

# ZnCl<sub>2</sub>/phosphonium halide: An efficient Lewis acid/base catalyst for the synthesis of cyclic carbonate

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## Abstract

An efficient Lewis acid/base catalyst composed of ZnCl<sub>2</sub> and phosphonium halide ([PR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>]<sup>+</sup>X<sup>-</sup>; X = Cl, Br, I) was developed and showed high activity and selectivity for the coupling reaction of CO<sub>2</sub> and epoxide under the mild conditions. The effects of reaction temperature, CO<sub>2</sub> pressure, various compositions of the catalysts have been investigated systematically. It was found that a 96.0% conversion of propylene oxide (PO) and high turnover frequency (TOF) value (4718.4 h<sup>-1</sup>) could be achieved in the presence of ZnCl<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (molar ratio = 1:6) at a low constant pressure of CO<sub>2</sub> (1.5 MPa) and mild temperature (120 °C) without any organic solvents, the catalyst was also proved to be applicable to other terminal epoxides. Additionally, the catalyst could be reused with little loss of catalytic activity after five times.

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**Keywords:** Chemical fixation; Carbon dioxide; Carbonates; Ionic liquids; Synthesis

## 1. Introduction

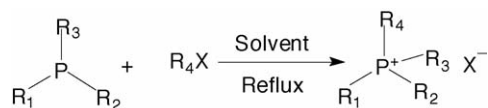
In recent years, much attention has been paid to the chemical fixation of carbon dioxide (CO<sub>2</sub>) because it is one of the greenhouse gases and is also recognized to be a naturally abundant, cheap, recyclable and non-toxic carbon source [1,2]. As one of the effective routes for chemical fixation of CO<sub>2</sub>, the synthesis of cyclic carbonates by the coupling reactions of epoxides and CO<sub>2</sub> has been extensively investigated [3–7].

Various catalysts such as alkali metal halides [8–11], metal oxides [12–15], transition-metal complexes [16–23], organic bases [24–26], porphyrin [27], zeolite [28–29], titanosilicates [22], smectites [30,31], and so on, have been studied. However, there are still some disadvantages such as high temperature, long reaction time, high CO<sub>2</sub> pressure, low turnover frequency (TOF) value, and/or toxic organic solvents, which should be solved before development and design of an industrial process. Recently, there are a number of researches concerning the appli-

cation of ionic liquids (ILs) as the catalyst, co-catalyst, activator, a new ligand, and/or solvent [32–43]. In 2001 [C<sub>4</sub>-mim]BF<sub>4</sub> ionic liquid was reported to be used as the catalyst for the synthesis of propylene carbonate (PC) [44], then, further researches [45] found that the addition of ZnCl<sub>2</sub> into [C<sub>4</sub>-mim]Br could show higher activity, while the TOF value was not satisfied (2717.0 h<sup>-1</sup>) yet. Moreover, the imidazolium halide and zinc halide could make the zinc tetrahalide complexes, which might be responsible for the decomposition of ethylene carbonate (EC) during the distillation process [46]. Kossev et al. [47] studied the CaCl<sub>2</sub>/triethylbenzylammonium chloride (TEBAC1) catalytic system, while the reaction temperature and pressure were high (170 °C, 4.0 MPa). Therefore, development of a highly efficient and environmentally benign catalytic system still remains a challenge for chemical fixation of CO<sub>2</sub> with epoxides under mild conditions.

From the previous researches [42–47], it was understood that the combination of Lewis base (such as imidazolium or ammonium halides) and Lewis acid (zinc halide) could show high catalytic activity for the coupling reaction between CO<sub>2</sub> and epoxide. Comparing with the ammonium halides ([NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>]<sup>+</sup>X<sup>-</sup>; X = Cl, Br, I), phosphonium halides are

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Scheme 1.

more thermally stable [48–50], and comparing with imidazolium halides, they were separated conveniently from the products due to their little potential interaction with the products [51]. Therefore, zinc halide/phosphonium halide catalytic systems were proposed and systematically investigated for the coupling reaction between epoxide and CO<sub>2</sub> in this work.

