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High-Efficiency Synthesis of Cyclic Carbonates from Epoxides and CO_2 over Hydroxyl Ionic Liquid Catalyst Grafted onto Cross-Linked Polymer

Wei-Li Dai · Lang Chen · Shuang-Feng Yin · Wen-Hua Li · Yuan-Yuan Zhang · Sheng-Lian Luo · Chak-Tong Au

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Abstract Hydroxyl ionic liquid grafted onto cross-linked divinylbenzene polymer (PDVB-HEIMBr) was fabricated and evaluated as a catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides without the use of any co-catalyst and organic solvent. The catalyst shows good performance across a wide range of epoxides, giving almost quantitative yield of carbonates (140 °C, 2.0 MPa of initial CO_2, and $\leq$4 h). The effects of reaction temperature, time and initial CO_2 pressure on product yield were investigated. It is suggested that the synergetic effect between the bromide ions and the hydroxyl groups facilitates the coupling reaction. Furthermore, the PDVB-HEIMBr catalyst shows excellent stability and reusability. From the viewpoint of industrial application, the catalyst is very attractive because of its simplicity, activity, stability, and reusability.

Keywords PDVB · Hydroxyl ionic liquid · Carbon dioxide · Epoxide · Cyclic carbonate

1 Introduction

Carbon dioxide is a green-house gas blamed for global warming. It is also a economical C1 resource that is abundant, nontoxic, and renewable [1, 2]. One of the most interesting processes using CO_2 as raw material is the synthesis of cyclic carbonate through the coupling of CO_2 with epoxide (Scheme 1). Cyclic carbonates, e.g., ethylene carbonate (EC) and propylene carbonate (PC), are valuable compounds that are used as polar solvents, as electrolytes in lithium secondary batteries, as precursors for synthesizing polycarbonates and polyurethanes, and as raw materials in a wide range of chemical reactions [1, 2].

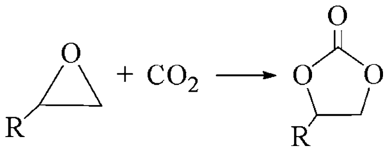
In the past decades, metallic complexes [3–7], phosphines [8, 9], organic bases [10–12], ionic liquids [13–16], metal oxides [17–19], modified molecular sieves [20–23], and supported catalysts [24–29] have been developed as catalysts for the coupling reaction. The homogeneous catalysts have been found to be efficient but the inherit disadvantage is the high cost for product separation and/or catalyst fabrication. Although heterogeneous catalysts (e.g., metal oxides [17–19], molecular sieves [20–23], and supported catalysts [24, 26, 27, 29]) have been explored, their application is limited because of low activity, and/or poor stability and reusability. In the past 10 years, ionic liquid attracted much interest in their uses as catalysts for synthesizing cyclic carbonates. As a strategy for the fabrication of stable and reusable heterogeneous catalysts, ionic liquids were immobilized on solid materials such as MgO, SiO_2, and MCM-41. However, catalyst reusability is far from satisfaction [27, 29–31].

Recently, Sun et al. [16] reported that the hydroxyl-containing ionic liquid (3-(2-hydroxyl-ethyl)-1-methyl-imidazolium bromide, HEMIMBr) showed good catalytic activity and selectivity for the coupling reaction. There was

W.-L. Dai · L. Chen · S.-F. Yin (✉) · W.-H. Li ·
Y.-Y. Zhang · S.-L. Luo (✉) · C.-T. Au
College of Chemistry and Chemical Engineering,
Hunan University, Changsha 410082, Hunan, China
e-mail: sfyin73@yahoo.com.cn

S.-L. Luo
e-mail: sllou@hnu.cn

C.-T. Au
Department of Chemistry, Hong Kong Baptist University,
Kowloon Tong, Hong Kong, China



