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Short communication

Zn–Mg mixed oxide as high-efficiency catalyst for the synthesis of propylene carbonate by urea alcoholysis

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ABSTRACT

Zn/Mg catalysts with different atomic ratios of zinc to magnesium were prepared via urea–precipitation. The products were characterized by XRD, BET, SEM, CO_2-TPD, and ICP. Compared with pure ZnO, the mixed oxide possessed appropriate alkaline density and high specific surface area. The catalyst with Zn/Mg of 1:4 exhibited high catalytic activity within 30 min and reliable production for propylene carbonate (PC) (94.8%). It was found that the PC yield was strongly related to the amount of alkali of unit specific surface area. Furthermore, the regeneration of ZnO–MgO catalyst was investigated and the ZM0.25 catalyst can be reused for up to 5 times with less changed PC yield.

1. Introduction

Propylene carbonate (PC) is a useful solvent and chemical intermediate. As an eco-friendly solvent, PC can be used in synthetic fiber, dyeing and gas purification, etc. [1,2]. Moreover, It can be utilized for pharmaceutical and polymer synthesis due to its high activity, especially for dimethyl carbonate (DMC) synthesis via transesterification with methanol [3,4]. Since PC was firstly produced from 1,2-propanediol and phosgene, there had been several environmentally compatible synthesis routes including transesterification of 1,2-propanediol (PG) with diethyl carbonate, direct oxidation of olefins with carbon dioxide, and cycloaddition of carbon dioxide [5–10]. However, due to the disadvantages of poisonous compounds and the low yield, all of the above processes are confronted with environmental pollution and lacking economic viability. Moreover, homogeneous catalysts are disadvantageous in terms of catalyst separation [11]. Compared with the traditional routes, the synthesis of PC from urea and PG presents the advantages of low cost, easily available feedstock and mild reaction condition. In addition, the PC cyclic reaction network including DMC synthesis via transesterification and PC synthesis is a green and environmentally friendly process for DMC synthesis, as shown in Scheme 1 [11].

Su and Speranza [12] studied the synthesis of alkylene carbonates from urea and alkylene glycol over toxic organic-tin with PC yield of 84% for the first time. Doya et al. [13] increased the yield of products by using zinc, magnesium and lead as catalysts under a vacuum. Li et al. [14] concluded that ZnO was more favorable to promote urea decomposition to form intermediate isocyanate species, and which was then converted into PC. In the pioneering work by several researchers, ZnO was used as high activity catalyst for the synthesis of PC [7–10]. The stronger alkaline catalyst can accelerate urea decomposition, resulting in the improvement of catalytic activity [11]. So far, few papers are available about the effect of the amount of alkali in different alkaline sites on the catalytic performance. Moreover, mixed metal oxides represented one of the most important and widely employed classes of solid catalysts, either as active phases or supports [15]. Yuan et al. [16] considered that mixed transition-metal oxides played significant roles for low-cost and environmentally friendly energy storage/conversion technologies. Gawande et al. [17,18] prepared nano-sized magnesia–zirconia mixed oxide catalyst from inexpensive precursors and reported their application as various important organic reactions. Prepared catalyst had high surface area, and was reusable and recyclable for many organic reactions.

In the present work, ZnO/MgO mixtures with different Zn/Mg molar ratios were prepared via urea–precipitation and tested for PC synthesis. A relationship between the strong alkaline sites on unit specific surface

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area of Zn–Mg mixed oxide and PC yield was well established. In addition, the regeneration of the catalyst performance was studied.

2. Experimental

2.1. Catalyst preparation

Catalysts with different $Zn(NO_3)_2 \cdot 6H_2O/Mg(NO_3)_2 \cdot 4H_2O$ atomic ratios (4–0.1) were prepared by urea–precipitation. The required amounts of $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 4H_2O$ and urea were dissolved in deionized water to reach a urea/metal ions molar ratio of 4.7. The clear solution was refluxed at 393 K for 48 h. The obtained precipitate was filtered, washed with deionized water and then dried at 373 K overnight, subsequently calcined at 873 K for 6 h. The calcined catalysts were denoted as ZMx (x represents the atomic ratio of $Zn(NO_3)_2 \cdot 6H_2O/Mg(NO_3)_2 \cdot 4H_2O$).

