



# Reusable and efficient polymer-supported task-specific ionic liquid catalyst for cycloaddition of epoxide with CO<sub>2</sub>

Jian Sun<sup>a,b</sup>, Weiguo Cheng<sup>a</sup>, Wei Fan<sup>c</sup>, Yaohong Wang<sup>a,b</sup>, Zhenying Meng<sup>a,b</sup>, Suojian Zhang<sup>a,\*</sup>

<sup>a</sup>State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, No. 1 Beier Tiao, Zhongguancun, Beijing 100190, PR China

<sup>b</sup>Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

<sup>c</sup>College of Chemical Engineering, Kaifeng University, Kaifeng 475004, PR China

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## ABSTRACT

1-(2-Hydroxyl-ethyl)-imidazolium-based ionic liquids (HEIMX, X = Cl, Br, I), which have both acidic and basic characteristics, were covalently anchored onto a highly cross-linked polystyrene resin. The catalytic activity of these heterogeneous catalysts for the synthesis of cyclic carbonates via cycloaddition reaction of CO<sub>2</sub> with epoxides was studied. The effects of parameters, such as anions of the catalysts, reaction temperature, pressure, reaction time, and the amount of catalyst used, on the reaction were also investigated. It was demonstrated that the hydroxyl group in the catalyst had synergetic effect with the halide anion. As a result, high yield (80–99%) and excellent selectivity (92–99%) of cyclic carbonates could be achieved at mild conditions (2.5 MPa, 120 °C and 4 h) without any co-solvent. In addition, the catalyst recycle test showed that the supported catalyst could be reused for as many as six times without loss of catalytic activity.

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## 1. Introduction

It has been well recognized that the efficient transformation of harmful wastes such as CO<sub>2</sub> into useful chemicals is an important contribution from the viewpoint of environmental protection and resource utilization [1]. In this respect, the CO<sub>2</sub> fixation reaction with epoxide to produce cyclic carbonates (Scheme 1), raw materials for polycarbonate and fine chemical intermediates, has received increasing attention recently [2].

Various heterogeneous catalysts [3–11] including heterogenization of ionic liquids (ILs) [12–19], have been widely developed for cycloaddition of epoxide with CO<sub>2</sub> to produce cyclic carbonate due to the facilitative catalyst separation. These catalysts can be found such as metal oxide [3,4], ion-exchange resin-supported gold nanoparticle [11], *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> [16], choline chloride-urea/molecular sieve [17], p([EVIm]<sub>2</sub>ZnBr<sub>2</sub>Cl<sub>2</sub>) [20], p([VBIM]Cl) [21], and CS-NMe<sub>3</sub>Cl [22]. However, unsatisfactory activities, high cost, low water/thermal stabilities of catalysts as well as the requirement of organic solvent (DMF, toluene or CH<sub>2</sub>Cl<sub>2</sub>) are still the disadvantages needed to be overcome. Additionally, to the best of our knowledge, immobilization of functionalized ILs to catalyze this reaction has not been received much attention up till now.

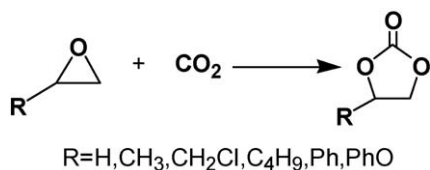
Being cheap, separable and easily surface-modified, polymeric materials are widely used substituting for silica in catalytic reactions [23–29]. However, the activities of polymer-supported ILs for the preparation of cyclic carbonate are needed to be improved [30]. In the continuous line of our study to develop recyclable catalysts with high performance for this reaction [31–33], we have found that hydroxyl-functionalized imidazolium-based ionic liquids (Scheme 2a) [32], which have both acidic and basic characteristics, are effective for CO<sub>2</sub> cycloaddition and can be easily chemically immobilized on polystyrene resin through covalent bonds. Herein, we highlight the use of high cross-linked polymeric material as support, and developed the polymer-supported 1-(2-hydroxyl-ethyl)-imidazolium-based ionic liquids (PS-HEIMX, X = Br, Cl) for the synthesis of cyclic carbonate (Scheme 2b). The catalytic performance of this kind of heterogeneous catalysts for cycloaddition of CO<sub>2</sub> to epoxide was investigated.

## 2. Experimental

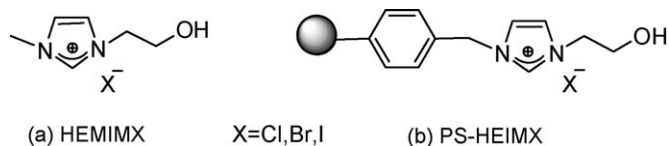
### 2.1. Chemical reagents

Highly cross-linked chloromethylated polystyrene (CPS) (D301, 18–19% Cl content and 6% cross-linked with divinylbenzene) was received as a gift from Jiangsu Suqing Water Treatment Co., Ltd. (China). CO<sub>2</sub> was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Propylene oxide, ethylene oxide and epichlorohydrin, all A.R. grade, were produced by Beijing Chemical

\* Corresponding author. Tel.: +86 10 8262 7080; fax: +86 10 8262 7080.  
E-mail address: [sjzhang@home.ipe.ac.cn](mailto:sjzhang@home.ipe.ac.cn) (S. Zhang).



