acid catalyst [24, 25]. A bifunctional material can be prepared by grinding the precursors of them [13, 26]. In our work, we found that the bifunctional materials can also be fabricated by chemical mixing. CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD analyses were used to present the basicity and acidity of the



Fig. 2 CO2-TPD (a) and NH3-TPD (b) patterns of catalysts calcined at 700 °C.  $282 \times 376 \text{ mm} (72 \times 72 \text{ DPI})$ 

prepared materials. Figure 2 shows the TPD profiles of different magnesium aluminum spinel catalysts. All the MgAl<sub>2</sub>O<sub>4</sub> spinel catalysts only show a single desorption peak, which means a single alkali type. As shown in Fig. 2a, a desorption peak starts to appear lower than 200 °C and extends into a broad peak in the sample MAO-0.5, which means it is weak alkaline on the surface. With the increasing of Mg, position of peaks is apt to appear at higher temperature, indicating the basicity of the catalysts is enhanced. For example, a single peak starts to form from around 220 °C in the MAO-2 sample, which suggests that the medium base sites are located on the surface of the catalyst. However, when the value of n(Mg)/n(Al) was three, the catalyst tends to show weak basicity, which is ascribed to the coexistence of MgO and MgAl<sub>2</sub>O<sub>4</sub>, which was proved by CO<sub>2</sub>-TPD test of pure MgO. A very broad CO<sub>2</sub> desorption peak extends from 150 to 400 °C, demonstrating the coexistence of weak and medium basic sites on the surface of MgO. In addition, Fig. 2b shows the

Table 1 The structure parameters of mesoporous MAO-x (x = 0.5, 1.5, 1, 2, 3)

Samples	BET surface area $(m^2 g^{-1})$	Mean pore size <sup>a</sup> (nm)	Pore vol. $(cm^3 g^{-1})$
MgO	15	3.3	0.049
MAO-3	109	9.6	0.348
MAO-2	205	12.5	1.003
MAO-1.5	142	12.3	0.583
MAO-1	164	12.2	0.536
MAO-0.5	133	12.4	0.535
$Al_2O_3$	131	12.5	0.584

 $^{\rm a}$  Calculated by the BJH model on the desorption branch of the  ${\rm N}_2$  adsorption/desorption isotherms

 $NH_3$ -TPD patterns of different catalysts. The typical streamed bread peaks are observed in all of the samples, which suggest that the acid sites on the surface of the magnesium aluminum spinel are not well-distributed [27]. The distribution temperature of desorption peaks indicates the existence of weak acid sites on the catalyst.  $NH_3$ -TPD of mesoporous alumina without Mg was also investigated. The profile of  $Al_2O_3$  expresses coexistence of weak acidity and strong acidity. Acid amount and base amount estimated from the area of TPD profiles can be treated as a function of catalytic activity. In this work, we concluded that the basicity of all samples seems to be more important for catalytic activity since acidity seems to be almost the same.

Furthermore, the structure parameters of MAO samples were investigated by N2 adsorption-desorption measurement and summarized in Table 1. Relatively higher specific surface area (205  $m^2 g^{-1}$ ) was obtained from MAO-2 material. It is worthy noticing that as the increase of Al species, the BET surface area decreases dramatically, and the specific surface area of pure Al<sub>2</sub>O<sub>3</sub> was 131 m<sup>2</sup> g<sup>-1</sup>. However, sample MAO-1.5 and MAO-3 show lower specific surface area, which is possibly due to the existence of MgO. In order to prove this, the BET of pure MgO powder was investigated and shown in Table 1 obtaining 14.7 m<sup>2</sup> g<sup>-1</sup>. The average pore size of MAO-x (x = 0.5-2) is around 12 nm, which is the specific characteristic of mesoporous (2-50 nm) materials [28]. In addition, pore size of MAO-3 is 9.6 nm since there is more MgO phase in MAO-3 (observed in Fig. 1). Comparing with the pore size reported earlier [15], we believe that the pore size here does not bring serious constraint of the diffusion of reactants.

## 3.2 Catalytic Performance

The activities of different catalysts for the reaction of DMC with DEC to synthesize EMC are summarized in Table 2.

