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Binary Mg–Fe oxide as a highly active and magnetically separable catalyst for the synthesis of ethyl methyl carbonate

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Magnetic binary Mg–Fe oxides were prepared by a co-precipitation method, characterized and tested in the synthesis of ethyl methyl carbonate (EMC) from di methyl carbonate (DMC) and diethyl carbonate (DEC). The obtained results showed that the Mg/Fe oxide catalyst with a 1 : 1 molar ratio and calcined at 400 °C exhibited superior catalytic activity. The yield of EMC could reach 66% (at 100 °C for 1.5 h) with a TOF of 220 mmol h⁻¹ g_{cat}⁻¹. The prepared catalysts could be magnetically separated, and reused for ten runs without noticeable deactivation. XRD and Mössbauer spectra revealed that there was a synergistic effect between Mg and Fe oxides in the catalysts, which was consistent with the results of TPR, *i.e.* the introduction of the Mg component favored the reduction of the Fe₂O₃. XPS and IR characterizations indicated that there were a large number of accessible Fe-OHs on the surface of MgFe-400, and combining the Fe-OHs with the basic MgO may be related to the highly catalytic performance.

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1. Introduction

Ethyl methyl carbonate (EMC) could be used as an important methylation, ethylization or carbonylation agent for the syntheses of numerous organic products. More importantly, EMC could be employed as a co-solvent in nonaqueous electrolytes to improve the energy density and discharge capacity of lithium ion cells.1-3 Traditionally, EMC could be produced from the esterification of methyl chloroformate with alcohol;4 however, this route generally involves environmentally hazardous chemicals. Another method for the synthesis of EMC is the transesterification of dimethyl carbonate (DMC) with ethanol, but the separation of EMC is very difficult due to the formation of three binary azeotropes.⁵ Alternatively, the transcarbonatation of DMC with diethyl carbonate (DEC) is considered as a promising approach to EMC, because all the reaction mixtures (DEC, DMC and EMC) can be used as solvents in nonaqueous electrolytes avoiding the separation problem. Moreover, the composition of products can be adjusted through controlling the conversion and the molar ratio of raw materials.

Although several homogenous catalytic systems have been reported previously for the transcarbonatation of DMC with

^bGraduate School of the Chinese Academy of Sciences, Beijing, 100039, China ^cNational Nanotechnology Research Center, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia DEC, such as Ti(OBu)₄, Bu₂SnO, and BuSnCl₃,⁶ the separation problems between homogeneous catalysts and EMC as well as the recovery of catalysts still remained in such processes. Gan *et al.* reported lithium diethylamide and lithiated carbon catalysts for EMC, which performed high activity for the reaction,⁷ whereas these catalysts are very expensive limiting their practical application. Other heterogeneous catalytic systems including the amorphous mesoporous aluminophosphate,⁸ basic metal oxides,⁹ Al-MCM-41 or Al-Zn-MCM-41,¹⁰ MOFs,¹¹ ZIF-8 (ref. 12) and ZIF-67 (ref. 13) were also found to be active catalysts for this reaction, but only <110 mmol h⁻¹ g_{cat}⁻¹ TOFs were obtained (Table 1). In this context, more effective catalystic system is still highly desired in view of the lower cost and time-/ energy-saving, thereby increasing the yield and simplifying the production separation process.

Since magnetic materials have emerged as efficient supports for catalysts, which can facilitate the separation from the reaction media using an external magnetic field,^{14,15} in this study, we prepared the magnetic binary Mg–Fe oxides as recoverable catalysts for the synthesis of EMC *via* the transcarbonatation of DMC with DEC. The resulting catalytic system exhibited superior activity and magnetical separability. XRD, BET, XPS, TPR, Mössbauer spectra, CO_2 -TPD and FT-IR studies were conducted to explore the relationship between structure and performance, and the corresponding mechanism was preliminarily proposed. Moreover, the influences of the catalysts with different components, optimal catalyst activation, and reaction variables (such as temperature, catalyst amount) were also investigated in a batch reactor system.