**Scheme 1.** Cycloaddition of epoxide with  $\text{CO}_2$  to produce cyclic carbonates.



**Scheme 2.** Structure of hydroxyl-functionalized ionic liquids (a) and polymer-supported hydroxyl-functionalized ionic liquids (b).

Plant. Other epoxides were purchased from Alfa Aesar China Co., Ltd. Styrene oxide was purified by distillation and other chemicals were used as received.

## 2.2. Polymer-supported ionic liquids preparation and characterization

The routes to synthesize the polymer-supported ionic liquids (PSILs) are shown in Schemes 3 and 4. Polymer-supported imidazole (PS-IM) was first prepared according to the following procedure (Scheme 3). A mixture of CPS (10.0 g, 53.4 mmol), imidazole (53.5 mmol) and acetonitrile (70 mL) was heated at  $80^\circ\text{C}$  for 24 h in a 125 mL three-necked flask. After cooled down to room temperature, the solid residue was collected by filtration and washed separately with ethyl acetate, 0.1 mol/L HCl, water and methanol. Then, the solid was dried under vacuum at  $60^\circ\text{C}$  for 12 h to give PS-IM a 98% yield. The loading of imidazole attached on the CPS was about 5.3 mmol/g determined by nitrogen content from elementary analysis.

Secondly, PSILs were prepared from PS-IM and the corresponding halide substituted alcohols. In a typical preparation, 2-bromide alcohol (54.0 mmol), PS-IM (10.0 g) and acetonitrile (70 mL) were added into a 125 mL three-necked flask equipped with a magnetic stirrer, and was heated at  $80^\circ\text{C}$  for 24 h with vigorous stirring. After reaction, the reaction mixture was cooled down to room temperature. The top phase was poured off, and the solid residue

was washed with ethyl acetate three times. Then, the solid was dried under vacuum at  $60^\circ\text{C}$  for 12 h to give the polymer-supported 1-(2-hydroxyl-ethyl)-imidazolium bromide (PS-HEIMBr) (Scheme 4a). Based on the similar procedure, PS-HEIMI, PS-HEIMCl, and polymer-supported ethyl-imidazolium bromide (PS-EIMBr) were synthesized, respectively (Scheme 4b–d).

## 2.3. Characterization of polymer-supported ionic liquids

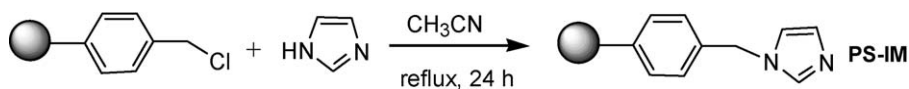
The amount of ionic liquid attached on the CPS was determined from elemental analysis (vario EL, Elementar Analysensysteme GmbH): PS-HEIMBr (loading, 3.2 mmol/g), PS-HEIMCl (loading, 3.1 mmol/g), PS-HEIMI (loading, 3.2 mmol/g), and PS-EIMBr (loading, 3.2 mmol/g). Thermogravimetric analysis (TGA) was performed using a TGA-50 (Shimadzu) in a nitrogen atmosphere between 25 and  $600^\circ\text{C}$  at a heating rate  $10^\circ\text{C}/\text{min}$ . Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 spectrophotometer with anhydrous KBr as standard (Thermo Electron Co.). The synthesized catalysts were pretreated by grinding before use.