Scheme 1 Coupling reaction of CO_2 with epoxide

no need of using any co-catalyst or organic solvent, and the catalytic performance is much higher than that of the traditional ionic liquids. The immobilization of hydroxyl ionic liquid (HIL) on a solid support for coupling reactions has been rarely studied [32–34]. Zhu et al. [32] reported that the molecular sieve-supported choline chloride/urea exhibited good catalytic activity, but urea was indispensable. We also fabricated hydroxyl ionic liquid catalyst immobilized SBA-15 molecular sieve, and found it showed good catalytic activity towards the coupling reaction [35]. But its reusability is not satisfactory, similar to the ionic liquid catalysts immobilized on MgO, SiO_2, or MCM-41 [27, 29–31]. Besides inorganic materials, high molecular polymers were also used as supports of heterogeneous catalysts. However, the use of polymer-supported ionic liquids as catalysts for the coupling of CO_2 with epoxides was only reported recently. Over the copolymer of 3-butyl-1-vinylimidazolium chloride and divinylbenzene and under rigorous reaction conditions (high pressure, long reaction time, and high catalyst concentration), Xie et al. [33] observed certain catalytic activity for coupling reaction and good reusability. Sun et al. [34] reported that imidazolium-base HIL immobilized on polystyrene resin showed good catalytic activity, but the employed amount of catalyst (1.6 mol.%) was high and catalyst reusability was not satisfactory. Herein, we report the grafting of HIL 3-(2-hydroxyl-ethyl)-1-(3-amino-propyl) imidazolium bromide onto cross-linked divinylbenzene polymer (PDVB). The catalyst (denoted as PDVB-HEIMBr hereinafter) is effective for the synthesis of cyclic carbonates from epoxides and CO_2, and catalyst reusability is excellent. The effects of reaction parameters such as temperature, time, and initial CO_2 pressure on product yield were systematically investigated.

2 Experimental

2.1 Reagents

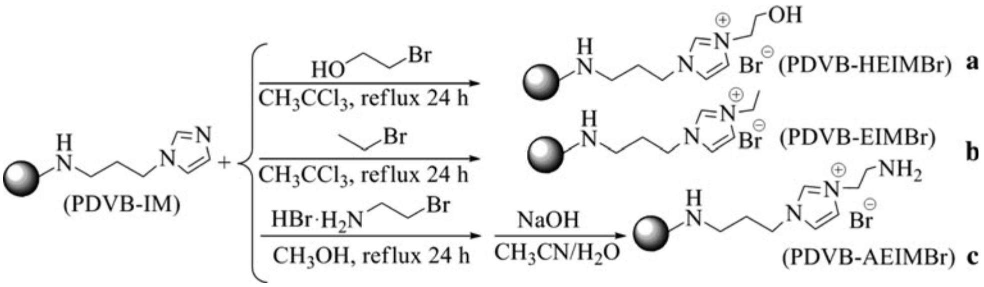
The PDVB grafted with 1-(3-amino-propyl) imidazole (denoted as PDVB-IM; QuadraPure IMDAZ, 100–400 μm particle size, content of labeling: 1.5 mmol/g loading, 1 % cross-linked with divinylbenzene), 2-bromoethanol, and 2-bromoethylamine hydrobromide were purchased from Aldrich Chemical Co. Propylene oxide, ethylene oxide, and bromoethane were produced by Sinopharm Chemical Reagent Co., Ltd. The other epoxides were purchased from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO_2 (99.9% purity) purchased from Changsha Gas Co. was used without further treatment.

2.2 Grafting of Ionic Liquids onto Polymer (PDVB)

Scheme 2a shows the steps for the grafting of (3-(2-hydroxyl-ethyl)-1-(3-amino-propyl) imidazolium bromide) onto PDVB. The as-fabricated catalyst is denoted as PDVB-HEIMBr. In a typical procedure, a mixture of 2-bromoethanol (6.0 mmol), 1,1,1-trichloroethane (20 mL), and 2.0 g PDVB-IM was refluxed for 24 h. The as-obtained solid was filtered out, washed three times with 1,1,1-trichloroethane, and dried at 60 °C for 6 h in vacuum to give the PDVB-HEIMBr catalyst. Similarly, the PDVB grafted with 3-ethyl-1-(3-amino-propyl) imidazolium bromide (denoted as PDVB-EIMBr) was fabricated (Scheme 2b).