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Catalyst	Operation conditions (temp., time, cat. amount)	DEC con. (%)	TOF (mmol $h^{-1} g_{cat}^{-1}$)
Lithiated diethylamide	25 °C, 48 h, 0.2 wt%	50	20
Alumino-phosphate	93 °C, 2 h, 5 wt%	50	25
MgO	103 °C, 4 h, 2.4 wt%	44.2	22
Al-Zn-MCM-41	175 °C, 5 h, 6 wt%, the flow rate 1.5 mL h^{-1}	85	_
MOFs	100 °C, 3 h, 2 wt%	50.1	41
ZIF-8	100 °C, 3 h, 1 wt%	50.7	81
ZIF-67	100 °C, 24 h, 2 wt%	83.4	17

Table 1 Summary of the work reported on synthesis of EMC from DMC and DEC over heterogeneous catalysts^a

^{*a*} TOF: based on the mole of DEC converted per gram catalyst per hour.

2. Experimental

2.1 Catalysts preparation and characterization

Chemicals used in this study including $Mg(NO_3)_2 \cdot 6H_2O$, FeSO₄·7H₂O and Na₂C₂O₄ obtained from Tianjin Chemical Reagent Factory (analytical reagent, >99%).

The binary Mg–Fe oxides were prepared by co-precipitation according to the literature procedures.¹⁶ A mixture of Mg(NO₃)₂- $^{\circ}$ 6H₂O and FeSO₄ $^{\circ}$ 7H₂O in designated ratios was dissolved into 100 mL distilled water. Subsequently, 40 mmol Na₂C₂O₄ was dissolved in to 100 mL water at 80 °C and then was added dropwise into the former solution under stirring. The resulting precipitate was aged, filtrated, washed, and calcined in static air for 3 h. The resulted catalysts are denoted as *x*MgFe-*T*, *x* is molar ratios of Mg and Fe, *T* is the calcination temperature.

The BET surface areas, pore volumes and average pore diameters of catalysts were obtained with physisorption of N_2 using a Micromeritics ASAP 2010.

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with Cu K α radiation (40 mA, 40 kV) over a 2 θ range of 20° to 80° and a position-sensitive detector using a step size of 0.01° and a step time of 0.15 s.

Surface analysis of the catalysts was performed by X-ray photoelectron spectroscopy (XPS) on VG ESCALAB210 using a Mg K α radiation at a pass energy of 20 eV. The energy scale was calibrated and corrected for charging using the C 1s (285.0 eV) line as the binding energy reference.

Temperature-programmed reduction (TPR) of H_2 was carried out on TPR/TPD flow system equipped with a TCD detector. TPR analysis was conducted with 10% H_2/Ar (50 mL min⁻¹). In a typical experiment, the solid sample (60 mg with particle size 160–200 µm) was pretreated at 400 °C for 1 h under air flow (50 mL min⁻¹) and then cooled to room temperature under argon gas flow (50 mL min⁻¹). The profile was recorded at a heating rate of 10 °C min⁻¹ from room temperature to 850 °C and maintained at this temperature until the TCD signal of H_2 returned to the baseline. Quantitative hydrogen consumptions were obtained by use of TPR calibration runs using a standard copper oxide sample (Micromeritics) in place of the catalyst.

The Mössbauer spectra were obtained at room temperature with a WissEL (Bench-MB500, Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}\text{Co/Pd}$ (activity $\cong 25$ m Ci) source and $\alpha\text{-Fe}$ standard were used. The experimentally obtained spectra were fitted to mathematical processing according to the least squares method.

