



Short communication

The role of zinc oxide in carbonylation of ethylene glycol to ethylene carbonate with urea: A precursor for homogeneous catalyst



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ABSTRACT

In carbonylation of ethylene glycol to ethylene carbonate with urea catalyzed by ZnO, which was considered as a heterogeneous catalyst. ZnO is observed to be dissolved in the reactants probably due to the formation of $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ making the reaction homogeneously catalyzed. To our knowledge, it is firstly reported that the reaction experienced three states including ZnO dissolution, homogeneous catalysis, and precipitate formation. The precipitate was characterized to be a mixture containing $\text{Zn}(\text{OH})_2$, ZnCO_3 , and $\text{Zn}(\text{NCO})_2$ with a ratio of 8.5:6.1:1. Possible mechanisms of ZnO dissolution and precipitation were proposed.

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1. Introduction

Ethylene carbonate (EC) is a commercially important starting chemical or intermediate for selective alkoxylation, carbamate formation, the processing agents of polymers etc. [1,2]. Most importantly EC is a critical reagent for dimethyl carbonate (DMC) production by transesterification with methanol. Equimolar amount of ethylene glycol (EG) and DMC is formed in this reaction [3]. While the commercialized path of EC is produced by the coupling of carbon dioxide and ethylene oxide cyclo-addition reaction [4], therefore, 1 mol of ethylene oxide needs to be consumed to produce 1 mol DMC and EG. However, ethylene oxide is more expensive than EG due to the different demands on EG and ethylene oxide in some places. Therefore, a new approach to produce EC has to be developed from an economic aspect.

EG can react with urea generating NH_3 and EC which can be transesterified to DMC with a side product of EG in the presence of methanol. The side product of EG here can be further recycled as a reactant in the production of EC. On the other hand, NH_3 , the side product of EC production, can be recycled as a reactant for urea production with CO_2 . Overall, as the reaction ($\text{EG} + \text{urea} = \text{EC} + \text{NH}_3$) start, only methanol and CO_2 need to be fed to produce DMC [5].

Various metal oxides have been prepared and utilized as catalysts for the carbonylation of EG to EC with urea, such as CaO , La_2O_3 , MgO , ZnO , Al_2O_3 , $\text{ZnO-Fe}_2\text{O}_3$, and $\text{ZnO-Cr}_2\text{O}_3$ [5–9]. Among them, Zn-contained catalysts show the best performance with high activity and selectivity. ZnO has been considered to be one of the candidates for this reaction.

The reactions in the presence of ZnO are often regarded as heterogeneously catalytic processes [5–9]. The amount and balance of acidic and basic sites have been taken into account as the key factors for the good catalytic performance of ZnO [9,10]. However, we observed that ZnO could be dissolved completely into the reactants as the temperature was increased, suggesting that ZnO possibly experienced a phase transition in the reaction. As a result, the reaction was in fact carried out in a homogeneous phase. Generally, ZnO is insoluble in EG. It has been reported that ZnO was dissolved during the reaction of urea and methanol to DMC [11,12]. Differently [12], precipitate was observed after the reaction proceeded for a certain period in the current case.

Hereby, we attempted to clarify the catalytic role of ZnO during synthesis of EC from urea and EG. In order to elucidate the mechanism, the precipitate was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis and differential scanning calorimetry (TG-DSC), inductively coupled plasma (ICP), and CNH elemental analysis.

2. Experimental

ZnO was prepared by a precipitant method. 0.8 mol of urea (AR, Shanghai Ling Feng Chemical Reagent Co., Ltd.) and 0.2 mol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, Chinese Medicine Group Chemical Reagent Co., Ltd.) was dissolved in 400 g of deionized water. The solution was heated and reacted at 100 °C for 4 h under reflux; and then aged for 12 h at ambient temperature. The precipitate was collected by filtration and washed by large amount of water. The obtained solid was dried at 100 °C overnight and calcined finally at 500 °C for 2 h. $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ was prepared according to the literature [15]. In detail, prepared ZnO

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and urea were charged in the molar ratio of 1:2 and refluxed at 150 °C for 45 min in a three-necked flask fitted with a thermometer pocket.

The catalytic reaction was carried out in a 500 ml three-necked flask equipped with a magnetic stirrer, a set of reflux condensers, and a gas-liquid separator. After 60 g (1 mol) of urea, 81 g (1.31 mol) of EG, and 2.82 g of ZnO (2 wt% of the reactant) were charged to the reactor, the reactor was heated to 150 °C with a heated ramp rate about 2 °C/min and maintained at 150 °C for 2 h under the reduced pressure of about 14 kPa. After reaction, the reactor was cooling down to ambient temperature and the solid catalyst was separated from liquid by filtration. The liquid products were analyzed by gas chromatography (GC9800) equipped with a VO-1701 capillary column and a FID detector. The spent catalyst was washed by ethanol and cyclohexane (each for 5 times), and then filtrated and dried at 100 °C.

