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Zn-based ionic liquids as highly efficient catalysts for chemical fixation of carbon dioxide to epoxides†

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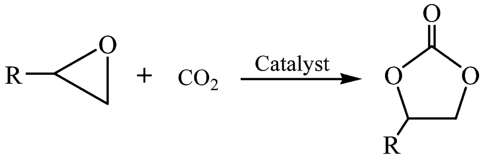
The novel Zn-based task-specific ionic liquids (Zn-TSILs) catalysts were developed for the coupling of carbon dioxide and epoxides to form cyclic carbonates under mild reaction conditions without using additional organic solvents and cocatalysts. Due to the synergistic effects of the cation and anion in this catalytic system, excellent yields and selectivities to cyclic carbonates were achieved with high TOF values up to 794 h^{-1}. Among the catalysts investigated, OH-containing Zn-TSILs showed better activity than COOH-containing Zn-TSILs, and $[(CH_2CH_2OH)Bim]ZnBr_3$ was found to be the best. Additionally, the influences of CO_2 pressure and catalyst concentration were also investigated over $[(CH_2CH_2OH)Bim]ZnBr_3$. In addition, the rate constants as well as the activation energies for the cycloaddition reaction catalyzed by Zn-TSIL and TSIL were comparatively determined. The activation energy was calculated to be 34.1 kJ mol^{-1} for bare TSIL catalyst, whereas the Zn-TSIL reduced the activation energy value by 14.7 kJ mol^{-1}. Moreover, the Zn-TSIL was easily recyclable without significant loss of activity, representing the exceptionally promising candidate for the effective fixation of CO_2 to epoxides.

1. Introduction

Carbon dioxide is has been in the spotlight as a renewable C1 feedstock because it is ubiquitous and readily available, either from decomposition of organic matter or artificial production by human activities. Conversion of CO_2 into industrially useful chemicals has dual significance in view of both environmental protection and sustainable chemistry.[1] One of the most promising strategies in this area is the synthesis of cyclic carbonates *via* the cycloaddition of epoxides and CO_2 (Scheme 1), especially the synthesis of propylene carbonate (PC) and ethylene carbonate (EC). The formation of cyclic carbonates is green for 100% atom efficiency and cyclic carbonates have found applications not only as polar aprotic solvents, electrolytes for lithium-ion batteries, and as intermediates in the manufacture of fine chemicals,[2–4] but are also used as constituents of oils and paints and as raw materials in the synthesis of polycarbonates[5,6] and polyurethanes[7,8] as shown in Scheme 2.

Because carbon dioxide contains carbon in its most oxidized state, it has inherent thermodynamic stability and kinetic inertness.[9] Therefore, catalysts are needed to reduce the activation energy of any reaction in which CO_2 is involved. Accordingly, a wide range of catalysts have been explored for the synthesis of cyclic carbonates, including metal oxides,[10,11] alkali metal salts,[12,13] quaternary ammonium salts,[14] phosphonium salts,[15] Schiff bases[16–18] and transition metal complexes.[19] However, in many cases, additives and/or cocatalysts as well as organic solvents are needed. In addition, unsatisfactory activity, harsh reaction conditions and inexhaustive separation of products from the catalysts are still drawbacks that need to be overcome. Hence, the design of a novel, solvent/cocatalyst-free catalyst with enhanced activity still remains to be developed toward effective conversion of CO_2.[20]

More recently, ionic liquids (ILs) have attracted considerable interest and CO_2 cycloaddition to epoxides has been effectively carried out in ILs, which possess unique characteristics, such as thermal and chemical stability, negligible vapor pressure, selective solubility towards organic and inorganic materials, and high reusability of the catalysts.[21] In 2001, Peng and Deng[22] first reported the quantitative conversion of propylene oxide



Scheme 1 Cycloaddition reaction of CO_2 with epoxides.

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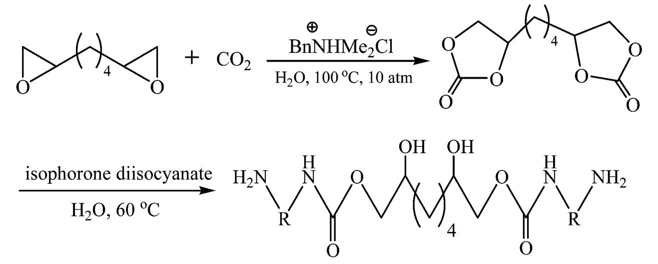
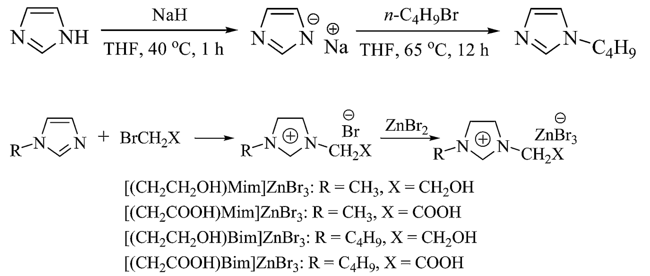


Scheme 2 Synthesis of polyurethanes *via* cyclic carbonates.[7]



Scheme 3 Synthesis process for Zn-based task-specific ionic liquids.

