

Short Communication

Efficient synthesis of 2-oxazolidinone from epoxides and carbamates with binary Mg–Fe oxides as a magnetic solid base catalyst

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ABSTRACT

Magnetic binary Mg–Fe oxides were prepared by co-precipitation method, characterized and tested in the synthesis of 2-oxazolidinones from epoxides and carbamates. The catalytic results showed that the catalyst with Mg/Fe molar ratio of 1 and calcined at 400 °C exhibited superior catalytic activity. The catalyst could be magnetically separated, recycled and reused for five runs without noticeable deactivation. Under the optimized conditions, various 2-oxazolidinones derivatives were successfully synthesized with good to excellent isolated yields.

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1. Introduction

2-oxazolidinones are important compounds in both fine chemicals and synthetic organic chemistry, which are widely applied in the synthesis of pharmaceuticals, pesticides, cosmetics, and so on [1–3]. Since the 2-oxazolidinones preparation generally uses highly toxic phosgene [4], and therefore involves environmental and safety problems, much efforts have been made to explore environmentally benign methods for 2-oxazolidinones synthesis. Several non-phosgene routes for 2-oxazolidinones synthesis have been developed: (1) oxidative carbonylation of β-aminoalcohols with CO/O₂, (2) carbonylation of β-aminoalcohols by dialkyl carbonate, (3) cycloaddition of CO₂ with β-aminoalcohols or aziridines. Although the oxidative carbonylation of β-aminoalcohols catalyzed by transition metal is an efficient way to produce 2-oxazolidinones [5–9], such route is not eco-friendly due to the potential explosion hazards and poisonous CO. As an alternative, dialkyl carbonates were used for the synthesis of 2-oxazolidinones [10–13]. It should be noted that dialkyl carbonates are mainly produced by phosgenation or oxidative carbonylation routes [14,15]. Under these circumstances, the direct synthesis of 2-oxazolidinones from CO₂ and β-aminoalcohols [16–18] or aziridines [19–22] is preferable from environmental and economical viewpoints; however, some stoichiometrically consumed dehydrating reagents and high pressure or high temperature are required in most of these works.

Since epoxy compounds are known to produce ring-opened addition products with nucleophilic reagents [23], another phosgene-free

route for 2-oxazolidinones synthesis is the reaction between epoxy compounds and carbamates, and then intramolecular cyclization to give the expected 2-oxazolidinones [24–26], Scheme 1. Till now, several homogenous base catalysts have been reported, such as tertiary amines, potassium hydroxide and betaines [24,27,28]. However, the separation and recovery problems of those catalysts are still maintained and accordingly limit their practical application. Therefore, the development of an effective and stable heterogeneous base catalyst is highly desirable.

Since magnetic materials have emerged as efficient supports for catalysts and can facilitate their separation from the reaction media using an external magnetic field [29,30], herein, we report the preparation binary Mg–Fe oxides as highly effective and recoverable magnetic solid base catalyst for the synthesis of 2-oxazolidinone from epoxides and carbamates.

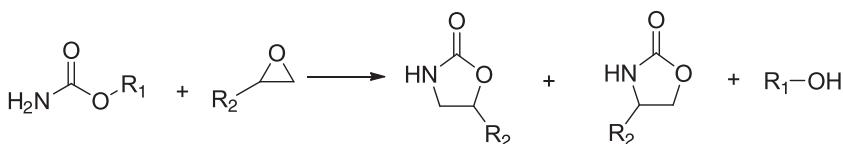
2. Experimental

2.1. Catalysts preparation

A mixture of given amount of Mg(NO₃)₂·6H₂O and Fe(SO₄)₂·7H₂O in designated ratios was dissolved into 100 mL distilled water under stirring. Subsequently, 40 mmol Na₂C₂O₄ was dissolved into 100 mL water at 80 °C and then was added dropwise into the former solution. The resulting precipitate then was aged for 2 h, filtrated, washed, and calcined in static air for 2 h. The obtained solids were denoted as xMgFe-T, where x represents the Mg/Fe molar ratio, and T is the calcination temperature.

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Scheme 1. Synthesis of 2-oxazolidinones from alkyl carbamate and epoxide.

2.2. Catalysts characterization

The BET surface areas, pore volumes and average pore diameters of catalysts were obtained with physisorption of N₂ using a Micromeritics ASAP 2010.

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu K α radiation (40 mA, 40 kV) over a 20 range of 15 to 85°.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB210 instrument. Mg K α radiation at an energy scale calibrated versus adventitious C1s peak at 285.00 eV was used.

