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Synthesis of diethyl carbonate from ethyl carbamate and ethanol over ZnO-PbO catalyst

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1. Introduction

Diethyl carbonate (DEC) is not only an important organic intermediate but also an attractive alternative oxygen-containing fuel additive. The processes for the synthesis of DEC mainly include phosgenation of ethanol [1], transesterification of organic carbonates [2], oxidative carbonylation of ethanol [3,4], ethanolysis of CO₂ [5] and ethanolysis of urea [6]. Among them, the ethanolysis of urea exhibits great advantages such as available raw materials and simple product separation. In such an approach, the intermediate ethyl carbamate (EC) is first produced from urea and ethanol and then further converted to DEC by consecutive reaction with ethanol. The reaction of EC with ethanol to DEC is the rate-control step. Several kinds of catalysts such as organometallic compounds, metal salts and metal oxides have been tested toward the reaction of urea and alcohols [7–9]. Among them, metal oxide catalysts have drawn much more attention because they can overcome the drawbacks in the separation of product and the recovery of the homogeneous catalysts [10,11].

In our previous work, lead oxide was found to be the most active catalyst for the reaction of EC and ethanol to DEC among a series of single metal oxides but DEC yield was still unsatisfactory [12]. Furthermore, it was found that the addition of a little lead oxide into some metal oxides could promote their catalytic performance. Therefore, in the present work, a series of double metal oxides

ABSTRACT

The synthesis of diethyl carbonate (DEC) from ethyl carbamate and ethanol was investigated over a series of double metal oxides. Among the catalysts, ZnO-PbO showed the best catalytic activity and the highest DEC yield was 20.6%. Furthermore, ZnO-PbO had an excellent reusability. According to the results of XRD measurement, IR and element analysis, ZnO and PbO in ZnO-PbO catalyst were separately converted to $Zn(NCO)_2(NH_3)_2$ and metal Pb during the reaction, indicating that the mixture of $Zn(NCO)_2(NH_3)_2$ and metal Pb may be the real active composition for DEC synthesis and ZnO-PbO is the precursor. In addition, a possible reaction mechanism for DEC synthesis was proposed.

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containing lead oxide were prepared and the activity evaluation results revealed that ZnO-PbO presented the highest catalytic activity. The effect of preparation conditions and DEC synthesis reaction parameters on the catalytic performance of ZnO-PbO was studied, and the catalysis and reusability of ZnO-PbO were discussed, and a possible reaction mechanism for DEC synthesis was proposed.

2. Experimental

2.1. Preparation of double metal oxides

All of double metal oxide catalyst samples were prepared by calcinating their corresponding metal compounds. The preparation process was as follows: the metal compounds were mixed and ground first and then calcined at a certain temperature for a period of time in air. For example, for the preparation of ZnO-PbO with PbO weight percentage of 10%, $Zn_2(OH)_2CO_3$ (41.3 g) and PbCO₃ (4.0 g) were mixed and then ground in a mortar by hand for about 3 min and finally calcined at 500 °C for 4 h in air.

2.2. DEC synthesis reaction

DEC synthesis reaction was carried out in a 500 mL stainless steel autoclave with a packed column and a back-pressure valve for ammonia gas removal. In a typical process, 30.5 g EC, 158 g ethanol and 1.9 g catalyst were introduced into the autoclave first, and then the mixture was rapidly heated to 180 °C under stirring and kept for 7 h. After the completion of reaction, the autoclave was cooled to room temperature and the product mixture was weighed and

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Table I		
Catalytic performa	ance of the doul	ole metal oxides

Catalyst	Precursor	Calcination temperature/°C	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
MgO-PbO	$Mg(NO_3)_2 \cdot 6H_2O$	500	18.8	4.7	25.0
CaO-PbO	CaCO ₃	900	37.4	9.4	25.1
SrO-PbO	$Sr(NO_3)_2$	1100	18.9	1.6	8.5
BaO-PbO	Ba(NO ₃) ₂	700	23.1	3.7	16.0
ZnO-PbO	$Zn_2(OH)_2CO_3$	500	33.9	13.8	40.7
ZrO ₂ -PbO	$Zr(NO_3)_4 \cdot 5H_2O$	500	26.5	5.4	20.4
Al ₂ O ₃ -PbO	$Al(NO_3)_3 \cdot 9H_2O$	500	20.1	1.4	7.0
Fe ₂ O ₃ -PbO	Fe (NO ₃) ₃ .9H ₂ O	500	26.1	5.8	22.2
CuO-PbO	CuCO ₃ ·Cu(OH) ₂ ·2H ₂ O	300	42.6	5.9	13.8
NiO-PbO	NiCO3·2Ni(OH)2·4H2O	300	26.2	4.5	17.2
TiO ₂ -PbO	TiO(OH) ₂	500	14.0	0.28	2.0
La ₂ O ₃ -PbO	$La(NO_3)_3 \cdot 6H_2O$	800	20.8	5.0	24.0
None			1.7	0.5	29.4