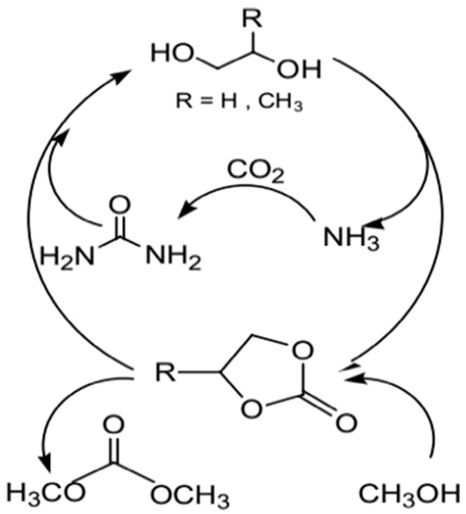
2.2. Catalytic test

The reaction was performed in a 250 ml three-necked-flask, which was equipped with a magnetic stirrer, double condenser pipe along with gas–liquid separators, vacuum pump and temperature-controlled instrument. Typically, 30 g urea, 57 g PG and 0.6 g catalyst were added into the reactor, heated and kept at 443 K for 30 min at the pressure of 300 mm Hg. After reaction, the product was cooled to room temperature and the solid catalyst was separated from the liquid by centrifuge.

The product was analyzed with a gas chromatography equipped with a DB210 (30 m × 0.32 mm) capillary column and a FID detector. The major components were PC and PG. Trace of dipropylene glycol (DPG), hydroxypropyl carbamate (HPC) and 4-methyl-2-azole alkane ketone (MOZD) was detected [14].

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Panalytical X'Pert Pro X-ray diffractometer with Cu Kα radiation. The specific surface areas of samples were determined by BET nitrogen adsorption method using a Micromeritics TriStar II 3020 instrument. The morphology of the powder was examined using a JSM-7001F scanning electron microscope (SEM) with an accelerating voltage of 10–500 kV. The elemental analysis was determined by an inductively coupled plasma (ICP) emission spectrometer (Perkin-Elmer ICP OPTIMA-3000). The distribution of basic sites was determined by temperature programmed desorption (TPD) of CO_2 pre-adsorbed at ambient temperature (Balzers Omnistar™ Mass spectrometer).



Scheme 1. The cycle routes of urea alcoholysis for the synthesis of DMC by transesterification.

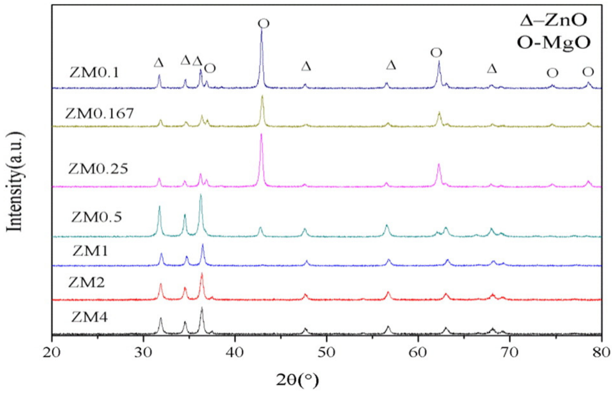


Fig. 1. XRD patterns of ZnO–MgO mixed metal oxide catalysts.

3. Results and discussion

3.1. Catalysts characterization

The XRD patterns of ZnO–MgO mixed oxide catalysts were shown in Fig. 1. It was likely that the mixed oxide of Zn and Mg did not form any specific structures but presented as separate oxide clusters: zincite phase of ZnO (JCPDS File No. 36-1451) and periclase structure of MgO (JCPDS File No. 45-0946). The previous study also showed that ZnO–MgO mixed oxide catalysts prepared by the co-precipitation method were generally consisted of a mixture of pure oxide crystals [19]. It was noticed that the diffraction peak of MgO at $2\theta = 42.92$ was absent for the Zn/Mg ratios decreased from 4 to 2, which was attributed to the high dispersion of MgO in the catalysts. Moreover, the intensity of ZnO diffraction peak decreased with the increase content of Mg.