The surface base properties of the catalysts were measured by temperature programmed desorption (TPD) of CO₂ and carried out on TPD flow system equipped with an MS detector (DM300, AMETEK, USA). In a typical experiment, the solid sample (200 mg with particle size 160–200 μ m) was pretreated at 400 °C for 1 h under argon gas flow (50 mL min⁻¹) and then cooled to room temperature. The sample was subsequently exposed to CO₂ stream (50 mL min⁻¹) at room temperature for 1 h and flushed again with argon gas for 1 h to remove any physico-adsorbed CO₂. The desorption profile was recorded at a heating rate of 10 °C min⁻¹ from room temperature to 400 °C and maintained until the MS signal of CO₂ returned to the baseline. The quantitative analysis for CO₂ desorption is calculated based on the integration of the corresponding TPD traces, preliminarily calibrated by the injection of pure CO₂ pulses.

Fourier transform infrared spectroscopy (FT-IR) transmission data were collected from pressed catalyst disk made with KBr in the range of 4000–400 cm⁻¹ with a Nicolet 5700 FT-IR.

2.2 EMC synthesis from DMC and DEC

Typical procedure for the synthesis of EMC: 50 mmol DMC, 50 mmol DEC and 0.104 g (1 wt%, based on the total mass of reactants) catalyst were charged into a 50 mL flask equipped with a magnetic stirring and a reflux condenser. The reaction mixture was then heated to 100 °C with continuous stirring for 1.5 h. After the reaction, the mixture was cooled to room temperature. The qualitative and quantitative analyses of the liquid mixture were conducted with GC-MS (Agilent 6890/5973) and GC (Agilent 7890) equipped with a SE-54 capillary column and a FID detector. In the experiment to test the reusability of catalyst, binary Mg–Fe catalyst was recovered using an external magnetic field and reused for the next time without further processing.

Results and discussion

3.1 Results of the catalysts characterization

The physico-chemical properties of MgO, Fe_2O_3 and binary Mg– Fe oxides are summarized in Table 2. Obviously, the BET

surface areas of pure MgO and Fe₂O₃ are much smaller than that of binary Mg-Fe oxides. For the binary Mg-Fe oxides, the porous volumes and BET surface area decreased with the increase of the Fe content, which might be due to the formation of different bulk Fe species. Meanwhile, the BET surface areas of Mg–Fe oxides decreased monotonically from 90 to 23 $m^2 g^{-1}$ with the increase of calcination temperatures from 400 to 600 °C, which could be attributed to the sintering effect. The obtained results suggested that both Fe content and calcination temperatures have strong impacts on the catalyst textures.

The X-ray diffractions of the binary Mg-Fe oxides are shown in Fig. 1. The characteristic diffraction peaks at 29.0, 33.7, 48.5 and 57.6° of Fe₂O₃ (JCPDS 24-0072) were detected for all the samples demonstrating the formation of Fe₂O₃. Besides, the peaks at 30.1, 35.5, 43.1 and 62.6° were observed in 0.5MgFe-400 (Fig. 1a), which could be well indexed to spinel MgFe₂O₄ (JCPDS 17-0464). Compared to the 0.5MgFe-400, the diffraction peaks of MgO at 43 and 63° occurred for 2MgFe-400 (Fig. 1b) and MgFe-400 (Fig. 1c), and the intensity of such diffraction peaks become stronger with higher Mg content, while the characteristic peaks of spinel MgFe2O4 disappeared. Moreover, the intensity of diffraction peaks of the MgFe₂O₄ in MgFe-600 (Fig. 1e) was much higher than that of MgFe-500 (Fig. 1d), indicating that the higher calcined temperature favored the formation of spinel MgFe₂O₄ from MgO and Fe₂O₃.¹⁶

The X-ray photoelectron spectroscopy (XPS) analyses of binary Mg-Fe oxides were also performed in this work. The binding energy of Mg 2p and Fe 2p varied slightly around 49.4 \pm 0.1 eV and 710.9 \pm 0.2 eV, respectively, suggesting that the chemical states of Mg and Fe species on the catalyst surface were mainly Mg²⁺ and Fe³⁺. From the high resolution O 1s XPS spectra (Fig. 2), two peaks could be observed in the prepared catalysts with binding energy of 529.9 and 531.6 eV, which could be assigned to lattice oxygen in oxides and hydroxyl groups derived from surface-adsorbed oxygen, respectively.^{17,18} It was found that the ratio of hydroxyl and oxide groups decreased with the calcined temperature elevating from 400 to 600 °C, implying that the hydroxyl partly converted to lattice oxygen at higher temperature. Furthermore, according to the XPS results, the surface atom ratios of Fe^{3+} and Mg^{2+} over MgFe-400, -500 and -600 are 3.6, 7.4 and 5.4, respectively, which are higher than the theoretical value 1, meaning that Fe species enriched on the