 Table 2
 Transesterification of DMC with DEC in the presence of different catalysts

Entry	Catalyst	Yield <sup>a</sup> (%)	Time to reach equilibrium (min)
1	None	_	_
2	MAO-2	49.0	30
3 <sup>b</sup>	MOF-5	50.1	180
4 <sup>c</sup>	ZIF-8	50.7	180
5	MgO	44.6	120
6	MAO-1	48.9	30
7	MAO-1.5	48.7	30

Reaction conditions: DMC (0.05 mol), DEC (0.05 mol), catalyst (0.5 g), 373 K and 30 min

<sup>a</sup> Determined by GC, calculated in terms of DEC

 $^{\rm b}$  Cited by literature [14], DMC (0.02 mol), DEC (0.02 mol), MOF-5(1 wt%), 373 K and 3 h

 $^{\rm c}$  Cited by literature [17], DMC (0.1 mol), DEC (0.1 mol), catalyst (0.208 g), 373 K and 3 h

Obviously, no catalytic activity could be observed in the experiment without addition of catalyst, which is consistent with previous articles [14, 16]. EMC yield of around 49.0 % (error bar < 0.3 %) was obtained after adding MAO-x (x = 1-2) catalyst and reacting for 30 min in our work. Comparatively, both ZIF-8 and MOF-5 perform higher activity in the total yield of products, but much more reaction time will be needed. Jia et al. [15] also reported that porous carbon-supported MgO catalyst (MgO/NC-2) can obtain the EMC yield of 49.3 % after reaction for 30 min but a full recovery of the MgO/NC-2 catalyst required a heat treatment under an argon atmosphere at 800 °C [16], while catalyst MAO-x (x = 1-2) can be reused directly after a simple filtration. In addition, the catalyst was fabricated by calcining at 700 °C, which also indicates the higher thermal stability of the catalyst. However, ZIF-8 was stable only under 400 °C according to the DTA results given in Wang's article [17]. Zhao et al. [14] reported that the framework of MOF-5 was unstable when exposed to air. It is noteworthy that the reaction could take place without stirring because the catalyst has a great number of big pores, which can contribute to the formation of gasification center and prevent serious bumping. Hence, catalyst MAO-x (x = 1-2) is a better heterogeneous catalyst for the reaction.

## 3.3 Effect of the Reaction Time

Figure 3 presents the effect of reaction time on the product yield in the presence of different catalysts for the transesterification. All the samples are active for the reaction with excellent selectivity (>97 %) towards EMC. Among the catalysts, the new prepared MAO-2 obviously performs



Fig. 3 Dependence of the EMC yield on the reaction time with different catalysts.  $289 \times 202 \text{ mm} (300 \times 300 \text{ DPI})$ 

higher activity, and the EMC yield of 48.6 % was achieved after reacting for 20 min. In addition, different activities of MgAl<sub>2</sub>O<sub>4</sub> catalysts were obtained. While sample MAO-2, MAO-1.5 and MAO-1 performed a quite similar catalytical activity in consideration of 0.3 % of error bars for the reaction, the equilibrium of the reaction was nearly reached in 30 min, because medium base are better than other bases for the reaction and higher specific area provides more opportunity for the active sites contacting with reactants [10]. The reason why MAO-x (x = 1-2) show similar activity is that they are all medium base, and the base amount seems to be at the same level and 140 m<sup>2</sup> g<sup>-1</sup> of specific surface area is enough for active sites contacting with reactants in a short time. However, the solid MAO-0.5 and MAO-3 materials did not show any effective activity for the reaction in a short time, which could be mainly ascribed to the lower basicity (Fig. 2). But after 2 h, the vield of nearly 47 % was obtained, which is maybe due to the reaction almost reaches the equilibrium within 2 h in the presence of the catalyst.

However, commercial MgO powder displays much lower activity in a short reaction time, which maybe due to the much lower surface area of MgO than MAO-x, affecting the interaction between active sites and reactants. The highest yield (44.6 %) of ethyl methyl carbonate was obtained at 103 °C over commercial MgO powder catalyst after 2 h. The yield is close to that (44.2 %) reported earlier [16]. Obviously, new prepared MAO-x (x = 1–2) solid catalyst is much more active than sample MgO powder. The activity of mesoporous Al<sub>2</sub>O<sub>3</sub> without Mg was also tested to prove the coaction effect. Yield of 36.7 % (not present in Fig. 3) was obtained after 2 h, which demonstrates that acid sites are also active for the reaction and shows lower activity than pure MgO. All these facts above



Fig. 4 Effect of time of different catalyst (MAO-2) amount on the yield of EMC, Reaction conditions:. n(DMC)/n(DEC) = 1,103 °C, 289 × 202 mm (300 × 300 DPI)

prove that the interaction between acid and base sites on the surface of the MAO-x (x = 1-2) materials play a crucial role in the reaction.