According to Scheme 2c, the PDVB grafted with 3-(2-amino-ethyl)-1-(3-amino-propyl) imidazolium bromide (denoted as PDVB-AEIMBr) was prepared. In a typical procedure, a mixture of 2-bromoethylamine hydrobromide (6.0 mmol), methanol (20 mL), and 2.0 g PDVB-IM was refluxed for 24 h. The as-obtained solid was filtered out and washed 3 times with methanol. Then 5 mL of CH_3CN/H_2O (1:1, v/v) and NaOH (6.0 mmol) was added to neutralize hydrobromide, and the mixture was stirred at room temperature overnight. Finally, the solid was filtered out, washed 3 times with CH_3CN/H_2O, and dried at 60 °C for 6 h in vacuum for the generation of PDVB-AEIMBr.

Scheme 2 Procedure for the grafting of ionic liquids on PDVB



2.3 Characterization

Scanning electron microscopic (SEM) observations were carried out over a HITACHI S-4800 microscope. Energy dispersive X-ray spectroscopy (EDX) was performed using accessory (Horiba 7593-H) of the HITACHI S-4800 instrument. TG-DSC analysis was performed on NETZSCH-STA-449C at a heating rate of 15 °C/min in N_2 flow.

2.4 Coupling Reaction

The coupling reactions were carried out in a 30 mL high-pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, the reactor was charged with epoxide (28.6 mmol), catalyst (0.44 mol.%, calculated according to the amount of ionic liquid), and an appropriate amount of biphenyl (as internal standard for GC analysis). After the reactor was fed with CO_2 to a desired pressure, the autoclave with its contents was heated to a designated temperature in an oil bath and stirred for a designated period of time. Then the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO_2 was released using an aspirator and absorbed in a solution (aqueous) saturated with K_2CO_3. The resulting mixture was defined by GC-mass spectrometry on a Hewlett Packard 6890-5973 MSD GC-mass spectrometer and by ^{1}H NMR on a Bruck400 superconductive nuclear magnetic resonance spectrometer using TMS as internal standard. All the products were quantitatively analyzed by a Hewlett Packard 6820 gas chromatograph equipped with a TCD and DB-wax capillary column (30 m × 0.45 mm × 0.85 μm).

Scale-up coupling reactions were carried out in a 1 L high-pressure stainless-steel autoclave equipped with a mechanical agitator and electronic heater. No particular caution was taken to avoid the effect of water absorption (in trace amount from air).

3 Results and Discussion

3.1 Catalyst Characterization

The morphology of PDVB-IM and PDVB-HEIMBr was studied by SEM. As shown in Fig. 1a and b, PDVB-IM has a smooth surface. With the grafting of HIL on the material, there is roughening of surface (Fig. 1c and d). The EDX spectrum of PDVB-HEIMBr (Fig. 2) shows the presence of bromine, suggesting that the ionic liquid has been successfully grafted on the support.

Depicted in Fig. 3 are the TG and DSC curves of PDVB-IM and PDVB-HEIMBr. It is clear that both materials are stable up to 300 °C. Upon heating to 450 °C, there is the pyrolysis of PDVB-IM and PDVB-HEIMBr. The decomposition of the latter involves two endothermic steps at 335 and 425 °C, plausibly due to the decomposition of HIL and polymer support, respectively. The results indicate that the as-fabricated PDVB-HEIMBr is thermally stable up to 300 °C.