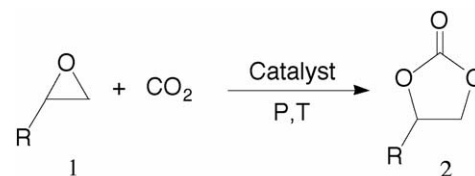
## 2. Experimental

### 2.1. Chemicals

PO, alkyl halides, ZnO, ZnCl<sub>2</sub> and other metal salts were supplied by Beijing Chemical Reagent Company. Other epoxides were purchased from J&K CHEMICA Company. All the chemicals were of analytical reagent grade and were used without further purification. CO<sub>2</sub> (>99.95%) was purchased from Beijing Analytical Instrument Factory.

### 2.2. Synthesis of phosphonium halides ([PR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>]<sup>+</sup>X<sup>-</sup>)

The phosphonium halides were synthesized according to the procedure in the literature [52–53], and the typical synthesis procedure is presented as Scheme 1. The mixture was refluxed for 24–48 h under a nitrogen atmosphere, then filtered



Scheme 2.

and washed three times with ethyl acetate. Finally, it was stripped under the vacuum condition at 60–90 °C in order to remove any volatile components in the product. The synthesized phosphonium halide was a white solid or yellow liquid with about 80.0%–93.0% yield.

### 2.3. Cycloaddition procedure

The reaction equation between CO<sub>2</sub> and epoxide to synthesize cyclic carbonate is shown in Scheme 2. All the coupling reactions were conducted in a 100 ml stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. A typical procedure was as follows: an appropriate amount of catalyst and PO was charged into the reactor without any solvent, stirred, and heated to a specified reaction temperature. Then CO<sub>2</sub> was charged into the reactor and the pressure of CO<sub>2</sub> was held constantly by means of a CO<sub>2</sub> reservoir connected to the reactor. After the proper reaction time, it was cooled to ambient temperature, and the remaining CO<sub>2</sub> was removed using an aspirator and absorbed in the saturation solution of Na<sub>2</sub>CO<sub>3</sub>. The propylene carbonate (PC) was distilled as a colorless liquid under reduce pressure, leaving the catalyst, which

Table 1  
Effects of different catalytic systems on the coupling reaction of CO<sub>2</sub> and PO<sup>a</sup>

Entry	Catalytic system	Yield (%)	Selectivity (%)	TOF (h <sup>-1</sup> ) <sup>d</sup>
1	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	96.0	>99.0	4718.4
2	ZnCl <sub>2</sub> /PPh <sub>3</sub> /C <sub>6</sub> H <sub>13</sub> Br	Trace	–	–
3	ZnCl <sub>2</sub> /PPh <sub>3</sub>	Trace	–	–
4 <sup>b</sup>	ZnCl <sub>2</sub> /KBr	Trace	–	–
5	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>2</sub> H <sub>5</sub> Br	93.0	>99.0	4570.9
6	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>4</sub> H <sub>9</sub> Br	95.0	>99.0	4669.2
7	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>8</sub> H <sub>17</sub> Br	97.1	>99.0	4767.5
8	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>10</sub> H <sub>21</sub> Br	98.5	>99.0	4841.2
9	ZnCl <sub>2</sub> /P(Bu) <sub>4</sub> Br	79.0	>99.0	3882.8
10	ZnCl <sub>2</sub> /PPh <sub>3</sub> iso-C <sub>4</sub> H <sub>9</sub> Br	94.2	>99.0	4629.8
11	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>3</sub> H <sub>7</sub> Cl	65.0	>99.0	3194.7
12	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>4</sub> H <sub>9</sub> Cl	67.0	>99.0	3293.1
13	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>5</sub> H <sub>11</sub> Cl	70.0	>99.0	3440.5
14	ZnCl <sub>2</sub> /PPh <sub>3</sub> C <sub>4</sub> H <sub>9</sub> I	95.1	>99.0	4674.1
15	ZnCl <sub>2</sub> /P(Bu) <sub>3</sub> C <sub>14</sub> H <sub>29</sub> Cl	75.2	>99.0	3696.1
16	ZnSO <sub>4</sub> /PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	60.0	>99.0	2949.0
17	Zn(Ac) <sub>2</sub> /PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	67.1	>99.0	3298.0
18	Zn(NO <sub>3</sub> ) <sub>2</sub> /PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	86.9	>98.0	4271.1
19 <sup>c</sup>	KI/ZnO/PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	29.5	>99.0	1449.9
20	KBr/ZnO/PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	21.6	>99.0	1059.3
21	KCl/ZnO/PPh <sub>3</sub> C <sub>6</sub> H <sub>13</sub> Br	10.0	>99.0	490.4

<sup>a</sup> Reaction conditions: PO (20.0 ml at 25 °C, 0.29 mol); Ionic liquid (0.35 mmol); Zinc salt (0.058 mmol); Temperature: 120 °C; CO<sub>2</sub> Pressure: 1.5 MPa; Reaction time: 1 h.