## 2.4. Typical procedure for the synthesis of cyclic carbonate from epoxide and $\text{CO}_2$

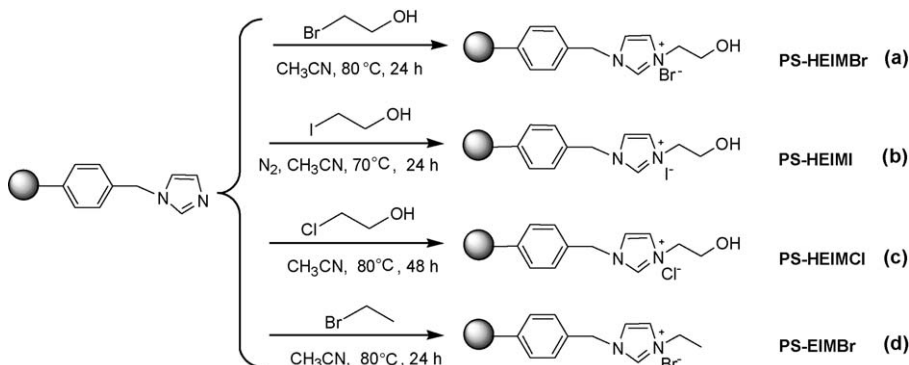
Experimental apparatus used for batch reaction was described in Scheme 5. All experiments were conducted in a 100 mL stainless-steel reactor equipped with a magnetic stirrer and an automatic temperature control system. The reactor was charged with known amounts of epoxide and an appropriate catalyst at room temperature, and then heated to a specified temperature with an addition of  $\text{CO}_2$  from a high-pressure reservoir tank to maintain a specified constant pressure for a desired time. After the reaction, the reactor was cooled to  $5^\circ\text{C}$  in an ice-water bath and  $\text{CO}_2$  was released slowly. The organic products were separated from the reaction mixture and analyzed by GC–MS and GC with acetophenone as the internal standard. Agilent 6890 GC was equipped with a flame ionization detector (FID) and a DB-624 column ( $30\text{ m} \times 0.53\text{ mm} \times 3\text{ }\mu\text{m}$ ).

## 2.5. Recycling experiment

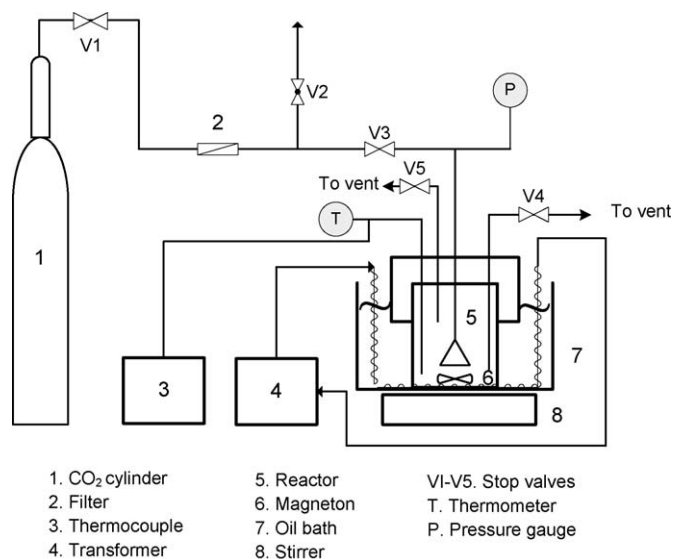
The reactor was charged with propylene oxide (PO) (0.10 mol) and PS-HEIMBr (0.5 g, 1.6 mol%). And then the reaction was performed at  $120^\circ\text{C}$  for 4 h under a  $\text{CO}_2$  pressure of 2.5 MPa. After reaction, the catalyst was recovered by filtration and washed with



**Scheme 3.** Synthesis of polymer-supported imidazole (PS-IM).



**Scheme 4.** Synthesis of polymer-supported ionic liquids (PSILs).



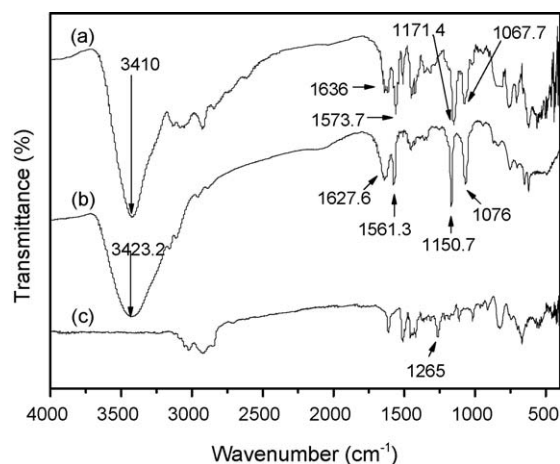
**Scheme 5.** Experimental apparatus used for batch reaction.

acetone for further used. The same procedure was repeated for the next five cycles.