The weight percentage of lead oxide in double metal oxides was 10% and the calcination time was 4 h.

Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 °C, and 7 h.

filtrated. The filtrate was analyzed by a SP 2100 gas chromatograph with a FID and a PEG-20 M capillary column using cyclohexanol as the internal standard. The yield and selectivity of DEC were calculated based on EC:

 $DEC \, yield(\%) = \frac{moles \, of \, DEC \, formed}{moles \, of \, EC \, charged} \times 100$

 $DEC selectivity(\%) = \frac{moles of DEC formed}{moles of EC converted} \times 100$

2.3. Catalyst characterization

XRD analysis of the catalyst was performed on a D/MAX-2500 diffractometer with Cu K α radiation operated at 40 kV and 100 mA. IR spectroscopic spectrum of the catalyst was recorded on a Bruker Vector 22 FT-IR spectrophotometer in the 4000–400 cm⁻¹ range. TG of the precursors (Zn₂(OH)₂CO₃ and PbCO₃) was carried out on a SDT Q600 simultaneous DSC-TGA instrument at a heating rate of 10 °C/min under a flow of air. Element analysis of the recovered catalyst was determined by a Flash EA1112 elemental analyzer.

3. Results and discussion

3.1. Screening for catalysts

As shown in Table 1, ZnO-PbO exhibits the highest activity among the prepared double metal oxide catalysts and the yield and selectivity of DEC are 13.8% and 40.7%, respectively. So it is necessary to study the effect of preparation conditions and DEC synthesis

Table 2

Catalytic performance of ZnO-PbO prepared from different precursor.

reaction parameters on the catalytic performance of ZnO-PbO catalyst.

3.2. Effect of preparation conditions

Reaction conditions for evaluating the catalytic performance of ZnO-PbO sample were as follows: molar ratio of ethanol/EC of 10:1, catalyst weight percentage of 1%, $180 \degree$ C, and 7 h.

3.2.1. Effect of precursor

The catalytic performance of ZnO-PbO samples prepared from different precursor is listed in Table 2. As a result, ZnO-PbO sample prepared with $Zn_2(OH)_2CO_3$ and PbCO₃ as the precursors shows the highest activity; the yield and selectivity of DEC are 13.8% and 40.7%, respectively. Hence, $Zn_2(OH)_2CO_3$ and PbCO₃ are selected as the precursors of ZnO-PbO catalyst.

3.2.2. Effect of calcination temperature

The effect of calcination temperature on the catalytic performance of ZnO-PbO is illustrated in Table 3. It can be seen that DEC selectivity reaches the maximum 40.7% at the calcination temperature of 500 °C (DEC yield 13.8%) while DEC yield attains the maximum 13.9% at the calcination temperature of 300 °C (DEC selectivity 38.2%). From the viewpoint of full use of reactants, the suitable calcination temperature is determined as 500 °C.

ZnO-PbO samples calcined between 300 °C and 600 °C were analyzed by XRD and the result is shown in Fig. 1. The diffraction peaks of ZnO in different samples can be indexed to hexagonal structured ZnO but lead oxides with different valence states and crystal forms can be observed at different calcination temperature. Tetragonal PbO is obtained from the samples prepared at 300 °C and 400 °C

