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COMMUNICATION

Catalysis by Lead Oxide for Diethyl Carbonate Synthesis from Ethyl Carbamate and Ethanol

GUO Lian, ZHAO Xinqiang*, AN Hualiang, WANG Yanji

Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, Hebei University of Technology, Tianjin 300130, China

Abstract: The catalysis by lead oxide in the reaction of ethyl carbamate (EC) with ethanol to form diethyl carbonate (DEC) was studied. The lead oxide catalyst exhibited an excellent stability, which could be reused five times without a significant loss in catalytic activity. X-Ray powder diffraction analysis showed that the recovered catalyst was a mixture of cubic metal Pb and orthorhombic PbO_2, with the latter shown to be the real active component for the synthesis of DEC. Verification experiments showed that the reaction between DEC and PbO was the main reason for the reduction of PbO to metal Pb.

Key words: diethyl carbonate; ethyl carbamate; lead oxide; ethanol; urea

Diethyl carbonate (DEC) is not only an important organic intermediate but also an attractive alternative oxygen-containing fuel additive. The DEC synthesis routes mainly include phosgenation of ethanol, transesterification of organic carbonates, oxidative carbonylation of ethanol, ethanolysis of CO_2, and ethanolysis of urea. The phosgenation of ethanol is gradually being phased out because phosgene is highly toxic and the byproduct hydrogen chloride causes serious corrosion [1]. The transesterification of organic carbonates is thermodynamically governed. Moreover, the starting material (such as propylene oxide) is sourced from depleting petroleum reserves [2,3]. The oxidative carbonylation of ethanol suffers from low single-pass conversion, high catalyst costs, and poor stability [4–8]. The ethanolysis of CO_2 is thermodynamically unfavorable and still in the stage of fundamental studies [9]. The ethanolysis of urea, however, is a potential route because it exhibits great advantages such as availability of raw materials and simple product separation [10].

The alcoholysis of urea can be divided into two steps: the synthesis of an intermediate alkyl carbamate from urea and an alcohol followed by reaction of the alkyl carbamate with the alcohol to form a dialkylcarbonate. The first step is fast and highly selective even without a catalyst, but the second step is more difficult [10]. Hence, it is important and necessary to study the second reaction. Zhao et al. [11] investigated the synthesis of dimethyl carbonate (DMC) from methyl carbamate (MC) and methanol over zinc compound catalysts. $ZnCl_2$ showed the highest catalytic activity and led to a DMC yield of 33.6% under the optimal conditions. The homogeneous nature of the metal salts lead to separation and recovery problems. Since heterogeneous catalysis can overcome these drawbacks, this type of catalyst has attracted much more attention. Wu et al. [12] have prepared Zn-based catalysts, and the DMC yield obtained was 12.7% over zinc powder. Wang et al. [13,14] investigated the catalytic performance of mixed oxide catalysts for the reaction for DMC synthesis, and zinc/iron mixed oxide possessed the best catalytic ability giving a DMC yield of 31.5%. Compared with many studies on DMC synthesis, there were a few reports on DEC synthesis. Zhao et al. [15] found that CaO had good catalytic activity for the reaction of ethyl carbamate (EC) and ethanol to DEC, and the yield of DEC was 10.8%.

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 metal oxides studied, and the DEC yield was 16.2% [16]. Hence, a further study on the catalysis and reus-

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*Corresponding author. Tel: +86-22-60202427; Fax: +86-22-60204294; E-mail: zhaoxq@hebut.edu.cn

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ability of lead oxide was carried out in this work. The reaction conditions in this work were identical to those described in our previous work [16].

Lead oxide was prepared by thermal decomposition of lead carbonate at 300 °C for 4 h in air. The 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 which was firstly purged with nitrogen and pressurized to 2 MPa. After that, the reaction mixture was heated to 180 °C with stirring. After the completion of reaction, the autoclave was cooled to room temperature and the product mixture was weighed, filtered, and analyzed.

The gaseous products were analyzed on a SP 3400 gas chromatograph with a PLOT-Q packed column. The analysis conditions were as follows: N_2 as carrier, TCD temperature 120 °C, the injection port temperature 120 °C, and column temperature 50 °C. The liquid products were analyzed on an SP 2100 gas chromatograph with a PEG-20M capillary column. The analysis conditions were as follows: N_2 as carrier, FID temperature 220 °C, the injection port temperature 200 °C, and the program-controlled column temperature. The reaction products were also qualitatively analyzed on a 6890/5973 GC-MS equipped with a HP-INNOWax column and mass spectra were obtained in a range of 10–500 amu. X-ray diffraction (XRD) analysis of the catalyst was performed on a D/MAX-2500 diffractometer with Cu K_α radiation, 40 kV tube voltage, 100 mA tube electric current, and scanning range of 5° to 90°.