XRD patterns were recorded on D/max2550V (Rigaku Co.) diffractometer using Cu K α 1 radiation (40 kV, 40 mA). FTIR analysis was carried out using FT/IR-610 (JASCO Co.) spectrometer. TG-DSC was measured on Setsys Evo (Setaram) with a heating ramp rate of 10 °C/min up to 800 °C under atmosphere. The contents of CNH and zinc were detected by an Elemental Analyzer (Vario EL III) and an inductively coupled plasma (ICP) emission spectroscopy (Perkin–Elmer, Nexlon 300 \times), respectively.

3. Results and discussion

Urea was completely dissolved to EG as the temperature was increased to about 80 °C. Interestingly, the white solid ZnO was disappeared when the temperature was increased to about 145 °C, resulting in the formation of a transparent solution. After 1 h at 150 °C, the color of the solution turned from colorless to light yellow. Precipitate was separated out from the solution after 1.5 h reaction at 150 °C. Therefore, it is apparent that the reaction experiences a period of homogeneous catalytic process.

XRD was used to ensure the synthesis of ZnO in our synthesis. Fig. 1a shows that the XRD pattern of the prepared catalyst can be assigned to wurtzite type of zinc oxide, confirming that ZnO is successfully prepared. Commercial ZnO (purchased from Chinese Medicine Group Chemical Reagent Co., Ltd.) was also tested in this reaction to make sure it is identical to ZnO we prepared. The same reaction phenomena were observed during reaction. These results substantiate the fact that ZnO can be transformed to a homogeneous catalyst during this reaction, at least under our experiment conditions. As shown in Fig. 1b, the XRD pattern of the spent catalyst (the precipitate after reaction) manifests an amorphous phase which further confirms the transformation of ZnO to a homogeneous catalyst. After the reaction, the collected

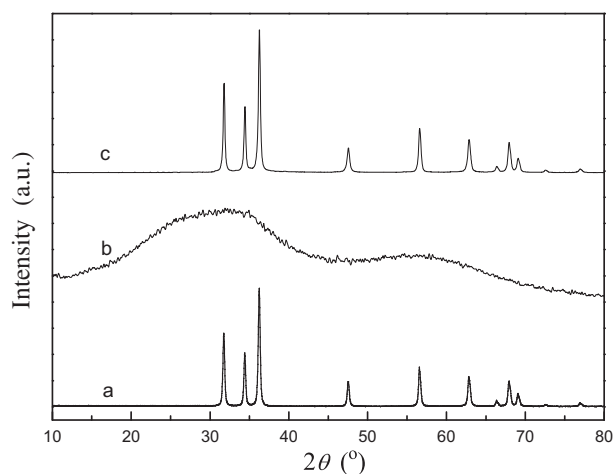


Fig. 1. XRD patterns of (a) as-prepared ZnO, (b) precipitate after reaction, (c) regenerated catalyst.

precipitate was regenerated by calcination at 500 °C for 2 h. The regenerated catalyst shows similar XRD pattern (Fig. 1c) as compared to the freshly prepared ZnO (Fig. 1a).

It is general that ZnO cannot be dissolved in alcohol and glycol even at high temperature. However, the dissolution of ZnO in urea and methanol was reported by Zhao et al. [12]. In their report, some precipitate was formed after the solution cooled down to ambient temperature, and the precipitate was identified to be $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$. The carbonylation of methanol to DMC with urea was in fact homogeneously catalyzed by $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$. Since the reactants in the present reaction (urea and EG) are very similar to their reaction (urea and methanol), we believed that $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ was formed and homogeneously catalyzed the synthesis of EC from EG and urea. According to the literature, the proposed formation mechanism of $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ is shown in Scheme 1. These reactions were based on the suggestion of the literatures [12,13]. The formation of HNCO was supported by the pyrolysis of urea reported by Schaber et al. [14]. Moreover, in a recent study, $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ was directly used as a homogeneous catalyst showing high selectivity and activity for the carbonylation of EG to EC in the presence of urea [15]. To ensure our proposed mechanism, $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ was prepared and used as a catalyst for the reaction under our experiment conditions. After homogeneously catalytic reaction performed for about 1.5 h at 150 °C, precipitate was observed. In a word, ZnO was firstly dissolved in the form of $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ which homogeneously catalyzed the carbonylation of EG to EC with urea under the present reaction conditions.