## 3.4 Effect of the Catalyst Amount on EMC Yield

The effect of mass ratio of catalyst MAO-2 to reactant was tested and shown in Fig. 4. Catalyst amount is ranged from 1.0 to 10.0 wt% based on the total reactant mixture. As shown in Fig. 4, the yield of EMC still increases after reacting for 30 min with a small amount of catalyst (<2 %), which means the reaction needs more time to reach the equilibrium. When the catalyst amount is higher than 3 %, EMC yield has no obvious distinction as time passes by, meaning that the reaction has reached equilibrium within 30 min. The result is ascribed to the explanation that more catalyst means more active acid-base sites for the reaction, and more catalyst amount (<5 %) will shorten the time of reaching equilibrium [17, 29]. In addition, at the optimal time (30 min), EMC yield increases with catalyst amount when it is lower than 5 %, and keeps constant as the addition of the catalyst's amount to 9 %. It is arresting that the maximum yield of small amount of catalyst (1 %) is similar to that of higher amount within 2 h, which is due to that the reaction is almost reaching equilibrium after reacting for 2 h. Thus, the catalyst MAO-2 performs well in catalyzing the reaction and the optimize amount for the reaction is 5 %.

# 3.5 Catalyst Recycling

The reusability of the catalyst is considered as another important property of catalyst. In this work, regeneration



Fig. 5 FT-IR spectra of fresh MAO-2 and reused. 289  $\times$  202 mm (300  $\times$  300 DPI)

of sample MAO-2 was also examined. After 30 min of reaction at 103 °C, the solid catalyst was filtered. After drying in oven at 80 °C for 5 h, the catalyst was reused for the next time. The recycle was repeated five times and only 1.2 % yield decrease was found. Favourably, after literaton, the catalyst can be used directly without drying and the activity had no significant change compared with the dried one, which is preferable for the future industrial applications. We also examined the fresh and reused catalyst by FT-IR (Fig. 5). According to previous work [30] the absorption band at  $1,639 \text{ cm}^{-1}$  is attributed to free water. The lower peak of reused catalyst is ascribed to the loss of free water due to the side reaction of reactants with water. Peak at around  $1,100 \text{ cm}^{-1}$  is related to C-O bonds [31]. This is due to the chemical absorption of diethyl carbonate and dimethyl carbonate during the reaction. Whilst the observed peaks at around 698 and 520 cm<sup>-1</sup> are corresponded to [AlO<sub>6</sub>] groups and Mg-O stretching. This indicates the formation of MgAL<sub>2</sub>O<sub>4</sub> and no structure changes in the used catalyst. In addition, TPD analyses of fresh and used catalyst was used to demonstrate the stability of acid-base sites. As shown in Fig. 6 CO<sub>2</sub>-TPD, the used catalyst still demonstrates a medium base, and base amount decreases slightly for reused catalyst, which may be the reason of the slight activity loss. From NH<sub>3</sub>-TPD profiles, we can conclude that the acid amount of the two catalyst seem to be same. Hence, the TPD analyses prove that the regeneration of used catalyst after filtration and drying in oven at 80 °C for 5 h. All the results demonstrate that the catalyst performs excellent reusability for the transesterification under the above-mentioned conditions.



Fig. 6 CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD profiles of fresh sample MAO-2 and reused.  $259 \times 400 \text{ mm} (72 \times 72 \text{ DPI})$ 

#### 4 Conclusion

MAO-x (x = 1–2), a highly effective acid–base bifunctionalization mesoporous catalyst was prepared for the transesterification of DMC with DEC to synthesize EMC. High ethyl methyl carbonate yield (49.0 %) with the reaction time of 30 min and excellent selectivity was achieved under optimal conditions. As a heterogeneous catalyst, MAO-x (x = 1–2) can be regenerated easily by simply drying in oven and reused for at least five times with 1.2 % decrease in catalytic activity. In addition, catalyst can be used continuously after filtration, which greatly promotes the industrial applications.

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