5 1	1 1	1			
Precursor of zinc oxide	Precursor of lead oxide	Calcination temperature/°C	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
$Zn_2(OH)_2CO_3$	PbCO ₃	500	33.9	13.8	40.7
$Zn_2(OH)_2CO_3$	Pb(NO ₃) ₂	500	21.6	9.5	44.0
$Zn_2(OH)_2CO_3$	Pb(CH ₃ COO) ₂	500	27.1	9.7	35.8
$Zn(NO_3)_2$	PbCO ₃	400	19.8	7.1	35.9
$Zn(NO_3)_2$	$Pb(NO_3)_2$	400	19.4	4.6	23.7
$Zn(NO_3)_2$	Pb(CH ₃ COO) ₂	400	17.8	6.9	38.8
$Zn(CH_3CO_2)_2$	PbCO ₃	400	29.7	11.0	37.0
$Zn(CH_3CO_2)_2$	$Pb(NO_3)_2$	400	23.4	7.0	29.9
$Zn(CH_3CO_2)_2$	Pb(CH ₃ COO) ₂	400	24.9	6.8	27.3
Zn(OH) ₂	PbCO ₃	500	27.8	10.9	39.2
Zn(OH) ₂	Pb(NO ₃) ₂	500	19.6	5.6	28.6
Zn(OH) ₂	Pb(CH ₃ COO) ₂	500	26.3	9.8	37.3

The weight percentage of lead oxide in double metal oxides was 10% and the calcination time was 4 h.

Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 °C, and 7 h.

Table 3

Effect of calcination temperature on the catalytic performance of ZnO-PbO.

Calcination temperature/°C	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
300	36.4	13.9	38.2
400	35.6	13.6	38.2
500	33.9	13.8	40.7
600	35.3	10.6	30.0

The double metal oxides were prepared using $Zn_2(OH)_2CO_3$ and PbCO₃ as the precursors which were calcined for 4 h, and the weight percentage of lead oxide in double metal oxides was 10%.

Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 $^\circ C$, and 7 h.



Fig. 1. XRD patterns of ZnO-PbO catalysts prepared at different calcination temperature. (1) 300 °C, (2) 400 °C, (3) 500 °C, (4) 600 °C. The double metal oxides were prepared using $Zn_2(OH)_2CO_3$ and PbCO₃ as the precursors which were calcined for 4 h, and the weight percentage of lead oxide in double metal oxides was 10%.

while orthorhombic PbO_2 is present in the sample prepared at 400 °C and 500 °C. Orthorhombic PbO appears and tetragonal PbO disappears when the calcination temperature is above 500 °C.

To investigate further the reason for similar catalytic behaviour of the samples, the thermal decomposition of precursors $(Zn_2(OH)_2CO_3 \text{ and PbCO}_3)$ was studied by thermal analyses and the result is shown in Fig. 2. TG curve indicates that the major weight loss is at around 190–330°C and there is no other weight loss when the temperature is higher than 330°C. XRD determination results (see Fig. 1) show that the precursors are decomposed completely



Fig. 2. TG curve of the mixture of Zn₂(OH)₂CO₃ and PbCO₃.

Table	4	
Effect	of lead	ovid

Effect of lead oxide content on the catalytic performance of ZnO-PbO.

Lead oxide content (%)	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
5	33.6	9.4	28.0
10	33.9	13.8	40.7
15	43.2	14.3	33.1
20	41.4	13.2	31.9
25	18.1	3.4	18.8

The double metal oxides were prepared using $Zn_2(OH)_2CO_3$ and $PbCO_3$ as the precursors which were calcined at 500 $^\circ C$ for 4 h.

Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 $^\circ$ C, and 7 h.

by calcining at 300 °C. The difference between TG and XRD may be caused by the calcination time, i.e. ZnO-PbO catalysts were calcined at 300 °C for 4 h, and TG analyses is only a process of temperature-programmed decomposition. After complete decomposition of the precursors, there does not exist any changes with increasing temperature in the TG curve, which may be responsible for the similar catalytic behavior for the samples prepared at different calcination temperatures.

3.2.3. Effect of lead oxide content

The effect of lead oxide content on the catalytic activity of ZnO-PbO is demonstrated in Table 4. When lead oxide weight percentage in ZnO-PbO sample reaches 10%, DEC selectivity attains the maximum 40.7% (DEC yield 13.8%) while the maximal DEC yield of 14.3% (DEC selectivity 33.1%) is obtained over the catalyst with lead oxide weight percentage of 15%. By comprehensive consideration of both DEC yield and selectivity, lead oxide weight percentage of 10% is selected.