<sup>b</sup> KBr (0.35 mmol).

<sup>c</sup> KI (0.116 mmol); ZnO (0.058 mmol).

<sup>d</sup> Moles of PC/moles of ZnCl<sub>2</sub>/hour.

was further recycled. The analyses were conducted by Agilent 6890/5973 GC-MS with chemstation containing a NIST Mass Spectral Database.

### 3. Results and discussion

#### 3.1. Synthesis of PC in the presence of phosphonium halides

##### 3.1.1. Effect of various catalytic systems

The effects of different phosphonium halides on the formation of PC were investigated, and the results are summarized in Table 1.

It can be seen that 96.0% conversion and >99.0% selectivity were obtained when ZnCl<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br catalytic system was used, and the corresponding TOF value was larger than 4690.0 h<sup>-1</sup> (Table 1, entry 1) under the mild conditions (120 °C, 1.5 MPa, 1 h), while the yield was unsatisfied with ZnCl<sub>2</sub>/PPh<sub>3</sub>/C<sub>6</sub>H<sub>13</sub>Br, ZnCl<sub>2</sub>/PPh<sub>3</sub>, and/or ZnCl<sub>2</sub>/KBr catalytic system (Table 1, entries 2–4). The activity of phosphonium halides were affected by their structure, which probably influences the behavior of anions, we tested a possible role exerted by the cations on this reaction. It was found that the catalytic activity increased with the phosphonium cations molecular weight increasing ([PPh<sub>3</sub>C<sub>n</sub>H<sub>2n+1</sub>]<sup>+</sup>, n = 2–10, entries 1, 5–8, 11–13), and the selectivity kept about 99% for all the cases. The possible reason may be that the nucleophilic attack of halide anion on the PO is accelerated by the less electrostatic interaction between the halide anion and the larger phosphonium cation. With different halide ions (entries 6, 12, 14), the activity varied in the order: I<sup>-</sup> ≥ Br<sup>-</sup> > Cl<sup>-</sup>. A possible reason was that I<sup>-</sup> ion locates away from cation more easily than Br<sup>-</sup> and Cl<sup>-</sup>.

In order to investigate the effect of the different zinc combination on the catalytic activity, the other catalysts, such as ZnSO<sub>4</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br, KI/ZnO/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br, and so on, were also studied. The results are presented in Table 1 (entries 16–21). It is obvious that Zn(NO<sub>3</sub>)<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br catalyst could also show high catalytic activity (yield > 86.0%) under the mild conditions, while the others did not.

##### 3.1.2. Effect of the composition of the catalytic systems

The influence of the composition of the catalytic system on the reaction was demonstrated by the dependence of the yield of PC on the molar ratio of ZnCl<sub>2</sub>: PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br. The mole of ZnCl<sub>2</sub> of the catalytic system was kept constant while that of the other one varied. The corresponding results are summarized in Table 2. Almost no activity was observed with ZnCl<sub>2</sub> alone (Table 2, entry 1). However, the combination of ZnCl<sub>2</sub> and PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br resulted in surprisingly high activity. With the increasing quantity of the PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br, the yield of PC was sharply increased until the molar ratio of the ZnCl<sub>2</sub>: PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br was 1:6.