Fig. 1 XRD patterns of (a) 0.5MgFe-400 (b) 2MgFe-400 (c) MgFe-400 (d) MgFe-500 and (e) MgFe-600.

surface of catalysts and the Fe amounts were obviously impacted by calcined temperature.

TPR results of MgO, Fe₂O₃ and MgFe-400 are described in Fig. 3. The pure MgO does not show any hydrogen consumption under the experimental conditions (Fig. 3a). As a reference, a



Fig. 2 O 1s XPS spectra of (a) MgFe-400 (b) MgFe-500 and (c) MgFe-600.

Table 2 Physico-chemical properties of the binary Mg-Fe oxides					
Catalyst	$\frac{S_{\text{BET}}}{(\text{m}^2 \text{ g}^{-1})}$	${d_{ m p}}^a_{ m (nm)}$	${\nu_{\rm p}}^{b}_{({\rm cm}^3 {\rm g}^{-1})}$	H_2 consumption ^c (mmol g ⁻¹)	Total basic amount ^d $(\mu mol g^{-1})$
2MgFe-400	156	9.4	0.54	3.6	249
MgFe-400	90	13.6	0.45	5.5	205
0.5MgFe-400	88	14.3	0.41	5.9	93
MgFe-500	62	16.1	0.32	—	113
MgO	29	26.3	0.21	0	69
MgFe-600	23	24.4	0.15	—	52
Fe_2O_3	10	25.6	0.05	5.8	32

^a Average pore size. ^b Average pore volume. ^c H₂ consumption calculated with respect to standard CuO-TPR run under similar conditions. ^d Determined by TPD.



Fig. 3 TPR-H₂ profiles of (a) MgO (b) Fe₂O₃ and (c) Mg-Fe-400.

sharp peak centered at 442 °C and a broad peak at 727 °C along with a shoulder at 800 °C could be observed in pure Fe₂O₃ (Fig. 3b). Generally, the peak at 442 °C is assigned to the reduction of Fe₂O₃ to Fe₃O₄, and the hydrogen consumed at this peak (2.05 mmol g^{-1}) corresponded well to the total consumption of Fe₂O₃ to Fe₃O₄ (2.08 mmol g^{-1}). Besides, the higher temperature peak could be ascribed to the subsequent reduction

of Fe₃O₄, ultimately involving the formation of metallic iron.¹⁹ In comparison with TPR profiles of pure Fe₂O₃, two reduction peaks at 422 and 668 °C were found over MgFe-400 (Fig. 3c). Based on the hydrogen consumed at the first peak (1.46 mmol g⁻¹), it could be determine that the actual ratio of Mg/Fe in the MgFe-400 was 1.17 : 1. However, the hydrogen consumed at the second peak (4.07 mmol g⁻¹) was about 9 times lesser than the corresponding consumption of Fe₃O₄ to Fe (35 mmol g⁻¹) in this catalyst, indicating that only part of Fe₃O₄ was reduced to Fe. Additionally, the shift in the reduction temperature from 442 to 422 °C indicated that some sort of interaction occurred between Mg species and Fe oxide, and the introduction of Mg component may favor the reduction of the Fe oxide.