First of all, the reusability of lead oxide catalyst was investigated. The used lead oxide catalyst was recovered by filtration, washed with ethanol, and dried at 80 °C for 12 h in vacuum. The activity evaluation shown in Table 1 reveals that both DEC yield and selectivity remained almost constant, indicating that lead oxide had high catalytic stability.

XRD patterns of the fresh, first recovered, third recovered, and fifth recovered lead oxide catalyst are shown in Fig. 1. Tetragonal PbO and orthorhombic PbO_2 were observed in the fresh catalyst while cubic metal Pb and orthorhombic PbO_2 appeared in the recovered catalyst. This suggested that tetragonal PbO had been transformed into cubic metal Pb during the reaction. Furthermore, we assumed that both cubic metal Pb and orthorhombic PbO_2 catalyze the reaction for DEC synthesis from EC and ethanol because the catalytic composition consisting of cubic metal Pb and orthorhombic PbO_2 had not changed since the second run.

Table 1 Reuse of lead oxide catalyst

Run	EC conversion (%)	DEC yield (%)	DEC selectivity (%)
1	36.5	15.7	43.0
2	36.8	16.2	44.0
3	37.0	16.1	43.5
4	33.4	15.1	45.2
5	36.7	16.4	44.7

Reaction conditions: n(ethanol):n(EC) = 10, catalyst concentration 1 wt%, 180 °C, 7 h, 2 MPa. EC—Ethyl carbamate; DEC—Diethyl carbonate.

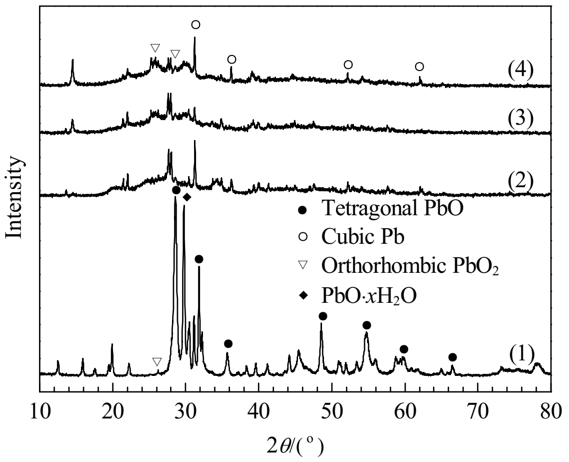

Fig. 1. XRD patterns of the fresh and recovered lead oxide catalysts. (1 Fresh; (2) First recovered; (3) Third recovered; (4) Fifth recovered.

In order to verify the correctness of this deduction, a metal lead sample was prepared firstly by reducing lead oxide with a mixture of H_2 and N_2 (volume ratio 1:1) at 300 °C for 6 h. Figure 2 shows the XRD pattern of the reduced lead oxide sample, and both cubic metal Pb and orthorhombic PbO_2 were observed. In Fig.1, PbO_2 showed diffraction peaks at around 2θ = 26° (110) and 2θ = 28° (111) while the diffraction peak of PbO_2 appeared only at around 2θ = 28° (111) in Fig. 2. This result may be caused by different treatment processes. Furthermore, the catalytic performance of PbO_2, pure metal Pb, and the metal lead sample prepared by reducing lead oxide was evaluated separately in the reaction of EC and ethanol. The results are listed in Table 2. Compared with the fresh lead oxide, the pure metal Pb exhibited a weak activity; PbO_2 displayed a slightly lower selectivity for DEC synthesis; the pre-

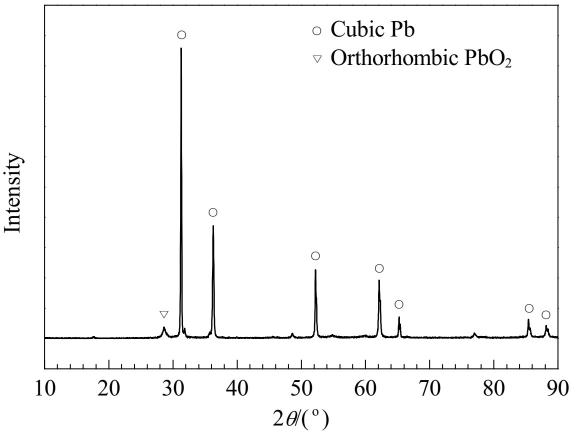

Fig. 2. XRD pattern of the sample prepared by reduction of the fresh lead oxide.

Table 2 Catalytic activity of different catalysts

Catalyst	EC conversion (%)	DEC yield (%)	DEC selectivity (%)
Pure metal Pb	12.1	1.9	15.7
PbO_2	34.6	11.3	32.7
Metal lead sample*	26.9	13.4	49.8
Pb + PbO_2	33.2	13.9	41.9
Fresh lead oxide	36.5	15.7	43.0

*Prepared by reducing lead oxide.