The experiments about the dependence of the PC yield on varying of ZnCl<sub>2</sub> amount (from 0 to 0.35 mmol) were also carried out in the presence of PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol). As shown in Fig. 1, PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br itself gave a low yield (15.4%), while the presence of ZnCl<sub>2</sub> enhanced the activity of PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br to

Table 2

Effects of the molar ratio of ZnCl<sub>2</sub> to PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br on the coupling reaction of CO<sub>2</sub> and PO to synthesize PC<sup>a</sup>

Entry	Ratio <sup>b</sup>	Yield (%)	Selectivity (%)	TOF (h <sup>-1</sup> ) <sup>c</sup>
1 <sup>d</sup>	∞	Trace	–	–
2	1:2	72.0	>99.0	3538.8
3	1:4	87.2	>99.0	4285.9
4	1:6	96.0	>99.0	4718.4
5	1:8	97.0	>99.0	4767.6

<sup>a</sup> Reaction conditions: PO (0.29 mol); ZnCl<sub>2</sub> (0.058 mmol); Temperature: 120 °C; CO<sub>2</sub> Pressure: 1.5 MPa; Reaction time: 1 h.

<sup>b</sup> The molar ratio of ZnCl<sub>2</sub>/ PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br.

<sup>c</sup> Moles of PC/moles of ZnCl<sub>2</sub>/hour.

<sup>d</sup> Without PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br.

a very great extent (84.0%). Surprisingly, another great change was taken place (PC yield, from 84.0% to 96.0%) when the molar ratio of ZnCl<sub>2</sub>: PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br was increased from 1:10 to 1:6. But, the TOF value was decreased sharply with the increasing amount of ZnCl<sub>2</sub>.

So the optimum molar ratio of ZnCl<sub>2</sub>: PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br was kept about 1:6 (ZnCl<sub>2</sub>: 0.058 mmol, PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br: 0.35 mmol), at which the higher TOF value (>4690.0 h<sup>-1</sup>) and high PC yield (96.0%) were obtained.

From the previous researches [13,17,20,41–43,46–47] and the experimental results, a possible mechanism was illustrated in Scheme 3.

It showed that the Lewis acid (ZnCl<sub>2</sub>) and Lewis base (phosphonium halide) might coordinately attack the different parts of epoxide firstly. The coordination of the zinc atom with the oxygen atom of epoxide through a donor–acceptor bond resulted in the polarization of C–O bonds, and the halide anion generated from the phosphonium halide, made the nucleophilic attack on the little bulkiness β-carbon atom of the epoxide at the same time. As a result, the ring of the epoxide was opened easily (step 1). Then, the interaction was occurred between the oxygen anion and CO<sub>2</sub>, and the alkylcarbonate anion was formed that would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step (step 2). Further

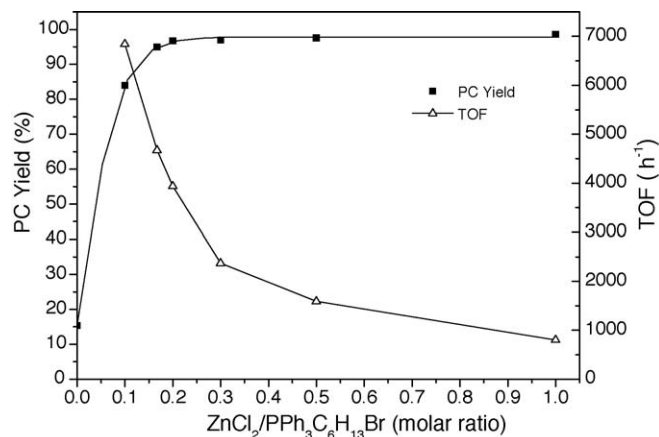
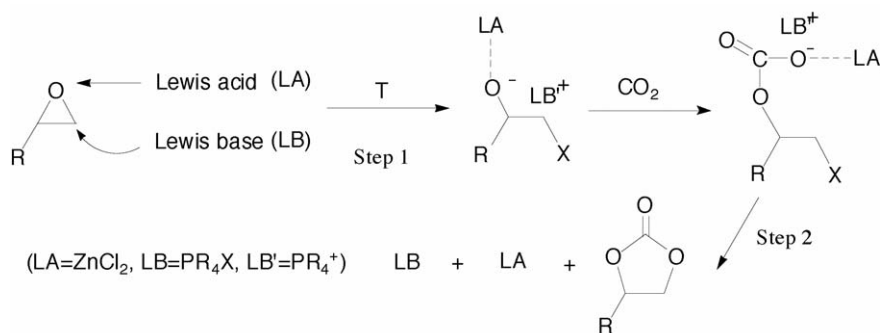


Fig. 1. The PC yields versus the molar ratio of ZnCl<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br. Reaction conditions: PO (0.29 mol); PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol); Temperature: 120 °C; CO<sub>2</sub> Pressure: 1.5 MPa; Reaction time: 1 h.



