

Research article

Synthesis of propylene carbonate from urea and propylene glycol over zinc oxide: A homogeneous reaction

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Abstract: In this work, several metal oxides and zinc salts were used to catalyze propylene carbonate (PC) synthesis from urea and propylene glycol (PG). According to the results of catalytic test and characterization, the catalytic pattern of ZnO was different from that of other metal oxides such as CaO, MgO and La₂O₃, but similar to that of zinc salts. In fact, the leaching of Zn species took place during reaction for ZnO. And ZnO was found to be the precursor of homogenous catalyst for reaction of urea and PG. Thus, the relationship between the amount of dissolved zinc species and the catalytic performance of employed ZnO was revealed. In addition, a possible reaction mechanism over ZnO was discussed based on the catalytic runs and the characterization of XRD, FTIR, and element analysis.

Keywords: Urea; 1,2-Propanediol; Propylene carbonate; Zinc oxide

1. Introduction

Propylene carbonate (PC), not only as a good organic solvent but also an important organic chemical, has been found numerous applications in the fields of electrochemistry, organic synthesis, gas separation and metal extraction, etc [1,2]. Up to now, PC could be produced from propylene glycol (PG) with phosgene, transesterification of PG with alkyl carbonate, direct oxidation of olefins with carbon dioxide and cycloaddition of carbon dioxide with propylene oxide. However, all these techniques suffer some corresponding disadvantages such as being poisonous, lack of economic viability, low conversion and easy explosion [3–8]. Thus, safer and economical alternative technologies are needed for the PC production scale-up. A new route of the PC synthesis from urea and PG has been developed owing to its advantages such as low cost, mild reaction conditions and safe operation. Even more important is, via the present route, that PG, as a byproduct in the

transesterification process for the production of dimethyl carbonate (DMC), can be reconverted as the raw material (See Figure 1). This would increase the efficiency of utilization of the raw material and greatly lower the cost of the DMC production. Besides, the byproduct ammonia released during reaction can be recycled for raw material urea synthesis by reaction with CO_2 . So the overall process is a green chemical cycle and can be considered as indirect utilization of CO_2 to produce green chemicals of organic carbonates. [9–11]. Many catalysts such as organic tin, metal oxides and metal salts have been tested towards PC synthesis from urea and PG [10,12,13]. Among them, zinc oxide was highly active to this reaction, and was considered as a typical heterogeneous catalyst in the previous work, where its catalytic ability was ascribed to its surface acid-base property [10]. However, in this study, it was found that ZnO might change to other species and dissolve into the liquid phase. Simultaneously, the PC yield was well correlated with the amount of the species dissolved. Thus, the reaction should occur in homogeneous phase. In a word, we attempted to clarify the catalytic role of ZnO by comparing the catalytic performances of metal oxides (such as ZnO, CaO, La_2O_3 and MgO) as well as that of several zinc salts, together with systematically characterization of catalysts and reaction liquid phases.

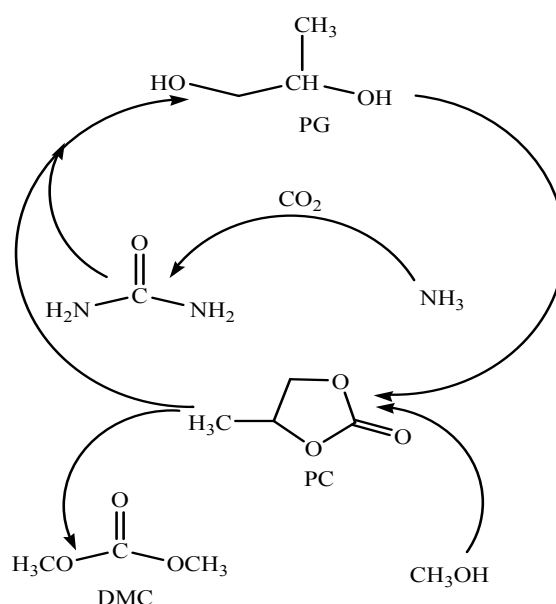


Figure 1. The cycle routes for synthesis of PC and DMC via urea alcoholysis.