The surface acid–base properties of the catalysts were measured by temperature programmed desorption of CO₂ and carried out on TPD flow system equipped with an MS detector (DM300, AMETEK, USA). The quantitative analysis for CO₂ desorption is calculated based on the integration of the corresponding TPD traces.

2.3. Catalytic testing

All reactions were carried out in a 90 mL stainless steel autoclave with a glass tube inside and magnetic stirring. In a typical test, 10 mmol propylene oxide (PO) (0.58 g), 15 mmol ethyl carbamate (EC) (1.33 g) and 58 mg binary Mg–Fe oxides catalyst were added in the reactor. The reaction mixture were heated up to 140 °C for 8–12 h. After the reaction was completed, the catalyst was recovered using an external magnetic field. The qualitative and quantitative analyses of the liquid mixture were conducted with GC-MS (Agilent 6890/5973) and GC (Agilent 7890) equipped with a FID detector.

3. Results and discussion

3.1. Catalysts characterization

The physical properties of the binary Mg–Fe oxides are summarized in Table 1. The BET surface area and porous volumes decreased monotonically from 156.1 to 23.1 m²/g and 0.54 to 0.15 cm³/g, respectively, while the average pores diameter was increased monotonically from 9.4 to 24.4 nm, with the decreasing of the Mg content and the increasing of calcination temperature from 400 to 600 °C. All those suggested that both the Mg content and the calcination temperatures have a strong impact on the texture of the binary Mg–Fe oxides. Moreover, the sintering effect, especially when the catalyst calcined at higher temperature (500 or 600 °C), may resulted in the decreasing of the BET surface area. As to the variation of the BET surface area with the Mg content, it might be duo to the different bulk

composition with different Mg content, which was confirmed with the results of XRD as discussed blow.

XRD patterns of MgO, Fe₂O₃, MgFe₂O₄ standards and binary Mg–Fe oxides are shown in Fig. 1. The results showed that the characteristic diffraction peaks of Fe₂O₃ (JCPDS 24–0072) were observed for all the samples and confirmed the Fe₂O₃ formation. For the 0.5MgFe-400, the peaks at 30.1, 35.5, 43.1 and 62.6° were also existed, which could be well indexed to spinel MgFe₂O₄ (JCPDS 17–0464). Compared to the 0.5MgFe-400, the diffraction peaks at 43 and 63° were also observed for MgFe-400 and 2MgFe-400, which could be ascribed to the (200) and (220) planes of MgO (JCPDS 87–0653), and the intensity of such diffraction peaks become significantly stronger in samples with higher Mg content. Therefore, the formation of additional crystalline MgO phase in MgFe-400 and 2MgFe-400 suggested that such materials could be used as solid base catalyst. Moreover, all the diffraction lines become slightly stronger and sharper after calcined at higher temperature, suggested that the higher calcinations temperature promoted the crystallization of the catalyst. Compared to the MgFe-500, however, the intensities of diffraction peaks of the MgO and Fe₂O₃ in MgFe-600 were much lower than that of MgFe-500, suggesting that the higher calcinations temperature favored the formation of spinel MgFe₂O₄ from MgO and Fe₂O₃.

The influence of the calcination temperature on the chemical states of the binary Mg–Fe oxides is shown in Fig. 2. The binding energy of Mg 2p and Fe 2p_{3/2} varied slightly around 49.4±0.1 and 710.9±0.2 eV, respectively, suggesting that the chemical states of Mg and Fe species on the catalyst surface were mainly Mg²⁺ and Fe³⁺ (Fig. 2a and b). As shown in Fig. 2c, two O 1s peaks could be well resolved with their binding energy at 529.9 and 531.6 eV, which should be assigned to oxygen of oxide and hydroxyl groups, respectively [31]. Moreover, the ratio of hydroxyl and oxide groups was decreased with the calcination temperature elevated from 400 to 600 °C. Since the surface of the MgO is easily hydroxylated due to dissociative chemisorption water when it was exposed to the air, it can be conjectured that the content of the MgO phase in binary