The Mössbauer spectra for the Fe₂O₃ and binary Mg–Fe oxides at room temperature are shown in Fig. 4, and the Mössbauer parameters are listed in Table 3. The formation of Fe₂O₃ was revealed by the sextet with the isomer shift (IS) of 0.367 mm s⁻¹ and quadrupole splitting (QS) -0.178 mm s⁻¹ in the Mössbauer spectra as shown in Fig. 4a. As Mg was introduced into the iron oxide (Fig. 4b), one sextet and two paramagnetic doublets were observed. In the two doublets, the doublet with IS = 0.331 mm s⁻¹ and QS = 0.653 mm s⁻¹ is typical of superparamagnetic Fe³⁺ species on the octahedral sites, denoted as Fe³⁺ (A) in Table 3, which may be assigned to MgFe₂O₄; another doublet peak with IS = 0.377 mm s⁻¹ and



Fig. 4 Mössbauer spectra of Fe₂O₃ and binary Mg–Fe oxides recorded at room temperature.

Table 3 Mössbauer parameters of Fe₂O₃ and binary Mg-Fe oxides at room temperature^a

Sample	Component	IS $(mm \ s^{-1}) \pm 0.002$	$\begin{array}{l} \mathrm{QS} \\ \mathrm{(mm~s}^{-1}) \pm \ 0.01 \end{array}$	$egin{array}{c} H_{ m hf} \ ({ m T})\pm 0.01 \end{array}$	$arGamma$ (mm s ⁻¹) \pm 0.006	Area (%)
Fe ₂ O ₃	Fe ₂ O ₃	0.367	-0.178	51.33	0.37	100
	Fe_2O_3	0.315	0.003	49.43	0.57	89.19
0.5MgFe-400	Fe^{3+} (A)	0.331	0.653	_	_	9.19
0	Fe^{3+} (B)	0.377	2.612	_	_	1.62
MgFe-400	Fe ₂ O ₃	0.315	0.011	49.92	0.53	100
2MgFe-400	Fe_2O_3	0.317	0.002	49.91	0.61	100
^{<i>a</i>} IS: isomer shift	. OS: quadrupole spl	itting. <i>H</i> _{bf} : hyper fine mag	netic fields. Γ: line width.			

 $QS = 2.612 \text{ mm s}^{-1}$ could be ascribed to high spin Fe^{3+} on the tetrahedral sites, denoted as Fe^{3+} (B). For MgFe-400 (Fig. 4c) and 2MgFe-400 (Fig. 4d), the raw spectra can also be fitted to one sextet but the relative intensity decreased compared to the pure Fe₂O₃. The reason may be due to the formation of MgO, which could be also confirmed by XRD. At the same time, the line width of the sextuplet in MgFe-400 was substantially broadened in comparison to the corresponding sextuplet of Fe_2O_3 , indicating the high dispersion of Fe_2O_3 in the sample, which may result from the occurrence of a random distribution of constituent Fe³⁺ cations in the presence of Mg²⁺.²⁰ In addition, the value of $H_{\rm hf}$ ($H_{\rm hf}$ = 49.92 T) for MgFe-400 was lower than that of the pure Fe_2O_3 ($H_{hf} = 51.33$ T), which demonstrated that the coordination environment of the Fe atom changed. The obtained results were consistent with the TPR analyses, *i.e.* the addition of Mg component favored the reduction of the Fe₂O₃.

The base properties of these oxide catalysts were studied by TPD of adsorbed CO₂. The CO₂-TPD results of Fe₂O₃, MgO and binary Mg–Fe oxide samples are exhibited in Fig. 5. For the MgO sample (Fig. 5a), a broad peak centered at 250 °C was observed, which was ascribed to medium strength basic sites of $O^{2-,21}$ In comparison with the MgO, only a small peak meaning the less basic sites was examined on the CO₂-TPD curves of pure Fe₂O₃ (Fig. 5b). It was found that all binary Mg– Fe oxide samples possessed broadened CO₂ desorption peaks in the region of 50–350 °C, which were derived from the weak and medium strength basic sites.¹⁶ From the quantitative results of CO₂-TPD (Table 2), it can be seen that the total basic amount decreased from 249 to 93 µmol g^{-1} with the decrease of the Mg content, suggesting that the basic site was mainly due to the MgO phase in the binary Mg–Fe oxides. Moreover, the total basic amount sharply decreased from 205 to 52 µmol g^{-1} with the calcination temperature elevating from 400 to 600 °C, which probably because of the decrease of content of MgO in catalyst.