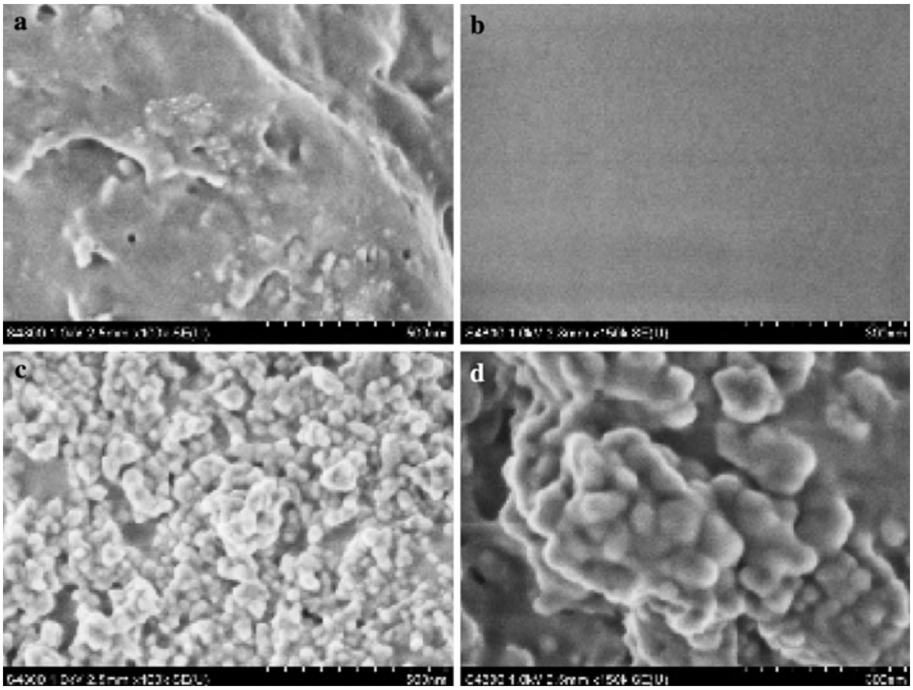


Fig. 1 SEM images of **a**, **b** PDVB-IM, and **c**, **d** PDVB-HEIMBr

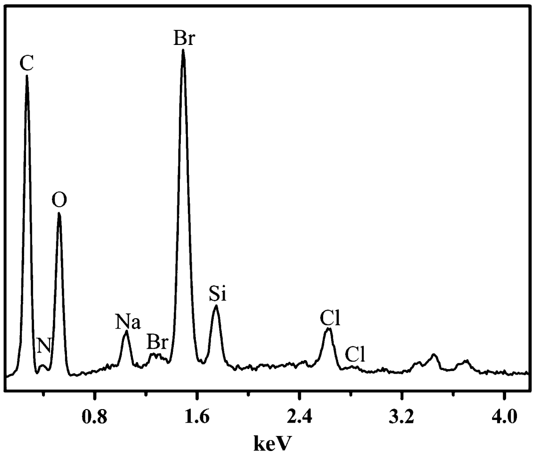


Fig. 2 EDX spectrum of PDVB-HEIMBr

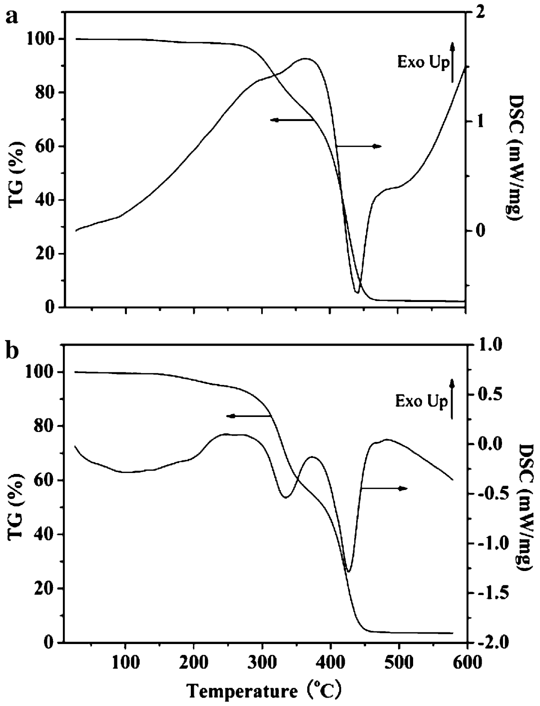


Fig. 3 TG and DSC curves of **a** PDVB-IM, **b** PDVB-HEIMBr

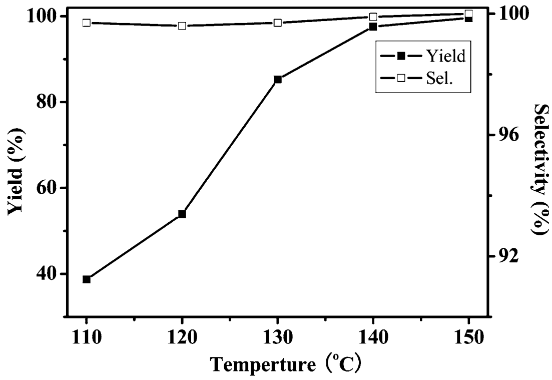


Fig. 4 Effects of reaction temperature on catalytic activity of PDVB-HEIMBr. Reaction conditions: PO 28.6 mmol, catalyst 0.1 g (0.44 mol.%), initial CO_2 pressure 2.0 MPa, time 4 h

3.2 Effects of Reaction Parameters on Catalytic Activity of PDVB–HEIMBr

It is generally accepted that reaction parameters such as temperature, time and initial CO_2 pressure have an effect on product yield. We used PO as a model substrate to evaluate the catalytic performance of PDVB-HEIMBr. The dependence of PC yield and selectivity on reaction temperature is shown in Fig. 4. With increase of temperature from 110 to 140 °C, PC yield increases from 38.7 to 97.6%. Further rise of temperature to 150 °C has only slight effect on PC yield. On the other hand, the selectivity to PC is almost independent of temperature: in the 110–150 °C range, PC selectivity is ≥99.6%, and only a minute amount of 1,2-propanediol generated from the hydrolysis of PO is detected as by-product.