3.3. Effect of reaction conditions

3.3.1. Effect of catalyst concentration

The effect of catalyst concentration on DEC synthesis reaction is shown in Fig. 3(a). The conversion of EC rises monotonically with an increase of catalyst concentration while DEC yield and selectivity reach their maximum 13.8% and 40.7% at the catalyst weight percentage of 1%. The main side-reaction in this reaction system is the *N*-ethylation of EC to *N*-ethyl ethyl carbamate (*N*-EEC). Higher catalyst concentration will promote this side-reaction and cause the consumption of DEC [6] so as to decrease the yield and selectivity of DEC. Therefore the suitable catalyst concentration is 1 wt%.

3.3.2. Effect of ethanol/EC molar ratio

Fig. 3(b) shows the influence of ethanol/EC molar ratio on the DEC synthesis reaction. The DEC yield and selectivity rise with an increase of ethanol/EC molar ratio first and then decrease. The DEC yield reaches the maximum 16.8% (DEC selectivity 36.6%) at ethanol/EC molar ratio of 7:1 while DEC selectivity attains the maximum 40.7% (DEC yield 13.8%) at ethanol/EC molar ratio of 10:1. When the molar ratio of ethanol/EC is lower, EC concentration is higher and the side reaction of *N*-ethylation of EC will take place easily so as to lower DEC yield and selectivity. However, too much higher molar ratio of ethanol/EC will result in the reduction of EC concentration. As a result, the reaction rate decreases and a lower DEC yield will be obtained. Based on the consideration of decreasing ethanol separation costs, the suitable molar ratio of ethanol/EC is 7.

3.3.3. Effect of reaction temperature

The effect of reaction temperature on the DEC synthesis reaction is presented in Fig. 3(c). The conversion of EC rises with an increase of reaction temperature but DEC yield and selectivity get



Fig. 3. Effect of reaction conditions on the reaction for DEC synthesis. (a) Effect of catalyst weight percentage. Reaction conditions: molar ratio of ethanol: EC = 10:1, 180 °C, and 7 h. (b) Effect of ethanol/EC molar ratio. Reaction conditions: catalyst weight percentage 1%, 180 °C, and 7 h. (c) Effect of reaction temperature. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Effect of reaction time. Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, and 7 h. (d) Ef

their maximum of 20.6% and 41.0% at 190 °C and then decrease. Since the synthesis of DEC is an endothermic reaction, it is beneficial at higher reaction temperature [6]. However, higher reaction temperature will accelerate the side-reaction of *N*-ethylization either and cause the decrease of DEC yield and selectivity beyond 190 °C. Hence, the reaction temperature of 190 °C is selected.

3.3.4. Effect of reaction time

The effect of reaction time on the DEC synthesis reaction is demonstrated in Fig. 3(d). As the reaction proceeds, the conversion of EC increases. However, DEC yield and selectivity reach their maximal value 20.6% and 41.0% at 7 h and then drop due to the side-reactions such as N-ethylization of EC. So the suitable reaction time is chosen as 7 h.

It could be concluded that the suitable reaction conditions for DEC synthesis over ZnO-PbO catalyst are as follows: catalyst concentration of 1 wt%, ethanol/EC molar ratio of 7:1, 190 °C, and 7 h. Under the above reaction conditions, the DEC yield was 20.6%. The catalytic performance of ZnO-PbO for dimethyl carbonate (DMC) synthesis from methyl carbamate and methanol was also evaluated and the yield and selectivity of DMC was 25.7% and 38.9%, respectively. The results indicate that ZnO-PbO is effective for the similar reactions.

3.4. Reusability of ZnO-PbO catalyst

To investigate the reusability of ZnO-PbO catalyst, the used ZnO-PbO was recovered by filtrating, washing with ethanol, and then drying at 80 °C for 12 h in vacuum. Their catalytic performance was evaluated and the results are listed in Table 5. With the reuse of ZnO-PbO catalyst, the conversion of EC decreases at the second run and then keeps almost unchanged, DEC selectivity rises firstly and then keeps even while DEC yield remains almost constant. It could be inferred that ZnO-PbO has an excellent reusability.

3.5. Analysis for catalysis of ZnO-PbO

3.5.1. XRD characterization

XRD patterns of the recovered ZnO-PbO catalyst are shown in Fig. 4(a). Hexagonal ZnO, orthorhombic PbO and orthorhombic PbO₂ are observed in the fresh catalyst but only cubic metal Pb and orthorhombic PbO₂ appear in the recovered catalyst. This suggests that ZnO has been transformed into an amorphous or microcrystal phase while orthorhombic PbO has been reduced to cubic metal Pb.