Fig. 6 displays the FT-IR spectra of the fresh (a) and reused MgFe-400 (b). The signal at around 3400 cm^{-1} could be attributed to the O-H stretch derived from the surface Fe-OH, and the intensity of this peak decreased after used 10 times because Fe-OHs were partially replaced by Fe-OCH₃ bonds. Meanwhile, the absorptions at 1632, 1100 and 816 cm⁻¹ were detected for fresh catalyst, which could be assigned to the H-O-H bending, Fe-O bending and Fe-OH-Fe bending, respectively.22 Compared to the fresh one, a new band at 2961 cm⁻¹ corresponding to the C-H stretching vibration was observed, which may be due to trace of methoxide species residing on the used catalyst surface;²³ and the peak 1024 cm⁻¹ owing to C-O vibration of methoxide group further confirmed that the methoxide group adsorbed on the catalyst surface. In addition, bicarbonate species formation involving surface hydroxyl groups emerged on reused catalyst, which characterized a C-OH



Fig. 5 CO_2 -TPD profiles of (a) MgO (b) Fe₂O₃ (c) MgFe-600 (d) MgFe-500 (e) 0.5MgFe-400 (f) MgFe-400 and (g) 2MgFe-400.



Fig. 6 FT-IR patterns of (a) fresh and (b) reused MgFe-400.

Table 4 Results of transcarbonatation of DMC and DEC over various catalysts⁴

Entry	Catalyst	n(DMC)/n(DEC)	Yield ^c (%)	TOF (mmol $h^{-1} g_{cat}^{-1}$)
1	Ma	1 • 1	7	22
2	Fe O	1.1	2	22
3	$MgO + Fe_2O_2^b$	1:1	4	13
4	0.5MgFe-400	1:1	46	153
5	MgFe-400	1:1	51	170
6	2MgFe-400	1:1	39	130
7	MgFe-500	1:1	16	55
8	MgFe-600	1:1	2	8
9	MgFe-400	2:1	66	220
10	MgFe-400	1:2	34	226

^{*a*} Reaction conditions: 50 mmol DMC, 50 mmol DEC, 0.104 g catalyst, 100 °C, 1.5 h. ^{*b*} Physically mixed MgO and Fe₂O₃ (molar ratio of Mg/Fe = 1 : 1). ^{*c*} Determined by GC, calculated in terms of DEC (moles of EMC/2 \times moles of DEC). TOF: calculated based on the mole of DEC converted per gram catalyst per hour.

bending mode at 1260 cm^{-1} as well as symmetric O–C–O stretching bands at 1480 cm^{-1} .²⁴

3.2 Results for synthesis of EMC

As shown in Table 4, the transcarbonatation of DMC and DEC for EMC was investigated over various catalysts with different proportions and activation temperatures. Only <10% of EMC yield were obtained over MgO, Fe₂O₃ and physical mixed oxide, indicating that those catalysts performed low activity for such transcarbonatation process (entries 1-3). As the binary Mg-Fe oxides with different proportions were used as catalysts, (entries 4-6), the yield of EMC was greatly improved. Above all, when the ratio of Mg and Fe was 1, 51% yield of EMC was achieved. It's worth mentioning that the TOF could be up to 170 mmol $h^{-1} g_{cat}^{-1}$ over MgFe-400, which was better than previously reported results to the best of our knowledge.⁶⁻¹³ If further increased the ratio of Mg and Fe to 2, the yield of EMC decreased to 39%. Obviously, the catalytic activity of binary Mg-Fe oxides was higher than that of the physical mixture, demonstrating that the integration of Mg and Fe components could remarkably enhance the catalytic activity and some synergistic effect probably occurred. Additionally, the yield of EMC was sharply decreased with the calcination temperature from 400 to 600 °C (entries 5, 7 and 8), indicating that 400 °C was the proper activation temperature for better catalytic activity. Generally, it was widely accepted that transesterification reaction was efficiently catalyzed by acid–base catalysts.²⁵ Therefore, it is reasonable to infer that the sharply decrease of catalytic activity might be due to the decrease of total basic sites (Table 2) with the calcination temperature elevating from 400 to 600 °C. Besides, the ratios of DMC and DEC from 2 : 1 to 1 : 2 were also studied (entries 9 and 10), and the yield of EMC could reach 67.8%. In this way, the molar ratio of the products mixture could be changed through adjusting the molar ratio of raw material.