The plots of PC yield at 140 and 150 °C versus reaction time are shown in Fig. 5. (Not shown is the PC selectivity which stays above 99.9% throughout.) At 140 °C, PC yield rises rapidly and reaches 87.3% within the first 3 h. It is 97.6% at the fourth hour and 99.5% at the fifth hour. At 150 °C, PC yield is 90.2% in the first 2 h. With prolonged reaction, almost quantitative yield of PC can be achieved: 96.6% at the third hour and 99.6% at the fourth hour. It is apparent that the coupling reaction is very sensitive to temperature (110–150 °C) and time.

Depicted in Fig. 6 is the plot of PC yield and selectivity at 140 °C versus initial CO_2 pressure. One can see that the catalytic activity of PDVB–HEIMBr is the highest at an initial CO_2 pressure of 2.0 MPa. Further rise of CO_2 pressure (from 2.0 to 4.0 MPa) results in a decrease of PO conversion. Such an effect of CO_2 pressure on catalytic

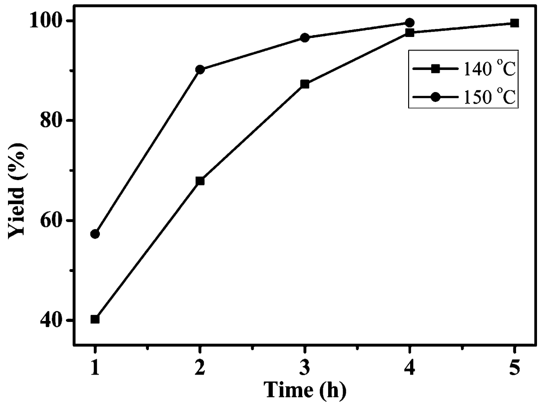


Fig. 5 Effects of reaction time on catalytic activity of PDVB-HEIMBr. Reaction conditions: PO 28.6 mmol, catalyst 0.1 g (0.44 mol.%), initial CO_2 pressure 2.0 MPa