### 3. Results and discussion

#### 3.1. Characterization of polymer-supported ionic liquids

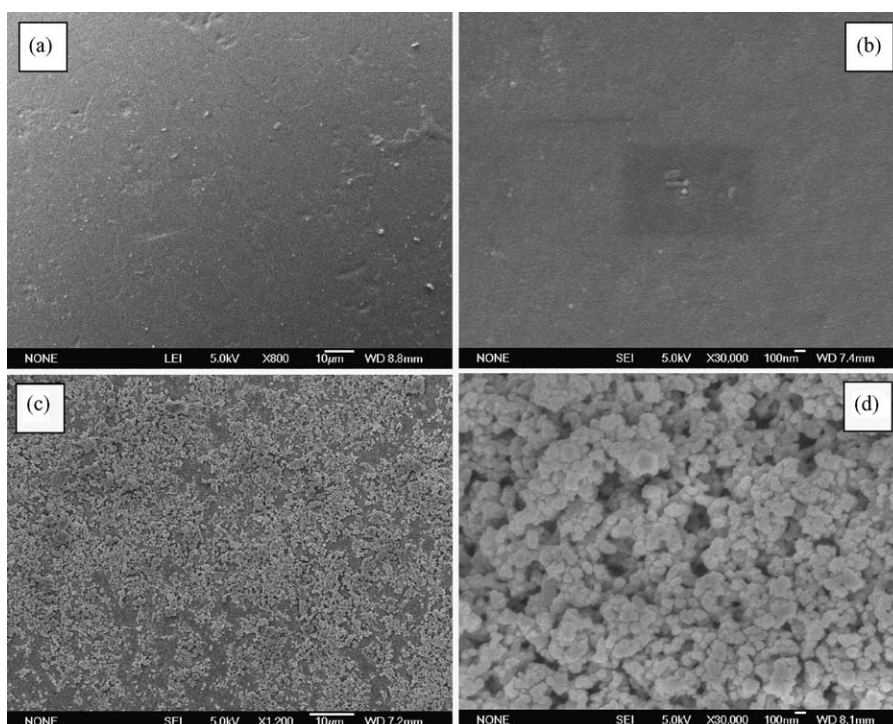
To confirm the immobilization of HEIMBr on a polymer, FT-IR spectroscopic studies were firstly carried out with PS-HEIMBr, support CPS and the active species HEIMBr. And the results were compared with those of the corresponding monomeric analogues. The samples were all dried over phosphorus pentoxide under vacuum at 70 °C for 48 h before detecting. Fig. 1a and b is the IR spectra of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide



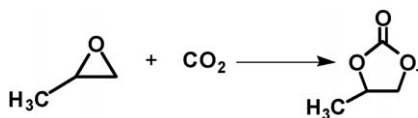
**Fig. 1.** FT-IR spectra comparison of the HEIMBr (a), PS-HEIMBr (b) and CPS (c).

(HEIMBr) and PS-HEIMBr, respectively. HEIMBr displays a typical strong peak corresponding to OH stretching frequency centered at about 3410  $\text{cm}^{-1}$ , and four typical peaks centered at 1067.7  $\text{cm}^{-1}$ , 1171.4  $\text{cm}^{-1}$ , 1573.7  $\text{cm}^{-1}$ , and 1636  $\text{cm}^{-1}$  associated with stretching frequencies of the imidazolium ring. When HEIMBr was immobilized on CPS, similar peaks corresponding to the ionic liquid can also be observed, but the discussed corresponding peaks shift to 3423.2  $\text{cm}^{-1}$ , 1076.0  $\text{cm}^{-1}$ , 1150.7  $\text{cm}^{-1}$ , 1561.3  $\text{cm}^{-1}$ , and 1627.6  $\text{cm}^{-1}$ , respectively, indicating the interactions of the ionic liquid and the support. As can be seen in Fig. 1, a typical peak centered at 1265  $\text{cm}^{-1}$  corresponding to the stretching frequency of the functional group  $-\text{CH}_2\text{Cl}$  disappears in the spectra of PS-HEIMBr (Fig. 1a), suggesting the complete modification of CPS. The above result is a clear indication of the chemical immobilization of the active catalyst on the support of CPS.

The morphology of the PS-HEIMBr and CPS was observed using scanning electron microscopy (SEM), and the images are shown in Fig. 2. CPS has a plain surface (a), while the supported-IL catalyst



**Fig. 2.** Scanning electron microscopy (SEM) images of CPS (a and b) and PS-HEIMBr (c and d).

**Table 1**Effect of various catalysts on the synthesis of propylene carbonate (PC)<sup>a</sup>

Entry	Catalyst	PO conversion (%)	Selectivity (%)
1 <sup>b</sup>	HEMIMBr	99	99
2 <sup>c</sup>	PS-HEIMBr	98	99
3	PS-EIMBr	64	99
4 <sup>d</sup>	PS-EIMBr/Ethanol	83	99
5	PS-IM	Trace	–
6	2-Bromide alcohol	4.0	99
7	Imidazole	Trace	–
8	CPS	Trace	–
9	PS-HEIMCl	59	99
10	PS-HEIMI	99	99
11 <sup>e</sup>	PS-HEIMBr	87	99

<sup>a</sup> Reaction conditions: PO (0.1 mol), catalyst (0.5 g, 1.6 mol%), 2.5 MPa CO<sub>2</sub>, 120 °C, 4 h.<sup>b</sup> HEMIMBr (1.6 mol%).<sup>c</sup> Grinding before use (particle size: 100 μm, 170–180 mesh).<sup>d</sup> Ethanol (1.6 mol%).<sup>e</sup> Using without grinding (particle size: 1 mm, 18 mesh).

has a rough surface (b). The sizes of the PS-HEIMBr particles are at the micrometer scale (170–180 mesh, 100 μm).