Reaction conditions: n(ethanol):n(EC) = 10, catalyst concentration 1 wt% , 180 °C, 7 h, 2 MPa.

pared metal lead sample showed an excellent activity and selectivity. DEC yield decreased slightly while DEC selectivity increased over the metal lead sample. Since the prepared metal lead sample was composed of metal Pb and PbO_2, the catalytic performance of Pb/PbO_2 mixture (mass ratio 1:1) prepared by physical mixing was also evaluated. DEC yield and selectivity were 13.9% and 41.9%, respectively, indicating that the catalytic activity of Pb/PbO_2 mixture was close to that of the fresh lead oxide catalyst. Hence, we are convinced that the mixture of metal Pb and PbO_2 is the catalytic agent and the synergistic action between metal Pb and PbO_2 is responsible for the high catalytic activity.

From Fig. 1 we know that tetragonal PbO was transformed into cubic metal Pb during the DEC synthesis reaction. In order to study the reason for the reduction of PbO in this reaction system, the following experiments were designed and conducted.

Experiment No.1: the reaction of ethanol and lead oxide (reaction conditions: mass ratio of ethanol to lead oxide = 60:1, 180 °C, 7 h). Acetaldehyde and ethylacetate were detected in the liquid phase after the reaction of ethanol and the lead oxide sample. Idriss et al. [17] investigated the reaction of ethanol with a series of metal oxides and found that the main reaction products in all cases were acetaldehyde and ethylacetate. They supposed that ethanol tended to dehydrogenate to acetaldehyde which further reacted to form ethylacetate via the Tishchenko reaction. The result of the reaction between ethanol and lead oxide was in agreement with Idriss's work [17]. Furthermore, the XRD characterization of the solid sample after the reaction revealed that no metal Pb was observed, indicating that the presence of ethanol was not the reason for the reduction of PbO to metal Pb.

Experiment No. 2: the reaction of EC and lead oxide (reaction conditions: water as solvent, mass ratio of EC to PbO = 15:1, 180 °C, 7 h). The XRD analysis of the solid sample revealed that no metal Pb was observed either, indicating that the presence of EC was not the reason for the reduction of PbO.

Experiment No. 3: the reaction of DEC and lead oxide (reaction conditions: mass ratio of DEC to PbO = 60:1, 180 °C, 7 h). The XRD analysis of the solid sample illustrated that tetragonal PbO was transformed into cubic metal Pb (Fig. 3), indicating that the presence of DEC was the main reason for the reduction of PbO.

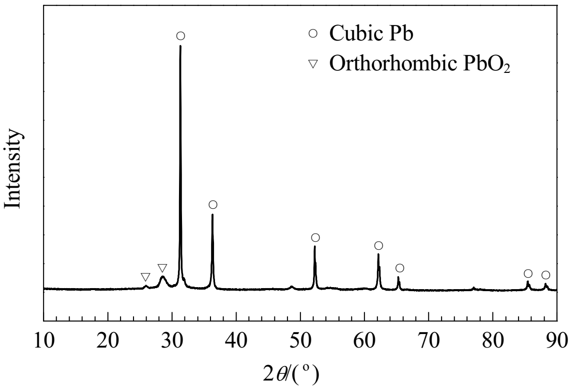

Fig. 3. XRD pattern of lead oxide reacted with DEC.

To investigate the reaction of DEC and lead oxide thoroughly, the gaseous products were collected and analyzed after reaction and the results showed the presence of hydrogen, ethylene, and carbon dioxide. Furthermore, the liquid products were qualitatively analyzed by GC-MS. The result showed that besides DEC, the main products in this reaction system were ethanol, diethylether, ethylacetate, and water. Notario and coworkers [18] found that DEC could decompose to ethanol, ethylene and carbon dioxide at temperatures of 280–440 °C. In our blank test, DEC did not decompose at 180 °C but did partially decompose at 180 °C in the presence of lead oxide. So we suppose that lead oxide can promote the decomposition of DEC.

Experiment No. 4: to test whether PbO could be reduced to metal Pb by the reaction products of experiment No. 3, the reaction between lead oxide and a mixture of diethylether, ethylacetate, acetaldehyde, and ethanol in the presence of gaseous mixture of hydrogen, ethylene, carbon dioxide, and nitrogen studied (reaction conditions: mass ratio of lead oxide to diethylether to ethylacetate to acetaldehyde to ethanol = 1:1:1:1:60, 180 °C, 7 h) was carried out. The XRD analysis of the solid sample after reaction revealed that PbO was not reduced to metal Pb, indicating that the above reaction system does not effect this reduction.

Based on the above experiments, it can be inferred that the reaction between DEC and PbO is the main reason for the reduction of PbO to metal Pb.