The morphology of the ZnO–MgO series catalysts with Zn/Mg ratios of 4, 1, 0.25, and 0.1 was examined by SEM, as shown in Fig. S1 (Supporting information S.1). In the Fig. S1(A), the catalyst was comprised of a homogeneous phase, which was with larger particles corresponding to ZnO particles mostly when the content of Mg is low for ZM4. Due to the merging and embedding of Mg particles into large Zn particles when the Zn/Mg ratio decreases to 1, the thin, flat crystal with the particles of various sizes was available, as shown in Fig. S1(B). Fig. S1(C) showed that the increasing content of Mg led to the formation of irregularly shape with small particles and larger pores. Moreover, the presence of MgO might contribute to the larger surface area of catalyst [20]. When the ratio of Zn and Mg decreased to 0.1, the size of catalyst was symmetrical and those particles were

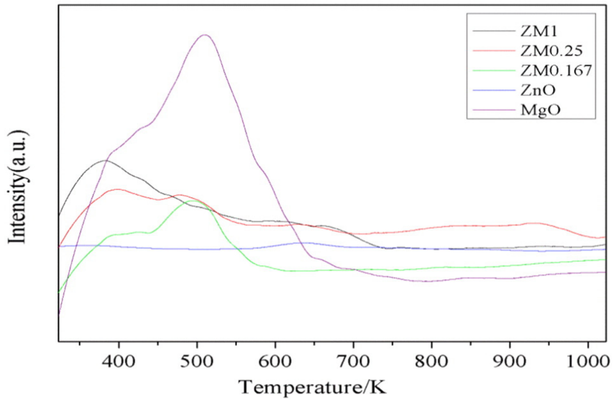


Fig. 2. CO_2-TPD profiles of the catalysts with different zinc/magnesium molar ratios.

Table 1
Texture structure and catalytic performance over different catalysts.

Entry	Catalyst	Zn/Mg$^{(a)}$	S_{BET} (m^2/g)	PC yield(%)
1	ZM4	12.56	3.49	58.2
2	ZM2	12.47	5.20	64.7
3	ZM1	6.71	6.96	74.8
4	ZM0.5	3.02	8.74	77.1
5	ZM0.25	0.75	15.06	94.8
6	ZM0.167	–	10.19	93.5
7	ZM0.1	–	3.83	80.4
8	ZnO	∞	6.2	55.2
9	MgO	0	21.0	72.9
10	ZM0.75^{m}	0.75	–	65.4
11	None			19.3

[a]Experiment Zn/Mg atomic ratio by ICP and m: ZnO/MgO mechanical mixing.
Reaction conditions: 443 K, 0.5 h, 300 mm Hg, PG: urea = 1.5 (the quality of urea 30 g), and catalyst: 0.6 g.

mostly MgO, as shown in Fig. S1(D). However, the presence of gathered MgO may contribute to the smaller specific surface areas.

Specific surface areas of the different materials were obtained using the BET methodology, seen in Table 2. The BET surface areas of catalyst increased from 3.49 m^2/g for ZM4 to 15.06 m^2/g for ZM0.25 since Mg suppressed the coalescence of ZnO (ZM4–0.25) effectively. The increase in MgO content with a porous structure increased the surface areas of a catalyst. However, when the Zn/Mg mole ratio decreased to 0.1, the BET surface area significantly decreased to 3.83 m^2/g due to the aggregation of crystals. As mentioned by Olutoye et al. [21], the MgO clusters significantly increased the surface area, altered the surface reactivity and led to the high activity. Generally, these results indicated that the surface areas of the catalyst by using BET were consistent well with the SEM.

The CO_2-TPD measurements were carried out to determine the total basicity and base strength distribution of the catalyst, shown in Fig. 2. The TPD profiles suggested that several alkaline sites were available on ZnO–MgO catalysts. The desorption peak was found at T_{max} ranging from 298 to 473 K, which was attributed to the interaction of CO_2 with the weak alkaline sites present in the catalyst. While, another desorption peak found at T_{max} varying from 473 to 773 K was due to the interaction of CO_2 with the medium alkaline sites of the catalyst. In addition, the ZnO–MgO exhibited the desorption peak at temperatures >773 K, which was ascribed to the strong alkaline sites that correspond to isolated O^{2-} anions located on a particular position on the mixed oxide catalyst surface [22]. With the increase of the content of Mg, the strength of the weak alkaline sites increased, while the amount of the weak alkaline sites decreased. The middle strong basic sites also increased. These results were in agreement with Olutoye's studies [21], in which the presence of a synergetic effect between Mg and Zn increased the catalytic basicity [20,23].