### 3.2. Activities of various catalysts for cycloaddition of CO<sub>2</sub> to PO

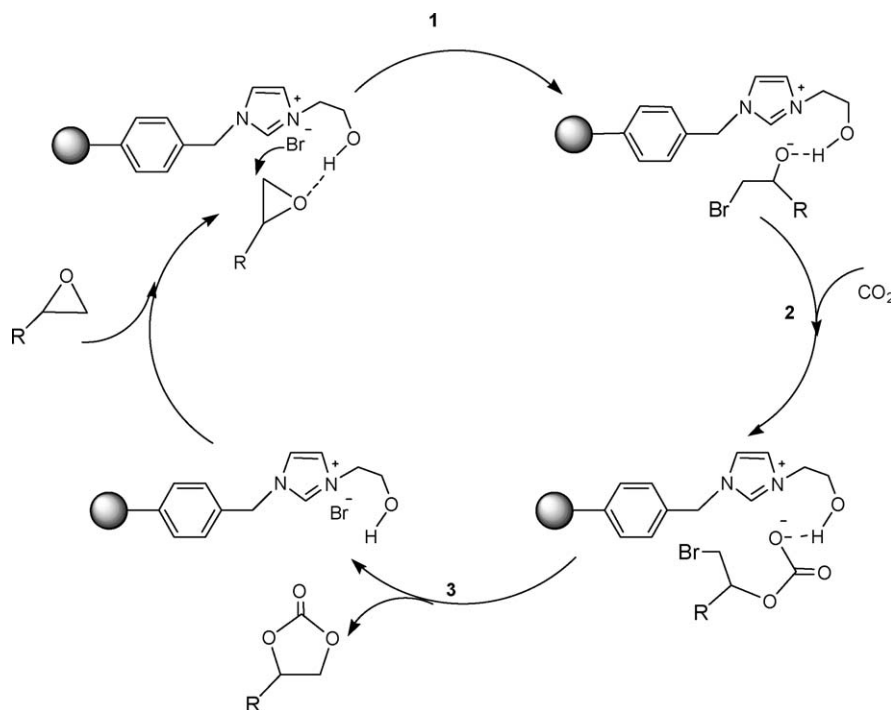
The activities of the prepared polymer-supported 1-(2-hydroxyl-ethyl)-imidazolium-based ionic liquids (PS-HEIMX, X = Cl, Br, and I) were first examined in cycloaddition reaction of CO<sub>2</sub> with propylene oxide (PO). And the corresponding results are presented in Table 1.

The catalytic activity of PS-HEIMBr (Table 1, entry 2) was comparable to that of the homogeneous ionic liquid catalyst, HEMIMBr (entry 1). The main reason for this was that miscibility of

the ionic liquid catalyst and the substrate was very poor, and IL phase could not be dispersed in the reaction system at the beginning which was observed in our experiments using the view cell. The inter-phase mass transfer reduced the reaction rate, while the PS-HEIMBr microparticles synthesized in this work could be well dispersed in the reaction mixture under stirring. Moreover, another advantage of the solid PS-HEIMBr was that it was insoluble in the product which was favorable with respect to the easy separation of the catalyst from the products, whereas the ionic liquid catalyst was soluble in the product. It was possibly because that the cross-linker DVB in the PSIL not only enhanced the activity but also prevented the dissolution of the catalyst [21].

The catalytic performance of PS-HEIMBr was also compared with the performance of polymer-supported 1-ethyl-3-methylimidazolium bromide (PS-EIMBr) and polymer-supported imidazole (PS-IM). As shown in Table 1, in the absence of OH group, the activity of PS-EIMBr in PC yield is much lower than that of PS-HEIMBr (entries 2 and 3). But, the activity of PS-EIMBr could be remarkably enhanced using ethanol as a co-catalyst (entry 4). Without OH group and Br anion, PS-IM is an ineffective catalyst as respected (entry 5). Almost no reactions occur by using 2-bromidethanol, imidazole, and polystyrene resin (CPS) (entries 6–8). The above results elucidated the respective roles of OH group and Br anion in PS-HEIMBr catalyst for accelerating the reaction [30,32]. As proposed in Scheme 6, the coordination of a H atom in the OH group with the O atom of the epoxide through a hydrogen bond resulted in the polarization of C–O bonds, and the Br anion made a nucleophilic attack on the less sterically hindered carbon atom of the epoxide at the same time, by which, the ring of the epoxide was opened easily. Then, the interaction occurred between the oxygen anion and CO<sub>2</sub>, forming an alkylcarbonate anion which would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step. From the viewpoint of exhibiting improved yield of PC, OH group could substitute for Lewis acid in some practical applications.