Table 5	
Reuse of ZnO-PbO Catalyst.	

Runs	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
1	50.2	20.6	41.0
2	43.9	19.4	44.2
3	44.6	20.2	45.3
4	42.4	19.1	45.0
5	48.7	21.6	44.4

Reaction conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 7:1, 190 $^\circ$ C, and 7 h.



Fig. 4. XRD patterns of the catalysts. (a) The fresh and recovered ZnO-PbO: (1) fresh, (2) first recovered, (3) third recovered, (4) fifth recovered. (b) The fresh and recovered ZnO catalyst: (1) fresh, (2) recovered. (c) The fresh and recovered ZnO-Pb: (1) fresh, (2) recovered

When ZnO alone was used in this reaction, hexagonal ZnO could be observed in the fresh and recovered catalyst (see Fig. 4(b)). So we suppose that the existence of lead oxide accelerates the transformation of ZnO into an amorphous or microcrystal phase in ZnO-PbO catalyst.



Fig. 5. IR spectra of the recovered catalysts. (1) First recovered, (2) third recovered.

From Table 5 and Fig. 4(a), it can be seen that orthorhombic PbO has been reduced to cubic metal Pb in the recovered ZnO-PbO catalyst and DEC selectivity is higher than that over the fresh catalyst. In order to find the correlation between them, ZnO-Pb sample was prepared by reducing ZnO-PbO sample with a mixture of H_2 and N_2 (volume ratio 1:1) at 450 °C for 4 h and then the catalytic performance of ZnO-Pb sample was evaluated. Under the reaction conditions of catalyst weight percentage of 1%, ethanol/EC molar ratio of 7:1, reaction temperature of 190°C and reaction time of 7 h. the vield and selectivity of DEC are 19.4% and 48.0%. respectively, indicating that ZnO-Pb sample possesses high catalytic performance. Fig. 4(c) shows the XRD patterns of the fresh and recovered ZnO-Pb catalyst. Hexagonal ZnO, orthorhombic PbO₂ and cubic metal Pb are observed in the fresh catalyst sample but the recovered catalyst sample does not show any ZnO characteristic peaks, illustrating that ZnO has been transformed into an amorphous or microcrystal phase either, in accordance with the result of ZnO-PbO catalyst. Compared with the catalytic performance of ZnO-PbO catalyst, DEC yield is roughly the same while DEC selectivity increases over ZnO-Pb catalyst, in agreement with the experimental results of the reuse of ZnO-PbO catalyst. This result illustrates that metal lead has better selectivity in DEC synthesis reaction from ethanol and EC, which may be the reason for DEC selectivity increase in the experiment of the reuse of ZnO-PbO catalyst.

3.5.2. IR analysis and element analysis

IR spectra of the recovered ZnO-PbO catalysts are presented in Fig. 5. For the recovered catalyst from the first run, stretching vibrations of NH appears at 3464 cm⁻¹ and the asymmetry deformation vibration of NH_3 is observed at 1624 cm^{-1} . The characteristic bands at 2215, 1263 and $619\,\mathrm{cm}^{-1}$ are attributed to the stretching vibrations of NC and CO as well as the asymmetry deformation vibration of NCO, respectively [13]. The recovered catalyst from the third run also possesses the characteristic bands of NCO and asymmetry deformation vibration of NH₃, suggesting that the recovered catalysts contain NCO group and NH₃. Zhao et al. [14] found that ZnO was transformed into Zn(NCO)₂(NH₃)₂ in the reaction of urea and alcohols. Hence, based on the IR analysis results, we presume that ZnO (in ZnO-PbO catalyst) is probably transformed into Zn(NCO)₂(NH₃)₂ either in DEC synthesis reaction from ethanol and EC. This is significantly supported by element analysis of the recovered catalysts, i.e., the measured molar ratio of Zn, N, C and H is 1:4:1.97:5.98, which is evidently consistent with the molecular formula of $Zn(NCO)_2(NH_3)_2$.



Scheme 1. Possible reaction mechanism for DEC synthesis from EC and ethanol.