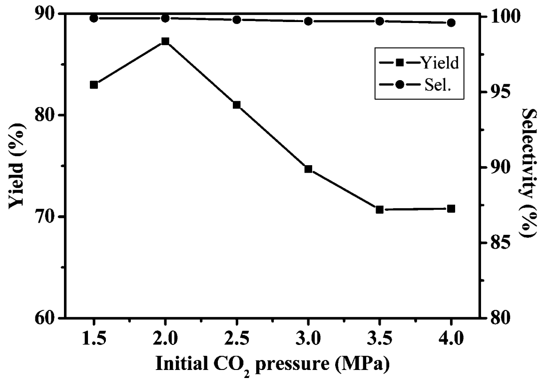


Fig. 6 Effects of initial CO_2 pressure on catalytic activity of PDVB-HEIMBr. Reaction conditions: PO 28.6 mmol, catalyst 0.1 g (0.44 mol.%), temperature 140 °C, time 3 h

Table 1 Catalytic activity of various catalyst systems

Entry	Catalyst	Catalytic results	
		Yield (%)	Sel. (%)
1[a]	2-Bromoethanol	23.8	99.0
2	PDVB-IM	8.9	97.4
3	PDVB-HEIMBr	97.6	99.9
4	PDVB-AEIMBr	83.3	99.9
5	PDVB-EIMBr	31.2	99.2
6[b]	PDVB-EIMBr/ethanol	30.9	98.7
7[c]	PDVB-EIMBr/ethanol	64.4	99.4
8[c]	PDVB-IM/ethanol	9.9	96.5
9[c]	Ethanol	Trace	–
10[d]	PSIL	74.9	99.1
11[e]	Zn–Mg–Al oxide	55.4	97.2

Reaction conditions: PO 28.6 mmol, catalyst 0.44 mol.%, initial CO_2 pressure 2.0 MPa, temperature 140 °C, time 4 h

[a] 2-Bromethanol 0.44 mol.%

[b] Ethanol 0.44 mol.%

[c] Ethanol 2.2 mol.%

[d] Prepared according to reference [32]; catalyst 0.44 mol.%

[e] Reported by us [42]; catalyst 0.5 g

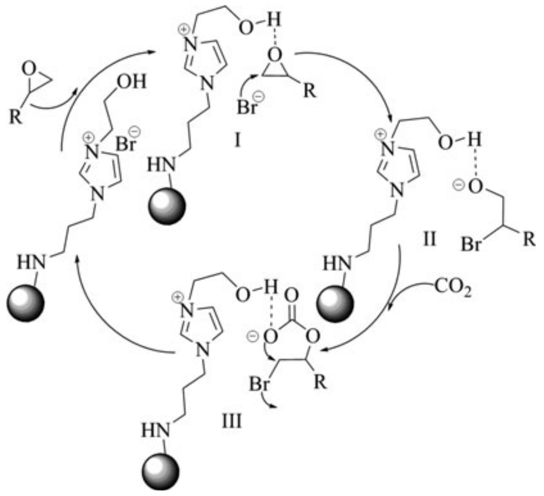
activity has been observed in other catalytic systems [15, 27]. The results are somewhat unexpected because PC is in its liquid form under the adopted reaction conditions and an increase of CO_2 pressure should be a favorable factor for PO conversion. A possible explanation is that acidic CO_2 dissolves in basic epoxide and liquefies due to CO_2-epoxide complexing [27, 36]. Thus rather than promoting the interaction between PO and catalyst, the high CO_2 pressure enhances the CO_2–PO complexing interaction, consequently leading to a decline of catalytic activity. However, PC selectivity is almost independent of the initial pressure of CO_2.