To further analyze the reason for the reduction of PbO to metal Pb, experiment No. 5 was designed to test the effect of reaction time on the reaction between DEC and PbO (reaction conditions: mass ratio of DEC to lead oxide = 60:1, 180 °C, 3 h). GC analysis showed that acetaldehyde appeared at 3 h but disappeared at 7 h (experiment No. 3) in the reaction solution, and other products did not change at 3 and 7 h. This means that the acetaldehyde formed must be further converted to other products such as ethylacetate [17]. Additionally, the DEC content decreased while ethanol content increased at 7 h in the reaction system, illustrating that prolonging the reaction time can promote the decomposition of DEC. Since acetaldehyde was detected in the reaction solution of DEC and lead oxide at the reaction time of 3 h, we suggest that the reaction between DEC and PbO takes place as follows:

$$(C_2H_5O)_2CO + PbO \longrightarrow C_2H_4 + CH_3CHO + CO_2 + H_2O + Pb \quad (1)$$

As mentioned above, ethanol, diethylether, ethylacetate, and hydrogen were detected in the reaction between DEC and lead oxide. We assume that ethanol can be formed by the decomposition of DEC [18], and the intermolecular dehydration of ethanol can generate diethylether [19]. Ethylacetate and hydrogen can be formed by the dehydrogenation of ethanol [20], and ethylacetate can be also produced via the Tishchenko reaction of acetaldehyde [17], as shown in the following equations:

$$(C_2H_5O)_2CO \longrightarrow C_2H_4 + C_2H_5OH + CO_2 \quad (2)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \quad (3)$$

$$2C_2H_5OH \longrightarrow CH_3COOC_2H_5 + 2H_2 \quad (4)$$

$$2CH_3CHO \longrightarrow CH_3COOC_2H_5 \quad (5)$$

In summary, the lead oxide catalyst displayed excellent stability. The recovered catalyst was found to be a mixture of cubic metal Pb and orthorhombic PbO_2, indicating that the synergistic action between them is responsible for the high catalytic activity observed. Furthermore, tetragonal PbO promoted the decomposition of DEC to ethanol, ethylene, and carbon dioxide, and PbO itself was simultaneously reduced to metal Pb. The catalytic mechanism of cubic metal Pb and orthorhombic PbO_2 in the synthesis of DEC from EC and ethanol is currently under investigation.

References

1 Muskat I E, Strain F. US 2 379 250. 1941

2 Frevel L K, Gilpin J A. US 3 642 858. 1972

3 Wang M, Zhao X Q, An H L, Wang Y J. *J Chem Eng Chin Univ*, 2010, **24**: 663

4 Fenton D M. US 3 227 740. 1966

5 Zhang P B, Huang S Y, Yang Y, Meng Q S, Wang S P, Ma X B. *Catal Today*, 2010, **149**: 202

6 Zhu D J, Mei F M, Chen L J, Mo W L, Li T , Li G X. *Fuel*, 2011, **90**: 2098

7 Zhang P B , Ma X B. *Chem Eng J*, 2010, **163**: 93

8 Ma X B, Huang Sh Y, Wang Sh P, Zhang P B. *Petrochem Technol*, 2010, **39**: 697

9 Gasc F, Thieloaud-Roux S, Moulougui Z. *J Supercrit Fluids*, 2009, **50**: 46

10 Wang D P, Yang B L, Zhai X W, Zhou L G. *Fuel Process Technol*, 2007, **88**: 807

11 Zhao W B, Wang F, Peng W C, Zhao N, Li J P, Xiao F K, Wei W, Sun Y H. *Ind Eng Chem Res*, 2008, **47**: 5913

12 Wu C C, Zhao X Q, Wang Y J. *Catal Commun*, 2005, **6**: 694

13 Wang D F, Zhang X L, Gao Y Y, Xiao F K, Wei W, Sun Y H. *Catal Commun*, 2010, **11**: 430

14 Wang D F, Zhang X L, Zhao W B, Peng W C, Zhao N, Xiao F K, Wei W, Sun Y H. *J Phys Chem Solids*, 2010, **71**: 427

15 Zhao W B, Peng W C, Wang D F, Zhao N, Li J P, Xiao F K, Wei W, Sun Y H. *Catal Commun*, 2009, **10**: 655

16 Zhao H L, Zhao X Q, An H L, Wang Y J. *Petrochem Technol*, 2009, **38**: 139

17 Idriss H, Seebauer E G. *J Mol Catal*, 2000, **152**: 201

18 Notario R, Quijano J, Sánchez C, Vélez E. *J Phys Org Chem*, 2005, **18**: 134

19 Varisli D, Dogu T, Dogu G. *Chem Eng Sci*, 2007, **62**: 5349

20 Inui K, Kurabayashi T, Sato S, Ichikawa N. *J Mol Catal*, 2004, **216**: 147