2. Materials and Methods

2.1. Catalyst Preparation

Several catalysts were used in the present work. CaO, MgO and La_2O_3 were prepared by decomposition of calcium carbonate, magnesium hydroxide and lanthanum carbonate at $800\text{ }^\circ\text{C}$ for 5 h in N_2 , respectively. The method for lanthanum carbonate synthesis was as follows: first, certain amount of ammonium carbonate solution was added to lanthanum nitrate solution till the pH value of the mixed solution reached to 10. Then the sample was obtained by drying at $100\text{ }^\circ\text{C}$ after it was

separated by filtration and washed several times with deionized water. $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{NO}_3)_2$ were obtained by evacuating $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 110°C for 24 h, respectively. Other chemicals and catalysts were commercial analytic reagents without further purification.

2.2. Characterization

The structure features of catalysts before and after reaction were examined by powder X-Ray diffraction (XRD) on a Rigaku D max III VC instrument with $\lambda = 0.1541\text{ nm}$, Cu-K α radiation in the 2θ range of $5\text{--}80^\circ$. BET surface areas of the samples were measured by nitrogen adsorption using a Micromeritics ASAP-2000 apparatus. The zinc content was determined using the inductively coupled plasma-optical (ICP) emission spectroscopy on a Perkin Elmer 3000 equipment. The contents of nitrogen, carbon and hydrogen in sample were determined by an Elemental Analyzer (Vario EL III). The FTIR spectra of liquid phases after reaction were examined on a Nicolet Magna 550 Fourier-transform infrared spectrometer in the region of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} .

2.3. Catalytic reaction

The catalysts were tested in a 100 mL three-necked-flask equipped with a magnetic agitator, sphere reflux condenser and thermocouple thermometer. In a typical process, 0.1 mol PG, 0.05 mol urea and 0.002 mol catalysts were charged into the reactor. While stirring, the reaction mixture was heated and kept at 180°C for 3 h in an oil bath at the pressure of 10 kPa. After the reaction, the reactor was cooled to room temperature and solid catalysts were separated by centrifugation or filtration. Then, the liquid products were analyzed by a GC-950 gas chromatography with a flame ionization detector and a HP-5 capillary column.

3. Results and discussion

3.1. Catalytic performance of different catalysts

According to previous works, the reaction for synthesis of PC from urea and PG appeared to proceed in two steps: 2-hydroxypropyl carbamate (HPC) formed first without catalyst and then it transformed into PC through the intramolecular interaction between the hydroxyl group and the carbonyl group [10]. Moreover, the byproduct 4-methyl-2-oxazolidone (MO) was formed over some catalysts because of the dehydration of HPC.

The four different solid metal oxide catalysts of ZnO, CaO, MgO and La_2O_3 used in the present work showed BET surface areas of 6.7, 9.5, 34.2 and $21.0\text{ m}^2/\text{g}$. The typical performance of different catalysts is summarized in Table 1. Without catalyst, the yield of HPC was higher than that of PC. Under the same reaction conditions, the PC yield increased swiftly and that of HPC decreased in the presence of catalysts. Zinc salts such as $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, ZnCl_2 and ZnSO_4 exhibited high activities towards PC synthesis, yielding 93.1%, 92.0%, 87.8% and 87.3% PC, respectively. This was the same for ZnO, it could improve PC yield to 82.3%. CaO, and MgO La_2O_3 gave smaller yields of PC compared with that of ZnO, and they also yielding 6.8%, 2.7% and 4.2% of MO, respectively. Thus, basic oxides were inclined to promote the formation of by-product. On the other hand, to our

surprise, ZnO that could not dissolve in PG even at extremely high temperature, dissolved in the reaction solution, which became transparent after about 30 min at 180 °C. Simultaneously, as that observed in zinc salts catalytic system, the color of the PG solution changed from colorless before reaction to yellow after reaction. More important, after the reaction solution was cooled to room temperature, some yellow precipitate appeared. Nevertheless, above phenomena were not observed for the catalysis in the presence of CaO, MgO and La₂O₃, and the three basic oxides were not dissolved in solution during the reaction. Thus, it was reasonable to conclude that among these metal oxides, ZnO was a special one and it might catalyze this reaction in a different way. This led to our interest in the role of ZnO in this reaction and so there is still room to examine the performance of these homogenous and heterogeneous catalysts.

Table 1. Catalytic performance of different catalysts for PC synthesis from urea and PG^a.