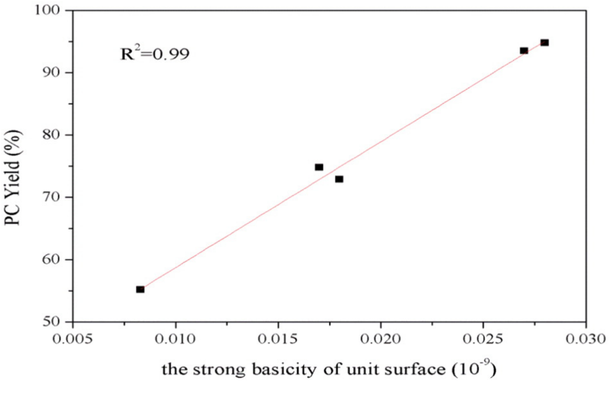


Fig. 3. The relationship between strong basic sites of unit surface and PC yield.

Table 2
The CO_2 diffraction peak intensity of the ZnO–MgO catalysts.

Catalyst	Amount of basic site (CO_2 stripping peak area/10^{-9})		
	T_{max} (<473 K)	T_{max} (473–773 K)	T_{max} (>773 K)
ZM1	3.21	0.83	0.12
ZM4	1.54	0.41	0.43
ZM0.167	0.52	1.37	0.27
ZnO	0.18	0.29	0.05
MgO	2.18	5.06	0.37

3.2. Catalytic activity

3.2.1. Effect of Zn/Mg ratio

Table 1 showed the catalytic performance for the prepared ZMx catalysts. Entries 1–5 disclosed that the Zn/Mg molar ratio of the catalysts was higher than that of the feed, which was caused by the greater affinity of Zn^{2+} ions to the precipitation than Mg^{2+} ions [24,25]. As a result, Mg^{2+} was partially retained in the mother solutions during preparation. The ZnO and MgO produced PC at the yields of 55.2% and 72.9%, respectively, which were lower than that of the mixed metal oxide. The PC yield increased from 58.2% for ZM4 to 94.8% for ZM0.25 with the increasing magnesium content. The increased catalytic activity of the binary oxide system might attribute to the modification of the electronic properties and porosity, and which could lead to the increase in basicity and specific surface areas [21]. However, the decrease of catalyst activity was observed for ZM0.1 (80.4%) because of the catalyst possessing the lower specific surface area.

3.2.2. Correlation between the strong basicity of unit specific surface area and PC yield

Fig. 3 illustrated the relationship between strong alkaline sites of unit surface and the PC yield. The amount of the alkaline sites was calculated by integrating the CO_2-TPD curves, shown in Table 2. A well established linear relationship ($R^2 = 0.99$) was obtained, which demonstrated that the catalytic activity depended on the base strength and density of the catalyst. Higher density of the strong basic sites was helpful to initiate the formation of isocyanate [14] and lead to better catalytic rate.

3.3. Regeneration and reusability of ZnO–MgO catalysts

Reusability is one of the most important features of a heterogeneous catalyst. In a typical regeneration procedure: the used catalysts were washed with ethanol for three times, followed by calcination at 873 K for 5 h. It was found that the ZM0.25 catalyst could be reused for up to 5 times with less changed PC yield in Fig. S2 (Supporting information S.2).

4. Conclusion

The mixed metal oxide of Zn–Mg prepared by the urea–precipitation method was used as a solid catalyst for the synthesis of PC by using urea and PG. ZnO–MgO binary system was superior to the individual bulk oxide of ZnO and MgO. ZM0.25 had high specific surface area and stronger alkaline density, which led to the highest PC yield. The PC yield was found to be related to the strong alkaline sites of unit and specific surface areas. Moreover, the ZM0.25 catalyst could be reused up to 5 times upon the removal of residual organics.

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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.2015.03.014.

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