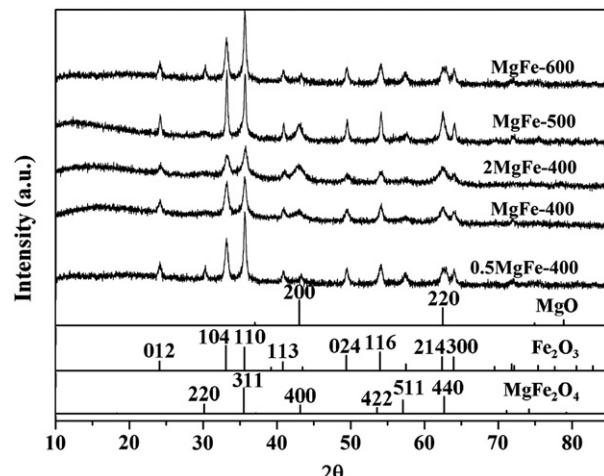


Fig. 1. XRD patterns of MgFe₂O₄ (JCPDS 17–0464), Fe₂O₃ (JCPDS 24–0072), MgO (JCPDS 87–0653), 0.5MgFe-400, MgFe-400, 2MgFe-400, MgFe-500 and MgFe-600.

Table 1
Physicochemical properties of the binary Mg–Fe oxides.

Entry	Catalysts	S _{BET} (m ² /g)	d _p (nm) ^a	v _p (cm ³ /g) ^b	Total basic sites (μmol/g)
1	2MgFe-400	156.1	9.4	0.54	249
2	MgFe-400	90.4	13.6	0.45	205
3	0.5MgFe-400	87.5	14.3	0.41	93
4	MgFe-500	61.8	16.1	0.32	113
5	MgFe-600	23.1	24.4	0.15	52

^a Average pore size.

^b Average pore volume.

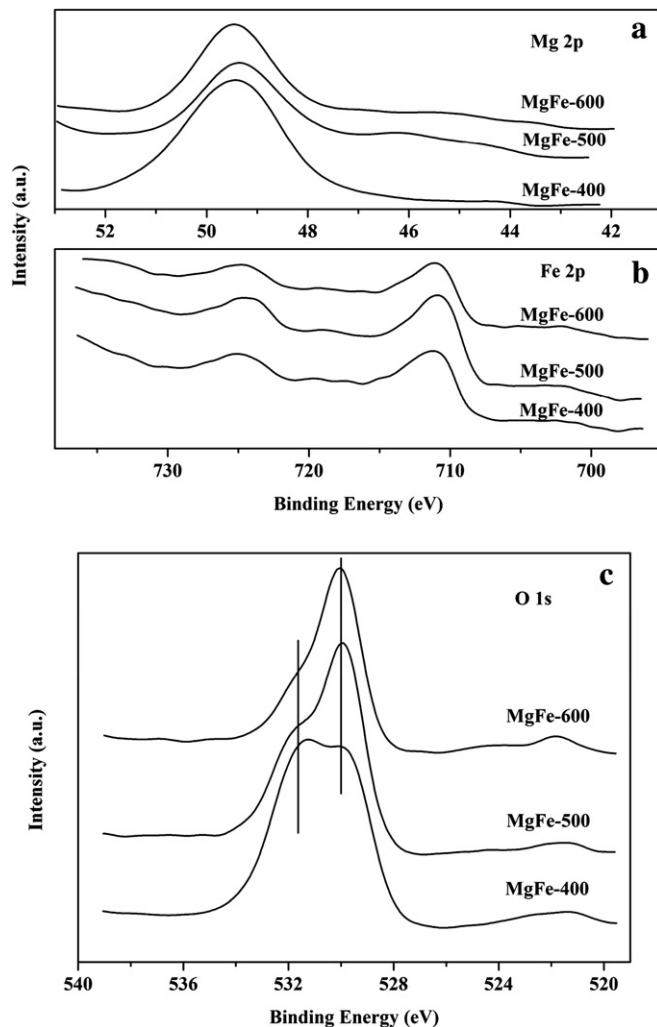


Fig. 2. XPS spectra of (a) Mg 2p, (b) Fe 2p and (c) O 1s spectra of MgFe-400, MgFe-500 and MgFe-600.

Mg–Fe oxide was decreased when it was calcined at higher temperature and the higher calcinations temperature was favorable to convert MgO to Mg₂O₄, which is consistent with the results of XRD.

