



Short Communication

Generation of solid base catalyst from waste slag for the efficient synthesis of diethyl carbonate from ethyl carbamate and ethanol

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ABSTRACT

The solid base derived from abundant waste slag was prepared by co-precipitation method, and tested in the diethyl carbonate synthesis via ethanolysis of ethyl carbamate. Compared to the previous reports, much higher catalytic activity and turnover frequency (TOF) of 2926 $\text{mg}_{\text{DEC}}/\text{g}_{\text{cat}} \cdot \text{h}^{-1}$ could be achieved. Accordingly, the correlation between the catalyst basic properties and the catalytic performance revealed that the appropriate strong basic sites facilitated the formation of DEC. Moreover, the catalyst could be readily recycled and reused for several times through facile calcination.

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1. Introduction

Diethyl carbonate (DEC) is an important dialkyl carbonate. It has been widely used as a carbonylation and an ethylation reagent and green solvent in the fields of organic syntheses [1,2]. Moreover, the DEC can be used as an excellent oxygen-containing fuel additive. Recently, great efforts were devoted to synthesize DEC via non-phosgene routes, including transesterification of dimethyl carbonate [3], oxidative carbonylation of ethanol [4], and ethanolysis of ethyl carbamate (EC) [5]. Among them, the latter route is promising due to the merits of low cost and simple product separation, as illustrated in Scheme 1. Notably, EC could be easily synthesized from ethanolysis of urea [6]. Meanwhile, urea could be produced from CO_2 and NH_3 in large scale industry. Hence, this route could be considered as indirect utilization of CO_2 to produce green chemicals of DEC.

Nevertheless, the reported catalytic system of ZnO–PbO suffered from low activity and easy leaching [5], resulting in the homogeneous species of $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$. Thus, the development of a more effective and stable catalyst system with low cost to improve the efficiency of DEC is highly desired.

Solid base is a very important type of catalyst in industrial manufacture [7]. Slag is inevitably generated in the steel production, which is approximately 10% of the total production. The usage of a huge amount of waste slag is an urgent topic due to the severe environmental

problems [8,9]. Meanwhile, slag primarily contains Mg, Ca, Al, Fe as well as other small amounts of metals, e.g. Ti, Mn, which are useful candidates to prepare solid base catalysts. Therefore, the effective utilization of slag to prepare cheap and effective solid base catalysts has great importance in the construction of low-carbon and sustainable society.

Herein, the solid base catalysts from slag were prepared by co-precipitation method and tested in the DEC synthesis via ethanolysis of EC. The compositions and structures of catalysts were characterized by X-ray fluorescence spectroscopy (XRF), N_2 sorption, X-ray diffraction (XRD), field-emission scanning electron microscope (FESEM), and temperature programmed desorption of CO_2 (CO_2 -TPD). The catalytic activities and recyclability of the catalysts were systematically studied. Moreover, the relationship between the structure and catalytic activity was studied.

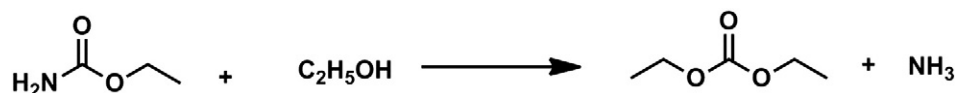
2. Experimental

2.1. Catalyst preparation

2.1.1. Slag-based catalyst preparation

The slag raw material (obtained from Capital Iron and Steel Company, China, the composition and morphology could be seen in Fig. S1) was dissolved by 3 mol/L HCl to form a solution containing the metal elements originating from slag; simultaneously most of the silicon species were eliminated. The resulting solution was co-precipitated by 2 mol/L NaOH to pH = 10.5. The precipitate was aged, filtrated, dried,

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Scheme 1. Synthesis of diethyl carbonate from ethyl carbamate and ethanol.

calcined in the regions of 350 °C to 650 °C for 3 h at regular intervals and denoted as SN-T, where T represents the calcination temperature.

2.1.2. Comparative catalyst preparation

The slag calcined at 450 °C for 3 h was denoted as slag-450. The oxides containing single metal composition were prepared by precipitation method aforementioned with the end point at varied pHs, i.e. pH = 6 for Al₂O₃, 10.5 for MgO and Fe₂O₃, and 12.5 for CaO, respectively. The Mg₃AlO_x derived from hydrotalcite was prepared by the method in reference [10] and used as reference catalysts. The physically mixed oxides with the same composition as slag or SN-T were prepared by mixing 0.0376 g MgO, 0.0495 g CaO, 0.0181 g Al₂O₃, 0.0300 g Fe₂O₃, 0.0148 g SiO₂ (denoted as S-Slag-450), and mixing 0.0823 g MgO, 0.0015 g CaO, 0.0246 g Al₂O₃, 0.0404 g Fe₂O₃, 0.0012 g SiO₂ (denoted as S-SN-450), respectively. These physical mixtures were also calcined at 450 °C for 3 h.