3.3 Effect of reaction conditions

In order to optimize reaction conditions, the influence of various reaction parameters was investigated. The impact of the amount of catalyst charged on the EMC synthesis was first examined varying from 0 to 3 wt% (respect to the total mass of raw materials) under 100 °C. As seen in Fig. 7A, EMC yield was very low without any catalyst. As 1 wt% catalyst was charged, 51% yield of EMC with >99% selectivity was achieved, however,



Fig. 7 Effect of reaction conditions on the catalytic performance of MgFe-400 influence of (A) the amount of catalyst charged; (B) the temperature; reaction conditions: 50 mmol DMC, 50 mmol DEC, 100 °C, 1.5 h.



Fig. 8 The reusability of MgFe-400 catalyst for EMC synthesis. Reaction conditions: 50 mmol DMC, 50 mmol DEC, 0.104 g catalyst, 100 $^\circ\text{C},$ 1.5 h.

as 2 wt% catalyst was used, no remarkable increase of EMC yield was observed, which suggested that 1 wt% catalyst might be sufficient for this process. In addition, the influence of temperature on EMC synthesis was also tested (Fig. 7B). It was found that the yield of EMC increased with the raising of reaction temperature, and the maximum yield (51%) was obtained at 100 °C. Therefore, 100 °C was the proper reaction temperature for the transcarbonatation process.

3.4 Recycling of the catalyst

The reusability of solid catalysts is a key parameter in determining their suitability in practical applications. Therefore, attempts were made to reuse the MgFe-400 catalyst 10 times by simple magnetic separation, and reused without any processing. The obtained results (Fig. 8) indicated that the catalyst could retain its activity performance during the recycles. The ICP-AES analyses showed that only 3 ppm of Mg and 7 ppm of Fe content were leached after 10 recycles, which indicated that MgFe-400 catalyst displayed excellent stability in this process.

3.5 The reaction mechanism

The mechanism for the transcarbonatation of DMC and DEC has been reported previously,⁸ in which DMC and DEC were



Scheme 1 A possible mechanism for the transcarbonatation between DMC with DEC.

chemisorbed on the Lewis acid sites and base sites of the catalyst to form intermediate. In this case, MgO activates the carbonyls of reactants, and the surface –OH groups play an important role in formation of reaction intermediate simultaneously. A possible mechanism for the transcarbonatation between DMC and DEC was proposed over the binary Mg–Fe oxides system (Scheme 1). First, chemisorption of DEC and DMC could occur on the Mg²⁺ of MgFe-400. Then two adjacent OH groups attack DEC and DMC carbonyl carbon to form the corresponding alkoxy groups and bicarbonate intermediate. Once the intermediate is produced, it would migrate to different regions where the alkoxy groups are available to yield mixtures of dialkyl products.

4. Conclusions

In summary, magnetic binary Mg–Fe oxides with different proportions were prepared by co-precipitation method, and MgFe-400 displayed high catalytic performance for the synthesis EMC from DMC and DEC (the highest TOF can reach 226 mmol $h^{-1} g_{cat}^{-1}$). It was found that the presence of Fe-OHs and basic sites of the MgO played a critical role on the activation of the reactants in the transcarbonatation reaction. Moreover, the catalyst could be easily isolated using an external magnetic field and recovered for 10 runs without significant loss of catalytic activity.

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