Entry	Catalysts	Urea conversion (%)	Yield (%)		
			PC	HPC	MO
1	–	85.3	30.4	54.9	0
2	Zn(NO ₃) ₂	94.9	93.1	1.8	0
3	Zn(CH ₃ COO) ₂	94.4	92.0	2.4	0
4	ZnCl ₂	90.7	87.8	2.9	0
5	ZnSO ₄	90.7	87.3	3.4	0
6	ZnO	86.9	82.3	4.6	0
7	CaO	85.8	71.4	7.6	6.8
8	MgO	88.1	77.3	8.1	2.7
9	La ₂ O ₃	86.0	74.9	6.9	4.2
10	Precipitate ^b	87.5	84.7	2.8	0

^a Reaction conditions: PG, 0.1 mol; urea, 0.05 mol; catalyst amount, 0.002 mol; reaction temperature, 180 °C; reaction time, 3 h, reaction pressure, 10 kPa.

^b The precipitate separated from the reaction mixture after the reaction.

3.2. FTIR spectra of liquid phases over zinc-containing catalysts and structure change of ZnO

FTIR measurements were made for the liquid phases of PG and urea after reaction runs in the absence and presence of zinc-containing catalyst (ZnO or zinc salts). Without catalyst, the characteristic bands of urea can be found at 1670 and 1620 cm⁻¹ due to C=O stretching vibration and N-H bending vibration, respectively (see Figure 2 (1)) [14]. Obviously, these two urea characteristic bands disappeared and some new FTIR bands became apparent at 2210, 1790, 1712, 1389, 1354 cm⁻¹ in the presence ZnO after reaction (see Figure 2 (2)). According to literatures, the band around 2210 cm⁻¹ was assigned to N=C=O asymmetric stretching vibration of isocyanate species [15]. The bands at 1788, 1389, 1354 and 775 cm⁻¹ were corresponding to $\nu_{\text{sy}}(\text{C}=\text{O})$, $\delta_{\text{sc}}(\text{CH}_3)$ and $\nu(\text{ring})$ of PC, respectively [16]. Besides, the absorption band at 1713 cm⁻¹ was assigned to intermediate carbamate species [17]. The same FTIR measurements were also made for the liquid phases using homogeneous catalysts such as ZnCl₂, Zn(CH₃COO)₂, ZnSO₄ and Zn(NO₃)₂ (see Figure 1 (3–6)). Interestingly, their FTIR spectra illustrated that some new absorption bands were also detected at very similar frequencies for these homogeneous catalysts as that observed with ZnO. Consequently,

it could be concluded that irrespective of the solid and salt zinc based catalysts used, similar Zn-containing complex should exist in the liquid phases during reaction, and it should be the active species for these catalysts. In other words, ZnO might be the precursor of homogenous catalyst for PC synthesis and catalyze this reaction as the same pattern as that of zinc salts.