ZnO in the catalytic synthesis of EC were considered as a heterogeneous catalyst in most of the previous reports [6,9,10]. The possible reasons for ignoring the homogeneous process on ZnO catalyst might be explained as the follows. Firstly, the opacity of the autoclave, which was used for this reaction in some cases [6], restricts the continuous observation on the reaction; ZnO catalyst for this reaction experiences three states of solid-dissolution-precipitate; the solid precipitate was seen as the autoclave was uncapped. Therefore, a possible homogeneous stage can be easily ignored. In addition, un-dissolved solid was remained when excess ZnO was added into the reaction causing the ignorance of the dissolved ZnO.

The abovementioned un-dissolved solid was identified to be ZnO from the XRD pattern (see Supporting information Fig. S1). According to the recent report, ZnO can completely convert to $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ in the presence of urea [15]. It is contradictory to the report that partial ZnO remained in the existence of urea and EG. One hypothesis based on the presence of EG is as follows. The carbonylation of EG to EC by urea can be separated to three consecutive steps: 1). urea decomposes to isocyanic acid (HNCO) and ammonia; 2). HNCO reacts with EG to produce 2-hydroxyethyl carbamate (HEC); 3). HEC cyclizes to EC [9,13]. From reaction (1) (Scheme 1), ammonia and HNCO is necessary for the transformation of ZnO to $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$. Since ammonia is continuously released through all the reaction process, the lack of HNCO should be the reason for the partial dissolution of ZnO. HNCO, decomposed from urea, is consumed by EG to form HEC. During the decomposition process, the decrease of urea concentration may cause the decrease of HNCO concentration. Meanwhile, the formed $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ has the possibility to accelerate the reaction of HNCO and EG to form HEC. The dissolution of ZnO is interrupted when the concentration of HNCO is lower than the threshold of ZnO dissolution. The discussion whether one or both of them is/are the major factor(s) need(s) to be further investigated in future work.



Scheme 1. Formation of $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$ in the reaction.

Table 1
Yields of EC on different catalysts.

Entry	Catalyst	Yield (%)
1	None	10.6
2	ZnO purchased	89.1
3	ZnO prepared	93.6
4	ZnO regenerated	93.3
5	Zn(NH ₃) ₂ (NCO) ₂	92.3

The yields on different catalysts are summarized in Table 1. The yield on prepared ZnO is as high as 93.6%. The regenerated catalyst shows a yield of 93.3%, which is close to the original yield of ZnO. However, the purchased ZnO shows a little lower yield of 89.1%. Although ZnO was dissolved to form a homogeneous catalyst, minor difference in physical or chemical properties of ZnO may affect the ratio of urea decomposition. The yield on prepared Zn(NCO)₂(NH₃)₂ is 92.3%, which is comparable to that on ZnO; this confirmed to some extent that Zn(NCO)₂(NH₃)₂ is possible present as the homogeneous catalyst during the reaction catalyzed by ZnO.

Different from carbonylation of methanol to DMC with urea catalyzed by ZnO, in which precipitate was formed as the temperature is cooling down to room temperature [12], precipitate was observed during the reaction as described above. The composition of the precipitate is attractive to be investigated. The elemental analysis by ICP (for Zn) and CNH element analysis is shown in Table 2. Beside the elements of Zn, N, C, and H, O is the most reasonable element presented in the precipitate; and that O is calculated to be 31.27 wt%. Since ZnO is formed after calcinations (Fig. 1c), the weight loss calculated on the basis of zinc by the formula $(100\% - \text{Zn}\% / M_{\text{Zn}} * M_{\text{ZnO}})$ is 26.2%, which is consisted to the results of TG (Fig. 2) in which 23.8% weight loss was determined. The FTIR spectra of the precipitate are distinctly different from those of ZnO, Zn(NCO)₂(NH₃)₂ and urea (Fig. 3). The vibration bands at 3500 cm⁻¹ can be assigned to OH group. The vibration bands at 2229 and 1344 cm⁻¹ can be assigned to the characteristic stretching vibrations of NCO group. The remained bands at 1200–1700 cm⁻¹ can be assigned to the characteristic peaks of carbonate. In addition, the exothermal peak of DSC (Fig. 2) at 350 °C is considered to be the transformation of Zn(NCO)₂ to ZnO according to the previous report [12]. The weak bands at 2850 and 2940 cm⁻¹ can be assigned to the symmetric and asymmetric stretching modes of C–H group which may come from organic contamination although the sample was rinsed by ethanol and cyclohexane for five times. Based on the above analysis, the most possible composition of the precipitate (Zn(OH)₂, ZnCO₃, Zn(NCO)₂) is 8.5:6.1:1. The content of remained zinc in the products is 9.34 ppm (g/g) obtained from ICP and that is about 0.97% of the originally charged zinc. The results suggest that most of the zinc was separated out as a precipitate after reaction.