Notably, the catalytic activity among PS-HEIMX (X = Cl, Br, I) strongly depended on the anion. The order of activity was found to be PS-HEIMI ≈ PS-HEIMBr > PS-HEIMCl, which was in accord with

**Scheme 6.** A possible mechanism.

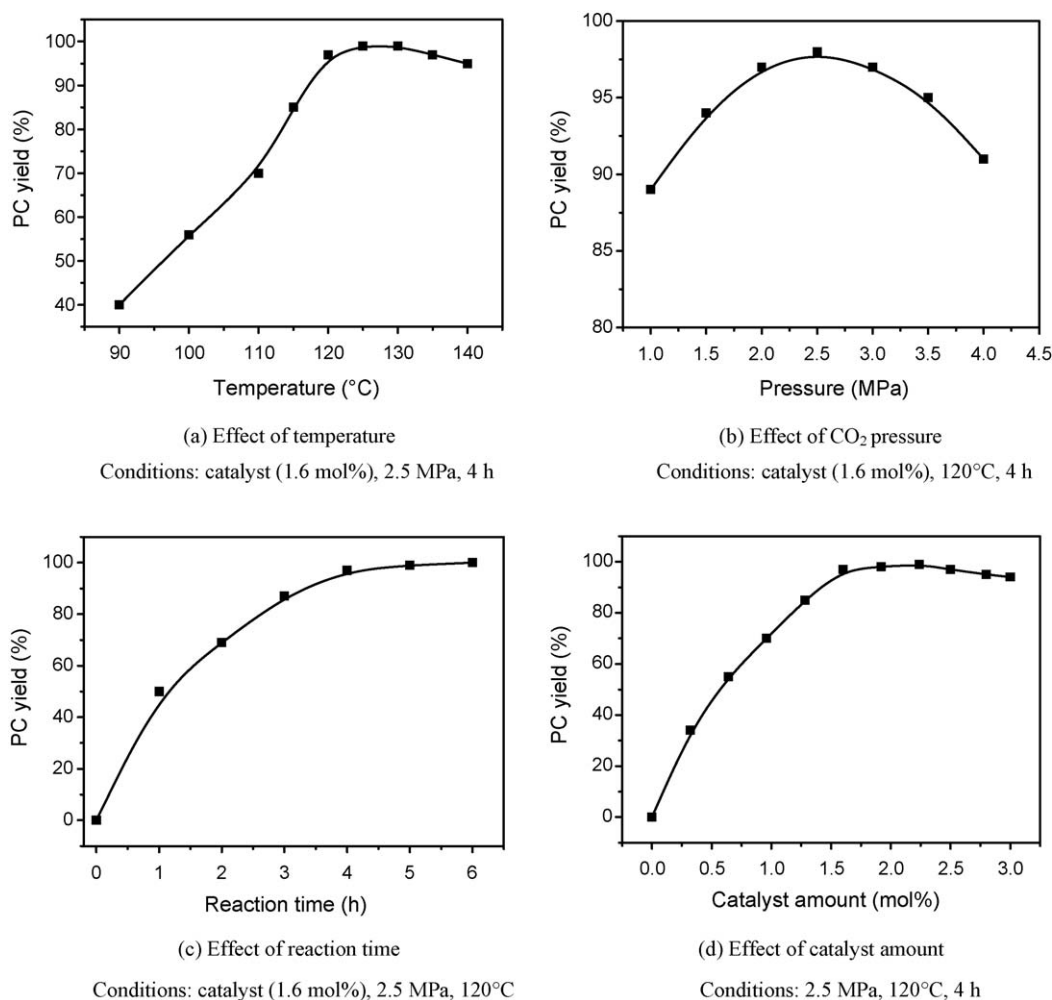


Fig. 3. Dependence of PC yields on different parameters catalyzed by PS-HEIMBr.

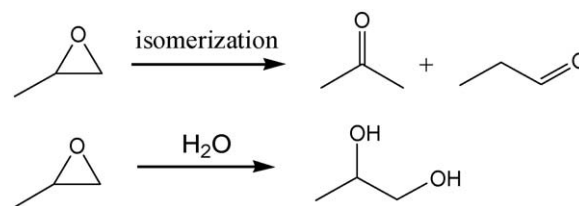
the order of nucleophilicity of the anions (entries 2, 9 and 10) [31,34]. Additionally, due to the possible strong hydrogen bond between the OH group and the chloride anion [36], PS-HEIMCl was much less reactive than PS-HEIMBr (entries 2 and 9). On the other hand, decreasing the particle size of PS-HEIMBr by grinding could enhance its activity (entries 2 and 11). Conclusively, due to the excellent activity and selectivity for the coupling reaction of PO and CO<sub>2</sub>, PS-HEIMBr was used for further investigation.