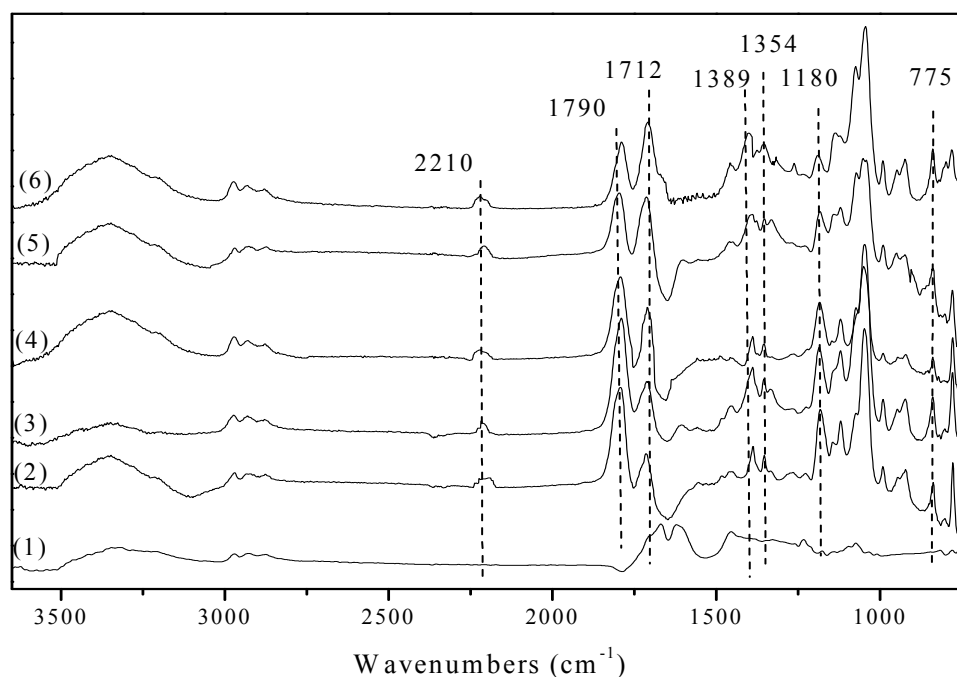


Figure 2. FTIR spectra of liquid phases after reaction of urea and PG in the presence and absence of Zn-containing catalysts. (1) blank; (2) ZnO; (3) ZnCl₂; (4) Zn(CH₃COO)₂; (5) ZnSO₄; (6) Zn(NO₃)₂.

In the other hand, after a reaction run over metal oxides, the catalysts were recovered from the reaction by filtration. Figure 3 gives XRD patterns of the solid catalysts before and after a reaction run. For CaO, MgO and La₂O₃, the XRD patterns clearly illustrated that their diffraction peak numbers in recovered catalyst were almost as the same as that of the fresh one. By contrast, as to ZnO, the XRD pattern of the yellow precipitate presented that the characteristic diffraction of ZnO almost disappeared completely. This suggested that ZnO had completely transformed to another substance, which was Zn(NCO)₂(NH₃)₂, according to the literature XRD data [18]. Furthermore, this was further significantly supported by element analysis of the precipitate. Based on the experimental data in Table 2, it could be calculated that its chemical formula was reasonably ZnC₂O₂N₄H₆. Meanwhile, the catalytic ability of this sample was evaluated. As showed in Table 2, it exhibited comparable activity to that of ZnO. From these experimental and characterization results, it was reasonable to assume that ZnO was the precursor of homogeneous catalyst, which would be related with the conversion of urea in the synthesis process of PC.

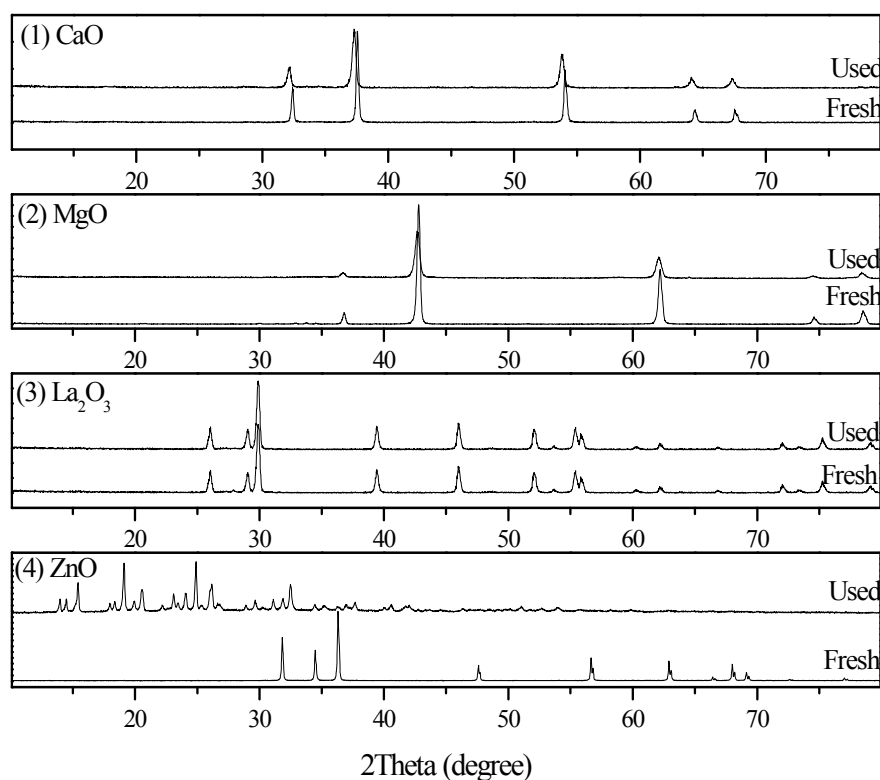


Figure 3. XRD patterns of metal oxide catalysts: (1), CaO; (2), MgO; (3), La₂O₃; (4), ZnO before and after reaction of urea and PG.