Fig. 3 shows the TPD-CO₂ profiles over various binary Mg–Fe oxides. Generally, broadened CO₂ desorption peaks in the temperature region of 50–350 °C were observed over all the tested samples, which were derived from the weak and medium strength basic sites. Other CO₂ desorption peaks appeared above 400 °C in 2MgFe-400 and MgFe-400 samples, which was attributed to strong strength basic sites by isolated O²⁻ in MgO. From the quantitative results of TPD-CO₂ (Table 1), it can be seen that the total basic sites decreased from 249 to 93 μmol/g with decreasing the ratio of Mg and Fe from 2 to 0.5, respectively, suggesting that the basic site mainly derived from the MgO phase in the binary Mg–Fe oxides. Moreover, the total basic sites sharply decreased from 205 to 52 μmol/g with the calcination temperature elevated from 400 to 600 °C, which most probably because of the relative lower surface area of MgFe-500 and MgFe-600 than that of MgFe-400.

3.2. Catalytic testing

The reaction of EC and PO for 5-methyl-2-oxazolidinone synthesis was investigated over various catalysts, Table 2. In the blank test (entry 1), the PO conversion was only 10%, suggested that catalyst was essential for such reaction proceeded successfully. The moderate to good PO conversions of 52–98% were achieved over the binary

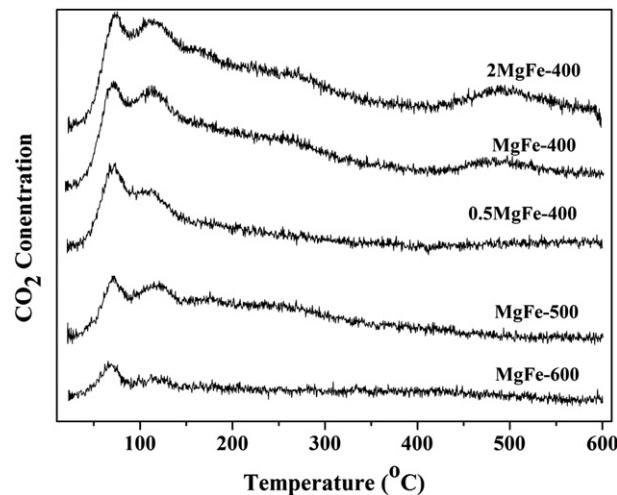
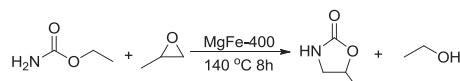


Fig. 3. TPD-CO₂ profiles of 2MgFe-400, MgFe-400, 0.5MgFe-400, MgFe-500 and MgFe-600.

Mg–Fe oxides with different calcinations temperature or ratios of Mg and Fe, entries 2–6. Among the catalysts calcined at different temperature, entries 2–4, the PO conversions were decreased with the catalysts calcination temperature elevated from 400 to 600 °C and the MgFe-400 exhibited superior catalytic activity with 97% PO conversion. Furthermore, the binary Mg–Fe oxides with different molar ratios of Mg and Fe calcined at 400 °C were also tested, entries 2 and 5–6. The conversions of PO were greatly improved and increased with increasing the ratio of Mg and Fe, reaches its maximum 97% at Mg/Fe molar ratio of 1:1. With further increasing the ratio of Mg and Fe to 2, the conversion of PO remained almost constant. That is, the catalyst with Mg/Fe molar ratio of 1:1 and calcined at 400 °C was the most active catalyst for 2-oxazolidinone synthesis. According to the quantitative results of TPD-CO₂, it could be found that the catalytic activity sequence is correlated to amounts of the basic site of the catalysts, which indicate that the catalytic activity is mostly determined by their relative basic strength. Furthermore, the larger amount of basic sites and the removal of carbonate from MgO surface at high temperature (>400 °C) could be the major reasons for the higher catalytic activity for MgFe-400. Moreover, the catalyst was recycled through simple magnetic separation, and washed with ethyl acetate and dried at 100 °C to remove the adsorbed organic

Table 2

Results of 5-methyl-2-oxazolidinone synthesis from EC and PO over different catalysts ^a.



Entry	Catalysts	Conv./%	Sel./%	Yield/% ^b
1	None	10	97	8
2	MgFe-400	97	99	95
3	MgFe-500	81	99	77
4	MgFe-600	52	98	48
5	0.5MgFe-400	75	98	73
6	2MgFe-400	98	99	95
7	Used MgFe-400 ^c	93	98	93
8	MgFe-400 ^d	42	98	40
9	MgFe-400 ^e	23	98	22
10	MgFe-400 ^f	98	99	97

^a Reaction conditions: PO, 10 mmol; EC, 15 mmol; catalysts, 58 mg (10 wt.%); reaction temperature, 140 °C; reaction time, 8 h. Conversions and selectivities were determined by gas chromatography.