Scheme 3.

research on the reaction mechanism is now undergoing in our laboratory.

### 3.1.3. Effect of reaction conditions

As shown in Fig. 2, the temperature had a pronounced positive effect on the coupling reaction when the temperature varied from 80 to 130 °C. The increasing rate of the PC yield was largest with temperature increasing from 90 to 100 °C. When the reaction was carried out at 80 °C or 90 °C, a dissatisfaction yield was given even though the reaction pressure was reached higher up to 2.0 MPa. For the continuous enhancement of the temperature gave only a slight increase in activity of the catalytic system, the optimum temperature was 120 °C, at which a satisfaction yield and a high TOF value were obtained.

Fig. 3 shows the dependence of the yield of PC on reaction pressure with a reaction time of 1 h. It can be observed that the higher yield of PC was achieved when the pressure was higher. This is possible because the higher pressure can improve the concentration of CO<sub>2</sub> in liquid and the communication between the gas–liquid two phases, and make the equilibrium of the reaction is shift towards the resulting carbonate, by which the conversion of PO was increased accordingly. Comparing to temperature, the effect of the pressure was quite moderate. It is obvious that nearly no change of the PC yield had been taken place even

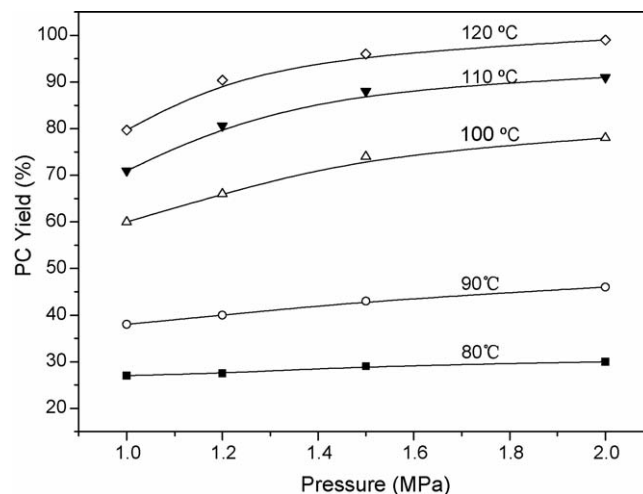


Fig. 3. Effect of pressure on the reaction results at different temperature from 80 to 120 °C. Reaction conditions: PO (0.29 mol); ZnCl<sub>2</sub> (0.058 mmol); PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol); Reaction time: 1 h.

though the pressure was enhanced from 1.0 to 2.0 MPa when the reaction was carried out at 80 or 90 °C. In order to obtain a satisfaction yield of the product under mild conditions, 1.5 MPa was suitable to operate.

### 3.2. Synthesis of cyclic carbonates via CO<sub>2</sub> cycloaddition to other epoxides

Under the optimized reaction conditions, the experiments of other terminal epoxides with CO<sub>2</sub> to synthesize the corresponding cyclic carbonates were also investigated. The results are summarized in Table 3. It was found that the catalytic system was also applicable to other terminal epoxides with high TOF value (3000.0 h<sup>-1</sup>) and >99.0% selectivity.

### 3.3. Recycling experiments

A series of reaction cycles were run in order to investigate the stability of the catalytic system. In each cycle, the catalytic system was separated by filtration under vacuum, and then used directly for the next experiment. The results were presented in Table 4, it can be found that this catalytic system can be reusable for at least five times with slight loss of activity, while the selectivity remains almost the same.