3.3 The Role of PDVB-HEIMBr Hydroxyl Groups

Sun et al. reported that in CO_2 coupling with epoxide, catalytic activity can be related to the coordination of hydroxyl group of HIL with the halide ion of HEMIMBr [16, 34]. The author also pointed out that when quaternary ammonium, imidazolium, or phosphonium halide was used as homogeneous catalyst, the –OH of water or that of OH-containing compounds could facilitate the coupling reaction [37]. Furthermore, Zhang et al. reported that hydroxyl groups such as those of silanols on amine-functionalized SiO_2 catalysts played an important role in the fixation of CO_2 [26]. In the present study, we investigated the role of hydroxyl groups of the PDVB–HEIMBr catalyst by comparing the activity of catalysts with different functional groups.

From the results listed in Table 1, one can see that the ingredients for the formation of PDVB–HEIMBr, viz. 2-bromoethanol and PDVB–IM are poor in catalytic activity (Table 1, entries 1, 2). In terms of PC yield and selectivity, the PDVB–HEIMBr catalyst that contains OH group is superior to PDVB–EIMBr that does not contain OH group (Table 1, entries 3, 5; scheme 2 for structural information). Moreover, the PDVB–AEIMBr (Table 1, entry 4) that contains an amino group is lower than PDVB–HEIMBr but much higher than PDVB–EIMBr in catalytic activity. It was reported that through amine modification, the activity of heterogeneous catalysts could be improved [25, 26, 38]. It is possible that the enhancement of catalyst basicity through the amino group is a reason for PDVB–AEIMBr being higher than PDVB–EIMBr in catalytic performance.

In most studies, it is regarded that epoxide and CO_2 are, respectively, activated by acid and basic sites. It was demonstrated that acid–base bifunctional catalysts performed well in the coupling reactions [13, 15, 18, 19, 39–41]. Sun et al. suggested that the hydroxyl groups and halide ions functioned as Lewis acid sites and basic sites, respectively, and their coordination was beneficial to the coupling reaction [16, 34, 37]. To further investigate the role of hydroxyl groups, we added ethanol deliberately to PDVB–EIMBr and PDVB–IM. Compared to the case of PDVB–EIMBr alone (Table 1, entry 5), there is little change in catalytic activity when the molar ratio of ethanol to the number of active sites on PDVB–EIMBr is 1.0, (Table 1, entry 6), likely to be due to the very low concentration of ethanol. When the ratio is raised to 5.0, there is significant rise in catalytic performance of PDVB-EIMBr (Table 1, entry 7). In the case of PDVB–IM/ethanol in the absence of bromide anions, the observed activity is poor (Table 1, entry 8). According to the results, we deduce that the presence of hydroxyl groups and the coordination of hydroxyl groups with bromide ions results in the promoted catalytic interaction. The deductions are in consistent with



Scheme 3 Proposed mechanism for the coupling reaction

the results of Sun et al. [16, 34, 37] and Zhang et al. [26]. It is noted that ethanol by itself shows no catalytic activity for the coupling reaction (Table 1, entry 9).

Based on the results of the present study and those in the literature [16, 26, 32, 34, 37], we propose a mechanism for the coupling reaction over the PDVB-HEIMBr catalyst (Scheme 3). First, the coordination of OH with the O atom of epoxide through hydrogen bonding results in the formation of intermediate **I** and polarization of the epoxide C–O bonds. Then, nucleophilic attack of bromide ion on the *β*-carbon atom of epoxide that is sterically less hindered occurs. Simultaneously, there is ring opening of epoxide and generation of oxy anion **II**. The insertion of CO_2 into the haloalkoxy species results in the formation of linear halocarbonate (**III**) that transforms into cyclic carbonate through intramolecular substitution of the bromide ion.