3.5.3. Possible formation route to $Zn(NCO)_2(NH_3)_2$

Combining the results of the present study and Zhao's work [14], a plausible formation route to $Zn(NCO)_2(NH_3)_2$ is put forward as follows:

$$\begin{array}{c} O \\ H \\ H \\ NH_2 COC_2 H_5 \end{array} \xrightarrow{Pb} H NCO + C_2 H_5 OH \end{array}$$
(1)

 $ZnO + 2HNCO \rightarrow Zn(NCO)_2 + H_2O$ (2)

$$Zn(NCO)_2 + 2NH_3 \rightleftharpoons Zn(NCO)_2(NH_3)_2$$
(3)

The decomposition reaction of EC was studied at 190 °C for 7 h in order to test whether metal lead could accelerate this reaction or not. The result shows that the yield of ethanol is separately 41.1% and 84.4% without a catalyst and over metal lead catalyst. This illustrates that metal lead indeed accelerates the decomposition of EC. Consequently, ZnO reacts with the resultant HNCO to give rise to $Zn(NCO)_2$ (Eq. (2)) and then $Zn(NCO)_2$ coordinates with NH₃ in the reaction system to form $Zn(NCO)_2(NH_3)_2$ (Eq. (3)). Since the deamination reaction of an ammonia complex can proceed at a high temperature, we presume that the reaction of $Zn(NCO)_2$ with NH₃ to $Zn(NCO)_2(NH_3)_2$ may be reversible in DEC synthesis process. While the temperature drops to room temperature, the complex is mainly in the form of $Zn(NCO)_2(NH_3)_2$.

3.5.4. Possible reaction mechanism

Since hexagonal ZnO and orthorhombic PbO were converted separately into $Zn(NCO)_2(NH_3)_2$ and cubic metal Pb at the first run, and they did not change at the following runs (see Fig. 4(a)), we presumed $Zn(NCO)_2(NH_3)_2$ and metal Pb were the real active components. To investigate whether the precursors of ZnO-PbO have the same catalytic performance as that of ZnO-PbO, the catalytic performance of $Zn_2(OH)_2CO_3 + PbCO_3$ was evaluated and the yield and selectivity of DEC was 15.5% and 34.4%, which was lower than that over ZnO-PbO. In the recovered $Zn_2(OH)_2CO_3 + PbCO_3$ catalyst, we found $Zn(NCO)_2(NH_3)_2$ but no metal Pb, suggesting that $Zn_2(OH)_2CO_3$ could convert to $Zn(NCO)_2(NH_3)_2$ while PbCO_3 could

not convert to metal Pb during the reaction. This result proves again that both $Zn(NCO)_2(NH_3)_2$ and metal Pb are the active components. Therefore we speculated the reaction mechanism for diethyl carbonate formation from ethyl carbamate and ethanol over metal Pb and $Zn(NCO)_2(NH_3)_2$ as shown in Scheme 1.

As a transition metal element, divalent Zn²⁺ ion with d¹⁰ electrons can coordinate with nitrogen, sulfur or phosphorus atom to reach the stable construction of 18 electrons. In this reaction system, $Zn(NCO)_2(NH_3)_2$ can convert to $Zn(NCO)_2$ and vice versa. Zn^{2+} ion coordinates with the nitrogen atom of amino group in a EC molecule so as to activate EC. Since there exists a resonance structure for EC molecule, the complex of EC activated by Zn(NCO)₂ has two kind of structures named as Species A and Species B in Scheme 1. The hybridized orbital of the nitrogen atom will change and most of sp² changes to sp³ once it coordinates with Zn²⁺ ion, and then the π -delocalized bond of the amide group becomes weak correspondingly. Firstly, 1 equiv. of Zn²⁺ ion reaches the stable construction of 18 electrons (the two nitrogen atoms in -NCO would provide one pair of electrons each) by the coordination of 2 equiv. of EC through the nitrogen atom of the amide group. The weak amino-carbonyl bond of Species B facilitates the nucleophilic attack of ethoxy group in an ethanol molecule. On the other hand, Pb atom inserts into an ethanol molecule between an ethoxy group and a hydrogen atom so as to activate ethanol, facilitating the dissociation of ethanol molecule into an ethoxy group and a hydrogen atom. Then, a lone pair of electrons of oxygen atom in the ethoxy group can form a bond with the electrophilic carbonyl carbon of Species B while the hydrogen proton breaking away from the ethanol molecule combines with the amino group leaving from EC molecule. As a result, a new Species C is formed while Pb atom is reduced back. The amino-carbonyl bond of Species C breaks to produce DEC and Species D. Because of the strong nucleophilic ability of EC and the dissociation of NH₃ in Species D, the NH₃ in the Species D can be substituted by EC to form Species A. Thus a catalytic circle finishes.