^b Isolated yield based on the charged PO.

^c Catalyst reused for five times.

^d Reaction conducted at 120 °C.

^e 11.6 mg MgFe-400 (2 wt.%).

^f 87 mg MgFe-400 (15 wt.%).

Table 3

Scope and limitation of MgFe-400 for catalytic syntheses various 2-oxazolidinones ^a.

Entry	Substrates		Major products	Conv. (%)	Sel. (%)		Yield (%) ^b
	Carbamate	Epoxide			major	minor	
1				98	98	2	94
2				97	99	1	95
3				97	97	3	94
4				96	100	-	90
5				97	96	4	94
6				98	99	1	95
7				97	98	2	93
8				97	99	1	94
9				95	76	24	92
10				85	100	-	82

^a Reaction conditions: epoxides, 5 mmol; alkyl carbamates, 7.5 mmol; catalyst, 10 wt.% based on the mass of charged epoxide; reaction temperature, 140 °C; reaction time, entries 1–5, 8 h; entries 6–10, 12 h. Conversions and selectivities were determined by gas chromatography.

^b Isolated yield based on the charged epoxides.

materials. The catalyst recycling test showed that the PO conversion of 93% was obtained even after five runs (entry 7), suggesting that the catalyst could be reused without significantly loss in activity after the fifth runs. Additionally, the leaching of the Mg and Fe after the reaction was determined with ICP analyses, and the results showed that the amount of Mg and Fe leached were 0.002 and 0.007% of the originally charged MgFe-400 catalyst, respectively, suggested that the catalytic activity should mainly be derived from the solid MgFe catalyst. Subsequently, the influence of the reaction temperature on the reaction was further investigated, entry 8. A significant increase in PO conversion from 42 to 97% was observed when the reaction temperature increased from 120 to 140 °C, and reached the maximum at 140 °C, indicating that such reaction was relatively sensitive to the temperature and the higher temperature favors the conversion of PO to 5-methyl-2-oxazolidinone. The effects of the amount of catalyst charged on the reaction was also investigated, entry 9 and 10. It can be seen that the PO conversion was increased from 23 to 97% when the amount of catalyst was increased from 2 to 10 wt.%, however, with further increasing the amount of catalyst to 15 wt.%, the conversion of the PO showed little changes. Notably, the 5-methyl-2-oxazolidinone was preferentially formed with high selectivities in all cases listed in Table 2. The major product corresponds to the nucleophilic ring opening of the PO at the less substitute site under basic conditions [23], followed by intramolecular cyclization to produce the corresponding 5-methyl-2-oxazolidinone. Moreover, the 4-methyl-2-oxazolidinone as byproduct was observed,

which was formed duo to nucleophilic ring-opening of PO at the methyl substitute site.

3.3. Scope of the catalysts

The scope of the MgFe-400 catalyst in 2-oxazolidinones synthesis with different alkyl carbamates and epoxides was further investigated, Table 3. Firstly, the corresponding 2-oxazolidinones were successfully synthesized with different alkyl carbamates and PO over MgFe-400, entries 1–3, suggested that the substituent on the oxygen atom of alkyl carbamate has little influence on such reaction. Then, various epoxides with different functional groups were further investigated. Excellent yields of the corresponding 2-oxazolidinones were obtained with terminal epoxides (entries 4–9), while the disubstituted epoxide, cyclohexene oxide (entry 10), gave lower activity towards the production of the corresponding 2-oxazolidinones, which might be due to the high hindrance of cyclohexene oxide. However, the selectivity of the 5-substituted-2-oxazolidinones for the styrene oxide (entry 9) was much lower than that of other epoxides, which might be ascribed to the conjugative effect derived from the benzene ring, which should favourably attack at the carbon atom at which phenyl substitute was connected to afford 4-substituted-2-oxazolidinones [32]. In one word, various 5-substituted-2-oxazolidinones were preferentially formed with high selectivities over the basic MgFe-400 catalyst.

4. Conclusions

In conclusion, binary Mg–Fe oxides were prepared by co-precipitation method and MgFe-400 was found to be effective catalyst for the synthesis 2-oxazolidinones from epoxides and carbamates. The total basic sites of the catalysts were considered to play an important role for the superior catalytic activity. The catalyst could be easily isolated using external magnetic field and recovered for several runs without significant loss of catalytic activity. In general, good to excellent yields of 2-oxazolidinones were obtained with various alkyl carbamates and epoxides.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2012.08.006>.

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