Table 2. Element analysis of the precipitate from the reaction of urea and PG over ZnO.

Element	Zn	N	C	H
Determined (Weight %)	35.8	30.2	13.2	3.3
Formula (Weight %)	35.6	30.5	13.1	3.3

3.3. Relationship between PC yield and Zn species dissolved

Figure 4 gives the effect of catalyst amount on PC yield using ZnO as catalyst. It could be seen that the yield of PC increased initially with catalyst amount increased, but remained almost unchanged when catalyst amount was > 1.0 mmol. Thereby, the PC yield was not simply dependent on the catalyst amount. Based on abovementioned XRD measurements and discussion, ZnO could be converted to a zinc complex $Zn(NCO)_2(NH_3)_2$, and it would be the active species homogeneously catalyze PC production. Thus, it was necessary to investigate the possibility of ZnO conversion as well as the relationship between ZnO amount and concentration of Zn species dissolved.

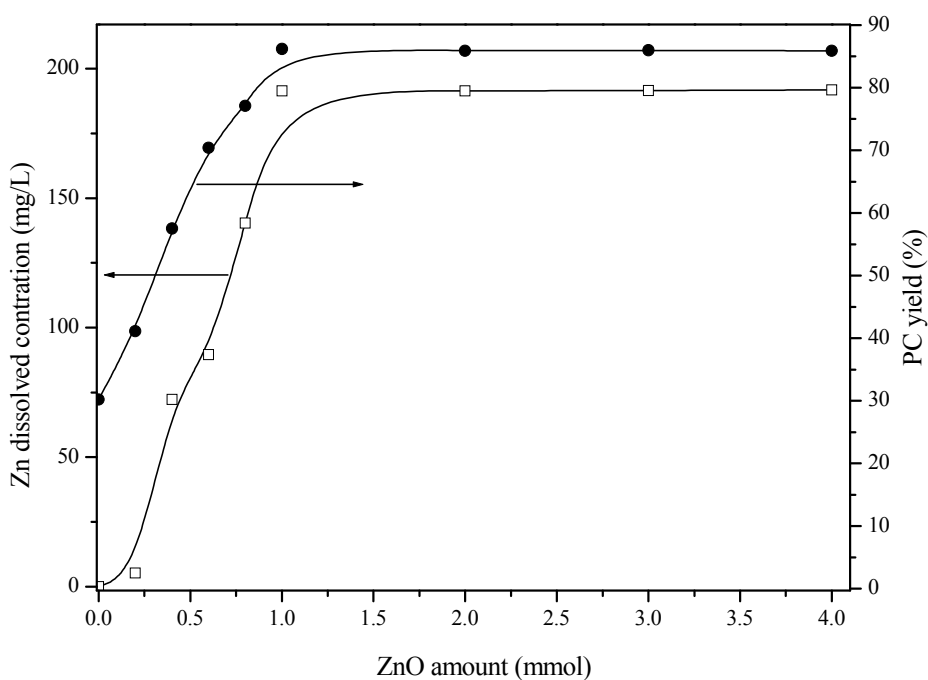


Figure 4. The effect of the initial amount of ZnO on the amount of Zn species dissolved and PC yield.

The reaction runs were carried out with different amounts of catalysts while the other reaction conditions were kept unchanged. The concentration of Zn species in the reaction solution was measured by element analysis. As depicted in Figure 4, the content of dissolved Zn complex increased sharply from null to about 190 mg/L with the increase of catalyst amount when it < 1.0 mmol, and then remained constant on further increase of the catalyst amount. This could be because of the limited solubility of the active species. More important, it should be worth to note that the concentration of Zn species dissolved and PC yield present the same trend with the increase of catalyst amount. Thereby, it could be concluded that the PC yield was well correlate with the concentration of dissolved Zn species in the liquid phase. This further provided the proof that ZnO was precursor of homogenous catalyst for this reaction and the PC yield determined by the active species dissolved in the reaction system.

Table 3. Catalytic results in the presence and absence (filtrate) of metal oxides for PC synthesis from urea and PG^a.