According to this catalytic mechanism, EC is activated by $Zn(NCO)_2$, which is in accordance with the activation of methyl

carbamate by $Zn(NCO)_2$ reported by Zhao et al. [14]. The reaction between PbO and EC could reduce PbO to metal Pb which was shown to be one of the real active component for the synthesis of DEC [15] and transition metal could catalyze dehydrogenation of ethanol to ethyl acetate [16], which give support for activition of ethanol by Pb. DEC yield was 2.3% over ZnO, 16.2% over PbO and 20.6% over ZnO-PbO. The higher catalytic activity of ZnO-PbO may be caused by the separate activation of EC and ethanol by Zn(NCO)₂ and metal Pb.

4. Conclusions

ZnO-PbO shows the highest catalytic performance; the yield and selectivity of DEC attain 20.6% and 41.0%, respectively. In addition, ZnO-PbO catalyst has an excellent reusability. On the basis of XRD characterization, IR and element analysis, it is found that $Zn(NCO)_2(NH_3)_2$ and metal Pb are the real active species for DEC synthesis while ZnO-PbO is the precursor. EC and ethanol are activated separately by $Zn(NCO)_2$ and metal Pb simultaneously in the reaction for DEC synthesis.

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References

- [1] I.E. Muskat, F. Strain, U.S. Patent 2,379,250 (1941).
- [2] M. Wang, X.Q. Zhao, H.L. An, Y.J. Wang, J. Chem. Eng. Chin. Univ. 24 (2010) 663–669 (in Chinese).
- [3] P.B. Zhang, S.Y. Huang, Y. Yang, Q.S. Meng, S.P. Wang, X.B. Ma, Catal. Today 149 (2010) 202–206.
- [4] D.N. Briggs, K.H. Lawrence, A.T. Bell, Appl. Catal. A 366 (2009) 71-83.
- [5] G. Fabien, T.R. Sophie, M. Zephirin, J. Supercrit. Fluids 50 (2009) 46-53.
- [6] D.P. Wang, B.L. Yang, X.W. Zhai, L.G. Zhou, Fuel Process. Technol. 88 (2007) 807-812.
- [7] R.Y. Saleh, R.C. Michaelson, E.N. Suciu, B. Kuhlmann, U.S. Patent 5,565,603 (1996).
- [8] D.F. Wang, X.L. Zhang, Y.Y. Gao, F.K. Xiao, W. Wei, Y.H. Sun, Fuel Process. Technol. 91 (2010) 1081–1086.
- [9] C.C. Wu, X.Q. Zhao, Y.J. Wang, Catal. Commun. 6 (2005) 694–698.
- [10] D.F. Wang, X.L. Zhang, Y.Y. Gao, F.K. Xiao, W. Wei, Y.H. Sun, Catal. Commun. 11 (2010) 430–433.
- [11] D.F. Wang, X.L. Zhang, W.B. Zhao, W.C. Peng, N. Zhao, F.K. Xiao, W. Wei, Y.H. Sun, J. Phys. Chem. Solids 71 (2010) 427–430.
- [12] H.L. Zhao, X.Q. Zhao, H.L. An, Y.J. Wang, Petrochem. Technol. 38 (2009) 139–144 (in Chinese).
- [13] H.G.M. Edwards, D.W. Farwell, I.R. Lewis, N. Webb, J. Mol. Struct. 271 (1992) 27-36.
- [14] W.B. Zhao, W.C. Peng, D.F. Wang, N. Zhao, J.P. Li, F.K. Xiao, W. Wei, Y.H. Sun, Catal. Commun. 10 (2009) 655–658.
- [15] L. Guo, X.Q. Zhao, H.L. An, Y.J. Wang, Chin. J. Catal. 33 (2012) 595-600.
- [16] L.X. Wang, Ph.D. Thesis, Jilin (2010).