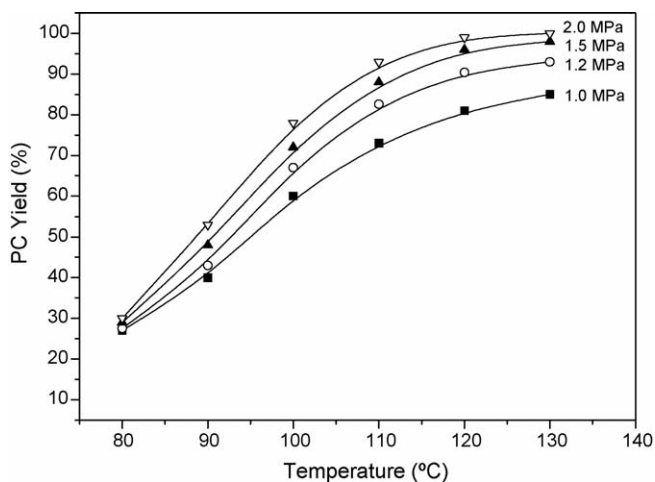
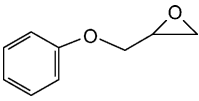
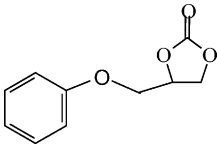
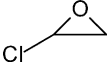
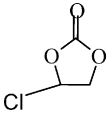
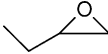
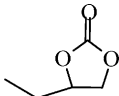

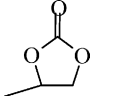
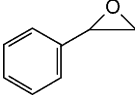
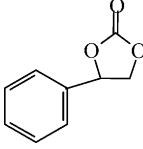
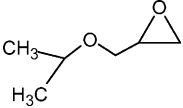
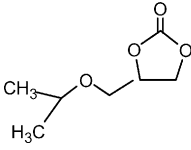


Fig. 2. Temperatures effect on the PC yields at different pressures. Reaction conditions: PO (0.29 mol); ZnCl<sub>2</sub> (0.058 mmol); PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol); Reaction time: 1 h.

Table 3  
Coupling reaction of CO<sub>2</sub> and various epoxides to synthesize cyclic carbonates<sup>a</sup>

Entry	Substrate	Product	Yield (%)	Selectivity (%)	TOF (h <sup>-1</sup> ) <sup>b</sup>
1			95.0	>99.0	2421.5
2			85.0	>99.0	3386.0
3			93.0	>99.0	3691.3
4			96.0	>99.0	4718.4
5			81.0	>99.0	2464.2
6			96.0	>99.0	2619.4

<sup>a</sup> Reaction conditions: Substrate (20.0 ml at 25 °C); ZnCl<sub>2</sub> (0.058 mmol); PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol); Temperature: 120 °C; CO<sub>2</sub> Pressure: 1.5 MPa; Reaction time: 1 h.

<sup>b</sup> Moles of cyclic carbonate/moles of ZnCl<sub>2</sub>/hour.

Table 4  
Investigation of catalyst recycle in coupling reaction of CO<sub>2</sub> and PO<sup>a</sup>

Entry	Recycle	Yield (%)	Selectivity (%)	TOF (h <sup>-1</sup> ) <sup>b</sup>
1	Fresh	96.0	>99.0	4718.4
2	1	95.5	>99.0	4693.8
3	2	95.0	>99.0	4669.3
4	3	94.7	>99.0	4654.5
5	4	94.5	>99.0	4644.7
6	5	94.3	>99.0	4634.8

<sup>a</sup> Reaction conditions: PO (0.29 mol); ZnCl<sub>2</sub> (0.058 mmol); PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (0.35 mmol); Temperature: 120 °C; CO<sub>2</sub> Pressure: 1.5 MPa; Reaction time: 1 h.

<sup>b</sup> Moles of PC/moles of ZnCl<sub>2</sub>/hour.

#### 4. Conclusions

The efficient Lewis acid/base catalytic system composed of ZnCl<sub>2</sub> and phosphonium halides ([PR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>]<sup>+</sup>X<sup>-</sup>; X = Cl, Br, I) was developed for the coupling reaction between epoxide and CO<sub>2</sub>. It was found that high conversion, more than 99.0% selectivity, and high TOF value could be achieved in the presence of ZnCl<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br (molar ratio = 1:6) for the synthesis of cyclic carbonates under the mild conditions (120 °C, 1.5 MPa, and 1 h). As to the efficient activity, and excellent stability of the ZnCl<sub>2</sub>/PPh<sub>3</sub>C<sub>6</sub>H<sub>13</sub>Br catalytic system, it could be considered as a potential industrial catalyst for the large-scale synthesis of cyclic carbonates.

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