### 3.3. Influence of reaction conditions on the synthesis of propylene carbonate

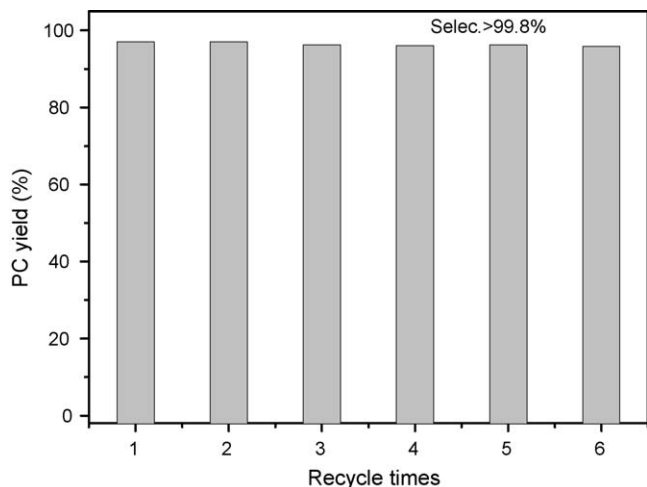
A significant drawback associated with using carbon dioxide as a reagent in organic synthesis is the potential dangers associated with operating at high temperatures and pressures, especially in the presence of heterogeneous catalytic system. So we investigated the dependencies of the yields of PC on the reaction conditions, especially temperatures and pressures of carbon dioxide. It is gratifying to discover that our catalyst system can operate very efficiently at mild conditions. As shown in Fig. 3(a), the reaction is very temperature-sensitive: with increasing temperature from 80 °C to 120 °C, PC yield varies remarkably, from below 30% to 98%. The continued increase of temperature beyond 120 °C up to 125 °C increases a little PO conversion. However, too high temperature would reduce PC yield though PO conversion remains >99%. The decrease of PC selectivity is plausibly a result of side reactions, such as PC polymerization [15], PO isomerization and the interaction between PO and water [16]

(Scheme 7). Therefore, 120 °C is considered suitable for the target reaction.

Because the diffusion may have an effect on the reaction kinetics in the mass transfer accompanied by chemical reactions between CO<sub>2</sub> and epoxide, there are optimum ranges of CO<sub>2</sub> pressure for the maximum conversion of PO [35]. In this work, the effect of CO<sub>2</sub> pressure on the yields of cyclic carbonates was studied at 120 °C with PS-HEIMBr as the catalyst, and the reaction time for PO was 4 h. Interestingly, an increase in CO<sub>2</sub> pressure resulted in a moderate increase in PC yield in the low-pressure region (1–3 MPa) but a decrease of yield in the high-pressure region (3–4.5 MPa) (Fig. 3(b)). Such an effect of CO<sub>2</sub> pressure on catalytic activity has been observed in other catalytic systems [15,16,21,26]. Based on these report, it could be explained that PC was in its liquid form under the adopted reaction conditions, and when the reaction was carried out in the low-pressure region, higher CO<sub>2</sub> pressure enhanced yield due to the higher CO<sub>2</sub> concentration in the liquid phase of the reaction system; but



Scheme 7. Possible side reactions.



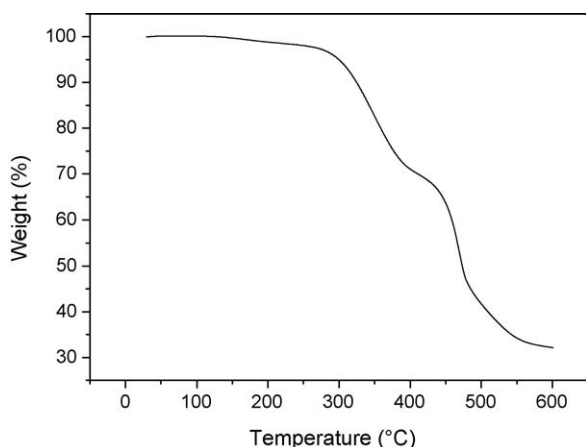
**Fig. 4.** Recycling experiments for PS-HEIMBr. Reaction conditions: PO (0.1 mol), PS-HEIMBr (1.6 mol%), 120 °C, 2.5 MPa CO<sub>2</sub>, 4 h

too high pressure would reduce PO conversion because of lowered PO concentration in the vicinity of the catalyst, a condition which was not favorable to the reaction because PO was also a reactant [21]. The competition of these opposite factors resulted in a maximum in the pressure versus yield curve. For better results, 2.5 MPa is chosen.