For comparison, the performance of a couple of known catalysts [33, 42] under equal reaction conditions are listed in Table 1. Over the copolymer of 3-butyl-1-vinylimidazolium chloride with cross-linker divinylbenzene (PSIL) reported by Xie et al. [33], PC yield and selectivity are 74.9 and 99.1%, respectively (Table 1, entry 10). Over Zn–Mg–Al composite oxide reported by us [42], PC yield and selectivity are only 55.4 and 97.2% (Table 1, entry 11). In other words, PDVB-HEIMBr is superior to the two catalysts in performance.

3.4 Coupling of CO_2 with Various Epoxides

To demonstrate the scope of PDVB-HEIMBr application, we examined the coupling reaction of CO_2 with various epoxides over the catalyst, and the results are depicted in Table 2. One can see that PDVB–HEIMBr is active for the selected substrates. Epichlorohydrin is the most reactive, and almost 100% yield of carbonate is achieved in 2 h (Table 2, entry 4). The reactivity of ethylene oxide (100% yield in 3 h (Table 2, entry 1) is lower than that of epichlorohydrin, but higher than that of PO (Table 2, entry 2) and styrene oxide (Table 2, entry 5). When cyclohexene oxide is adopted as substrate, much longer time is needed for complete conversion (Table 2, entry 6), plausibly due to the sterical hindrance originated from the two rings of cyclohexene oxide. From the results, one can see that the reactivity of the adopted substrates is in the order of epichlorohydrin > ethylene oxide > styrene oxide ≈ PO > 1,2-butylene oxide ≫ cyclohexene oxide.

Table 2 Coupling of CO_2 with various epoxides catalyzed by PDVB-HEIMBr

Entry	Epoxides	Time (h)	Catalytic results	
			Yield (%)	Sel. (%)
1	Ethylene oxide	3	100	100
2	Propylene oxide	4	97.6	99.9
3	1,2-Butylene oxide	4	79.0	100
4	Epichlorohydrin	2	97.5	97.5
5	Styrene oxide	4	99.5	100
6	Cyclohexene oxide	24	72.9	99.2

Reaction conditions: epoxide 28.6 mmol, catalyst 0.1 g (0.44 mol.%), initial CO_2 pressure 2.0 MPa, 140 °C

3.5 Catalyst Recycling and Scale-Up Reaction

Using PO as substrate, we performed experiments at 140 °C and initial CO_2 pressure 2.0 MPa to examine the reusability of PDVB–HEIMBr. After each reaction cycle, PDVB–HEIMBr was recovered by filtration and then rinsed with PO. After drying, the catalyst was reused for the next run. In each run, the selectivity to PC is ≥99.8%. It was noted that there is no significant loss of catalytic activity after eight runs. The results indicate that PDVB–HEIMBr shows excellent reusability and stability for the coupling reaction. We also checked the recycled catalyst by SEM and TG analysis techniques, and found there was no obvious difference between the fresh and recycled catalysts.

Moreover, we conducted scaled-up reaction under the conditions of: PO (1.0 mol), catalyst (0.44 mol.%, calculated based on the amount of ionic liquid), temperature 140 °C, initial CO_2 pressure 2.0 MPa in a 1 L high-pressure autoclave. It is noted that PC was obtained quantitatively (99.5%) in 4 h (PC selectivity = 99.9%). The results reported so far demonstrate that the catalyst is suitable for industrial applications.

4 Conclusion

Hydroxyl ionic liquid (3-(2-hydroxyl-ethyl)-1-(3-aminopropyl) imidazolium bromide) grafted on cross-linked divinylbenzene polymer is an effective heterogeneous catalyst for the solventless synthesis of cyclic carbonates through the coupling of CO_2 with epoxides. The adopted reaction conditions are not harsh and there is no need of using a co-catalyst or an organic solvent. The excellent performance is ascribed to the OH groups and the coordination of OH groups with bromide ions. Moreover, the catalyst shows good thermal stability, and excellent reusability. From the viewpoint of industrial application, the catalyst is attractive because of its simplicity, stability, and reusability.

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