Catalyst	Reaction time (h)	PC yiled (%)	HPC yield (%)	MO yield (%)
(1) ZnO	1	30.7	60.1	0
	5 ^b	85.7	2.2	0
	5 ^c	86.4	1.8	0
(2) CaO	1	30.6	55.1	0
	5 ^b	31.8	56.3	1.4
	5 ^c	80.3	5.1	8.2
(3) MgO	1	29.4	54.5	0
	5 ^b	30.5	53.4	0.6
	5 ^c	82.8	7.3	6.4
(4) La ₂ O ₃	1	29.1	56.5	0
	5 ^b	30.9	54.2	1.2
	5 ^c	76.6	6.7	6.9

^a Reaction conditions: PG, 0.1 mol; urea, 0.05 mol; catalyst amount, 0.002 mol; reaction temperature, 180 °C; reaction time, 3 h; reaction pressure, 10 kPa.

^b The reaction was carried out in the presence of catalysts for 1 h, it was separated by filtration, and then the filtrate was kept to stand at 180 °C for 4 h, total 5 h.

^c The reaction was carried out in the presence of catalysts for 5 h.

The homogenous nature of the PC synthesis from urea and PG over ZnO was further investigated with the liquid phase alone after reaction using solid catalysts. In principle, a model solid heterogeneous catalyst preparing PC should be insoluble in PG solution during reaction procedure. As a result, the liquid phase separated from solid catalysts should be inactive for PC production. In this work, after reaction occurred 1 h, all the metal oxide catalysts were separated from the reaction mixture by filtration, and the liquid phases were further kept to stand for 4 h under the same reaction conditions. Table 3 shows the yield comparison of PC obtained with these liquid phases after reaction over the different catalysts. Obviously, used CaO as catalyst, PC yield did not increase obviously. Thus, the liquid phase was almost inactive towards the PC synthesis. This was the same for MgO and La₂O₃. In contrast, for ZnO, the liquid phase obtained from the reaction mixture exhibited high catalytic ability and the PC yield was almost as the same as that acquired from the reactions carried out for 5 h in the presence of ZnO. These catalytic test results also illustrated that PC synthesized from PG and urea conducted homogeneously with the zinc species dissolved in the liquid phase. This conclusion was consistent with the results provided in previous reports [18,19].

3.4. Possible mechanism over ZnO

It was well known that urea could decompose into isocyanic acid and ammonia very easily at high temperature, especially higher than that its melting point (134 °C) [20]. Simultaneously, stable complexes were easily formed by ZnO coordinated with nitrogen and oxygen atoms [18,21]. On the basis of these facts, as well as the experimental results obtained in the present case, the reaction

mechanism of PC synthesis from urea and PG catalyzed over ZnO was proposed and shown in Figure 5.