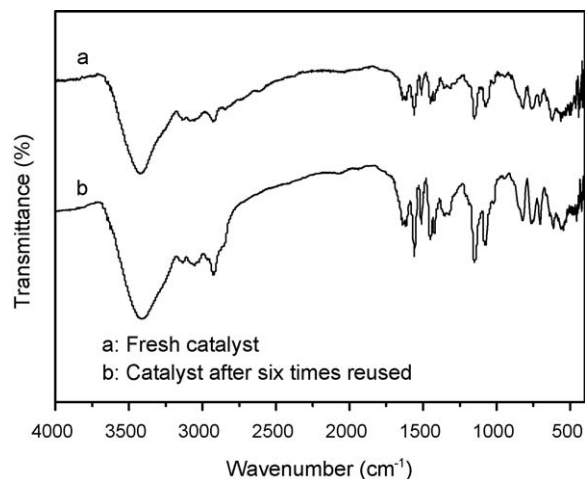
Fig. 3(c) shows that the yield of PC is very sensitive to reaction time: a 98% PO conversion could be realized in about 4 h at 120 °C and 2.5 MPa CO<sub>2</sub>. The reaction proceeds rapidly within first 3 h, and as high as 90% PO conversion could be obtained in 3 h. Prolonging reaction time beyond 4 h gives a little increase in PC yield indicating that 4 h is optimal. In all the experiments depicted in Fig. 3(c), the by-products were not detectable. As shown in Fig. 3(d), catalyst amount remarkably affects PC yield: the best yield could be obtained at a range of catalyst amount for 1.2–1.8 mol%. Beyond that, a lowered activity can be observed, which is because that the excess catalyst could not be well dispersed in the reaction mixture and limited the mass transfer between the active sites and reactants.

### 3.4. Recycling experiments

With PO as the substrate, experiments were carried out to examine the recyclability of PS-HEIMBr at 120 °C and 2.5 MPa in 4 h. As shown in Fig. 4, no decrease in PC yields for six repeated runs indicates the high stability of the catalyst. In addition,



**Fig. 5.** Thermogravimetric curves for PS-HEIMBr.




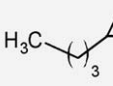
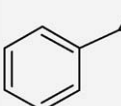
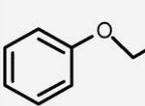



**Fig. 6.** FT-IR spectra comparison of the fresh and the six times reused PS-HEIMBr.

thermogravimetric analysis (TGA) result (Fig. 5) proved that PS-HEIMBr could endure about 280 °C with little loss of its weight. The decomposition of CPS started from about 430 °C, showing the high thermal stability of the support.

**Table 2**

Catalytic activity of the reaction of various epoxides with CO<sub>2</sub><sup>a</sup>.

Entry	Epoxide	Temperature (°C)	Time (h)	Selectivity (%)	GC Yield (%)
1	 <b>1a</b>	115	2.5	99	99
2	 <b>1b</b>	120	4	99	98
3	 <b>1c</b>	115	3	92	92
4	 <b>1d</b>	120	4	99	96
5	 <b>1e</b>	120	6	99	93
6	 <b>1f</b>	115	3	99	99
7	 <b>1g</b>	125	20	99	80

<sup>a</sup> Reaction conditions: epoxide (0.1 mol), catalyst (1.6 mol%), 2.5 MPa.

The FT-IR spectra comparison of PS-HEIMBr and six times reused PS-HEIMBr were listed in Fig. 6. The FT-IR curves compared the fresh and six times used catalyst indicating that the structure of the PS-HEIMBr catalyst hardly changes after six times reuse.

### 3.5. Catalytic activity of the reaction of various epoxides with CO<sub>2</sub>

The above results indicated that PS-HEIMBr was an effective catalyst for the cycloaddition of PO with CO<sub>2</sub> in solvent-free conditions. In order to survey the applicability of various epoxides to this process, we also examined the reactions of other epoxides with CO<sub>2</sub> and the results were summarized in Table 2. The catalyst (PS-HEIMBr) is found to be applicable to a variety of terminal epoxides, insuring high yields and high selectivities of the corresponding cyclic carbonates. Among the epoxides surveyed, ethylene oxide **1a** (entry 1) is the most reactive epoxide, and the reaction could completely finish in about 1 h with a 99% ethylene carbonate (EC) selectivity. Due to the higher hindrance originated from the two rings, cyclohexene oxide **1g** (entry 7) exhibits relatively low activity. The selectivity of the reactions to cyclic carbonates is mostly >99% except epichlorohydrin **1c** (entry 3), for which it is 92% as high as reported [17].

## 4. Conclusions

Polystyrene resin-supported hydroxyl-functionalized ionic liquids are effective catalysts for the synthesis of cyclic carbonates via the cycloaddition of epoxides with CO<sub>2</sub>. The hydroxyl group in ionic liquid cation can greatly accelerate the reactions and showed a synergetic effect with halide anions. The reactions can proceed smoothly under much milder conditions as compared to those using supported conventional ionic liquids. As a results, a 98% PO conversion and >99% selectivity could be realized using PS-HEIMBr at 2.5 MPa and 120 °C in 4 h. Also the catalyst can be easily separated from the products and reused for up to six times without the loss of its catalytic activity. The organic solvent-free green process presented here could show potential application in industry due to its easy product separation and high efficiency.

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