2.2. Procedure of the reaction

In a typical catalytic test, 3.0 g EC, 20 mL ethanol and 0.15 g catalyst were added into a 100 mL stainless steel autoclave reactor and sealed. The reactor was heated and stirred constantly at desired temperature. After the reaction, the reactor was cooled to room temperature and depressurized. The products were quantitatively analyzed by a gas chromatograph (Shimadzu) equipped with a FID and automatic operation controller (auto injector/auto sampler) to eliminate the manual injection bias. The relative standard error for the same sample through six sampling analyses is less than 0.2%. After the reaction, the catalyst was recycled by centrifugation, washed with ethanol, dried or re-calcined, and then reused.

2.3. Characterization

The composition of samples was measured by XRF (AXIOS). XRD patterns were recorded by using Empyrean XRD with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). Nitrogen adsorption–desorption isotherms were measured by using Autosorb-1-C-TCD. The surface basicities of the catalysts were evaluated by temperature programmed desorption of CO₂ and carried out on TPD flow system equipped with a TCD (AutoChem II 2920). The TPD of CO₂ was carried out from room temperature to 700 °C under helium flow (30 mL/min) with a heating rate of 10 °C/min. According to the region of desorbed temperature, the corresponding surface basic strengths were defined as weak ($T < 200 \text{ °C}$), medium ($200 \text{ °C} < T < 400 \text{ °C}$) and strong ($T > 400 \text{ °C}$). If necessary, the CO₂ desorbed temperature above 600 °C could be deemed as very strong basicities. The quantitative analysis of the basic amount is based on the integration of the corresponding TPD traces and the basic amounts were expressed as the number of CO₂ molecules per gram of catalyst ($\mu\text{mol CO}_2/\text{g}$).

3. Results and discussion

3.1. Catalyst characterization

The catalyst components and textures are shown in Table 1. Besides non-metal elements of oxygen and Si, the other primary metal components of slag are various contents of Mg, Ca, Al, and Fe. When the slag was treated by the preparation method aforementioned, the contents of Ca and Si in the samples decreased distinctly, while Mg, Fe and Al remained as the main metal components.

The textural parameters of samples, such as specific surface area (S_{BET}), pore volume (V_p), average pore diameter (d_p), are listed in Table 1. Obviously, the raw slag has an extremely small surface area of 2.9 m²/g. In contrast, 298.4 m²/g of high surface area was obtained after calcination at 350 °C. Subsequently, the surface area gradually decreased with an increase in the calcination temperature, and reduced to 156.9 m²/g at 650 °C. The declined surface area could be probably attributed to the sintering effect at higher calcination temperatures. All these samples possessed the hysteresis loop in the adsorption–desorption isotherms (Fig. S2(b)), which are the typical features of a mesoporous structure. Meanwhile, the average pore diameter gradually increased, and the corresponding shape of the pore size distribution became broader with increasing calcination temperature (Fig. 2(d)). These results suggested that the pores gradually changed to textural ones upon calcination temperature via dehydroxylation and sintering [11]. Briefly, solid bases were successfully prepared with high surface areas and meso-structured pores, which could be beneficial for the diffusion of reactants and provide more accessible active sites.

Fig. S3(b) shows the XRD patterns of the various catalysts derived from the slag. The characteristic peaks at (111), (200), (220), (222) crystal planes of the cubic-phase MgO could be observed for all those samples with different intensities (JCPDS Card No. 01-077-2179). As can be seen, the diffraction lines are stronger for the samples calcined at higher temperatures than those at lower temperatures or prepared at higher pH. However, the peaks are weak and broad, which is probably because the samples are formed by small grains. It can be concluded that the poor crystalline MgO was the dominant phase, and no other phases were obviously observed.

The morphology evolution of the sample with increasing calcination temperature is shown in Fig. S4. As can be seen, SN-350 primarily consists of irregular agglomerated particles with the sizes smaller than 100 nm. After calcined at higher temperatures, SN-450 and SN-550 show sponge-like surface morphologies. Meanwhile, smooth platelet morphology is observed for SN-650, indicating the occurrence of serious agglomeration.

In general, the calcination temperature could modulate the catalyst basicity and has a significant influence on the basicity distribution [12]. To disclose the influence of calcination temperature on the catalyst basic property, the samples were characterized by CO₂-TPD, as shown in Fig. 1. The corresponding CO₂ amounts desorbed from the catalyst

Table 1
The main compositions and sample textures.

Catalyst	Main chemical component/wt.%				N ₂ ads-des			
	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	S_{BET} (m ² /g)	V_p (cm ³ /g)	d_p (nm)
Slag	23.9	31.5	11.5	19.1	9.4	2.9	0.015	20.5
SN-350	48.1	0.9	14.4	23.6	0.7	298.4	0.326	4.4
SN-450						231.7	0.365	6.3
SN-550						172.0	0.426	9.9
SN-650						156.9	0.482	12.3
Used ^a						203.3	0.562	11.1
SN-11.5-450 ^b	48.2	1.0	12.9	28.4	1.6	238.5	0.267	4.5
SA-450 ^c	49.5	0.3	16.1	20.1	2.3	159.2	0.320	8.1

^a SN-450 reused for seven cycles.

^b Precipitated at pH = 11.5.

^c NH₃ · H₂O as precipitant.

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