The formation of precipitate at the end of the reaction was deduced as follows. At the end of the reaction, the concentration of HNCO is negligible since the urea was totally consumed. The formation rate of ammonia decreased because the concentration of the intermediate HEC is decreased, and the reaction rate of cyclization of HEC to EC was decreased. It has been reported that the ammonia in Zn(NCO)₂(NH₃)₂ was unstable and was easy to be released [15]. Therefore, the ammonia in Zn(NCO)₂(NH₃)₂ was not stable enough to maintain the structure under reduced ammonia pressure, resulting in the decomposition of Zn(NCO)₂(NH₃)₂ to Zn(NCO)₂ and ammonia. Zn(NCO)₂ could be hydrolyzed to Zn(OH)₂ and HNCO. HNCO is continuously hydrolyzed to ammonia and CO₂, resulting in the formation of ZnCO₃. The water could

Table 2
Elemental analysis result of the precipitate after EG and urea reacted on ZnO.

Element	Zn	C	N	H
Content (wt%)	59.2	6.02	1.74	1.77

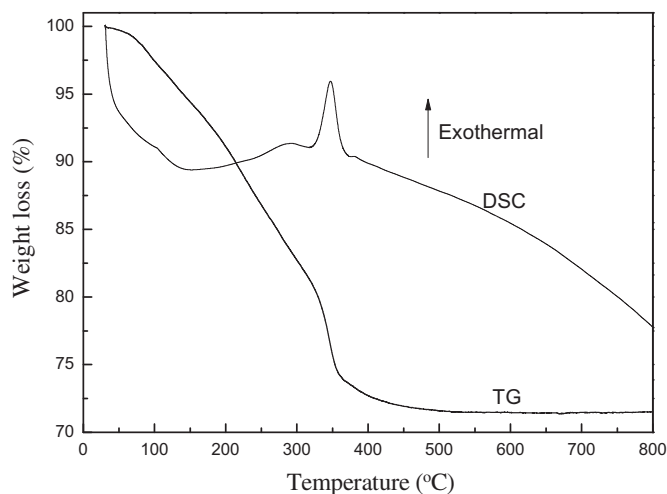


Fig. 2. TG-DSC curves of the precipitate after EG and urea reacted on ZnO.

be originated from the contamination of EG, the process of ZnO dissolution, and the dimerization of EG to diethylene glycol. The proposed mechanism is shown in Scheme 2.

The reaction experienced three states including ZnO dissolution, homogeneous catalysis, and precipitate formation. Although the main reaction was homogeneously catalyzed by Zn(NCO)₂(NH₃)₂, the presence of precipitate at the last period suggested that the process was homogeneous and heterogeneous without deciding on the mechanistic part of any process. The process may be in precisely defined as a pseudo homogeneous versus catalytic process.

4. Conclusion

In the reaction of carbonylation of EG to EC with urea, ZnO is a precursor for the formation of homogenous catalyst Zn(NCO)₂(NH₃)₂ rather than a heterogeneous catalyst. The reaction experienced three periods, the dissolution of ZnO, the homogeneous catalysis, and precipitate formation. To the best of our knowledge, it is the first time on the report of Zn(NCO)₂(NH₃)₂ homogeneously catalyzed this reaction when ZnO is used. The precipitate after reaction has been analyzed to be a mixture of Zn(OH)₂, ZnCO₃, Zn(NCO)₂ with ratio of 8.5:6.1:1.

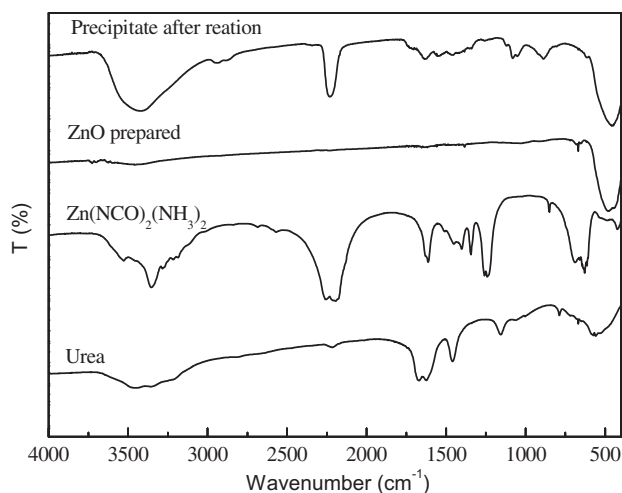


Fig. 3. FTIR spectra of the precipitate, the prepared ZnO, the prepared Zn(NCO)₂(NH₃)₂, and urea.



Scheme 2. Possible route for the formation of precipitates.

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2016.10.016.

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