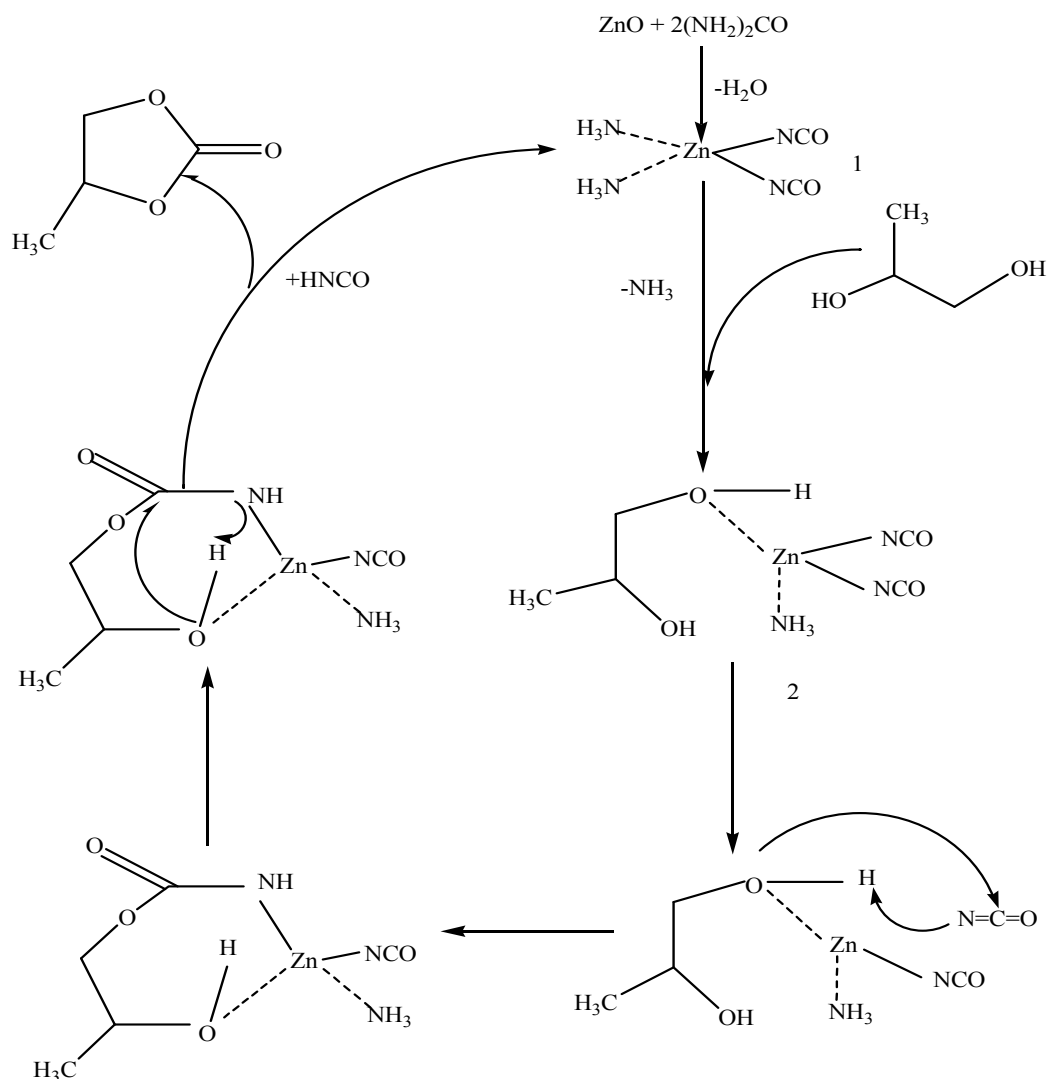


Figure 5. Proposed reaction mechanism for PC synthesis from urea and PG over ZnO.

At first, ZnO reacted with HCNCO produced from urea, and then it was converted to $\text{Zn}(\text{NCO})_2(\text{NH}_3)_2$, in which Zn^{2+} coordination with four N atoms to reach stable construction of 18 electrons. This was proved by both XRD characterization and element analysis. Compared to isocyanic acid, ammonia molecules were weakly coordinated with Zn^{2+} ion. As a result, one ammonia molecule would be substituted by one PC molecule to produce a complex 2, in which PC interacted with Zn^{2+} via its hydroxyl group oxygen atom. This made the oxygen atom of interacting hydroxyl group of PG easily attack the carbon atom in the neighboring isocyanate group, resulting in production a carbamate complex 3. As a result, the electrons of C-N bond in this complex would be redistributed and then, the proton moved to the carbon atom with the appearance of carbocation and nitrogen anion. This was favorable for the nucleophilic replacement of carbamate with another hydroxyl group. At the same time, considering of existence of HCNCO decomposed from urea in the reaction system, an ammonia molecule was released and it was a drive force for this step. Finally, the

ammonia and isocyanate group were linked to Zn^{2+} and the intermediate complex 1 was regenerated to finish the catalytic circle.

4. Conclusions

Unlike CaO, MgO and La_2O_3 , ZnO was the precursor of homogeneous catalyst rather than a heterogeneous catalyst for the synthesis of PC from urea and PG. Under the both influence of urea and PG, ZnO exhibited high activity due to the dissolved Zn species, which was the active homogeneous intermediate for the conversion of urea and PG to PC. More important, ZnO had the same catalytic pattern as that of zinc salts and its catalytic performance was well correlate with the concentration of dissolved Zn species in the liquid phase when ZnO was used as the catalyst. According to catalytic test as well as XRD, FTIR and element analysis characterization, the active species could be a complex of $Zn(NCO)_2(NH_3)_2$, in which Zn (II) ion coordinated stably with $N=C=O$ and NH_3 .

Acknowledgments

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Conflict of Interest

All authors declare no conflict of interest in this paper.

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