(PO) to PC catalyzed by 1-butyl-3-methylimidazolium ($BmimBF_4$) ionic liquid. Thereafter, series of imidazolium salts,[23–25] quaternary ammonium salts,[26] quaternary phosphonium salts,[27] pyridinium salts,[28] guanidinium salts,[29] polymeric[30,31] and other immobilized ILs[32,33] were developed as catalysts for the cycloaddition of CO_2 into epoxides. Among these, Kim's group found that imidazolium zinc tetrahalides showed surprisingly high activities for the coupling reaction of CO_2 and ethylene oxide or propylene oxide to produce corresponding cyclic carbonates and the highest TOF were up to 3545 h^{-1} for 1-butyl-3-methylimidazolium bromide-$ZnBr_2$ at 100 °C and 3.5 MPa.[34] Sun[35] and Zhou *et al.*[36] have reported that hydroxyl-functionalized (HFILs)/carboxyl-functionalized ionic liquids (CFILs) could coordinate with the oxygen atom of epoxides and thus lead to the activation of the epoxide. Furthermore, a theoretical study also indicated that the formation of hydrogen bonds between catalyst and epoxide could accelerate the ring-opening reaction of the epoxide, enhancing the activity significantly.[37] However, the catalytic activity was unsatisfactory and needed further improvement. Previous literature also reported that zinc halides could coordinate with the oxygen atom to activate the epoxide by forming the zinc-epoxide adduct.[15,38,39] Herein, we designed novel Zn-based task-specific ionic liquids composed of $ZnBr_2$ and hydroxyl/or carboxyl group-functionalized ILs, which are expected to be excellent catalysts for the CO_2 cycloaddition reaction. The Zn-based task-specific ionic liquids (Zn-TSILs) were facilely obtained from the reaction of $ZnBr_2$ with HFILs/or CFILs. The catalytic activities were examined for CO_2 coupling with PO as well as other epoxides, especially the less active epoxides, such as styrene oxide and cyclohexene oxide. Systematic investigations on the effects of CO_2 pressure and catalyst concentration on the target reaction were also conducted. Additionally, the contrast calculations for the activation energies were provided over HFIL and Zn-HFIL catalysts. A plausible reaction mechanism was proposed based on the experimental results.

2. Experimental

2.1. General information

Carbon dioxide with purity of 99.99% was purchased from Harbin Qinghua Industrial gases Co. Ltd. PO, sodium hydride (60%), imidazole (99%), *N*-methylimidazole (99%), *n*-butyl bromide (≥99%), 2-bromoethanol (96%), bromoacetic acid (98%), tetrahydrofuran (extra dry, >99%) were purchased

Table 1 Effect of various catalysts on the cycloaddition reaction of PO and CO_2[a]

Entry	Catalyst	Conversion[b] (%)	Yield[b] (%)	TOF[c] (h^{-1})
1	None	Trace	Trace	—
2	$ZnBr_2$	Trace	Trace	—
3	[Emim]Br	33	32	276
4	[Bmim]Br	35	35	302
5	$BrCH_2CH_2OH$	Trace	Trace	—
6	$BrCH_2COOH$	Trace	Trace	—
7	$[(CH_2CH_2OH)Mim]Br$	54	53	457
8	$[(CH_2COOH)Mim]Br$	49	48	414
9	$[(CH_2CH_2OH)Bim]Br$	55	54	466
10	$[(CH_2COOH)Bim]Br$	53	51	440
11	$[(CH_2CH_2OH)Mim]ZnBr_3$	90	89	768
12	$[(CH_2COOH)Mim]ZnBr_3$	83	81	699
13	$[(CH_2CH_2OH)Bim]ZnBr_3$	93	92	794
14	$[(CH_2COOH)Bim]ZnBr_3$	85	83	716
15[d]	$[(CH_2CH_2OH)Bim]ZnBr_3$	86	86	742
16[e]	$[(CH_2CH_2OH)Bim]ZnBr_3$	91	90	776
17[f]	$[(CH_2CH_2OH)Bim]ZnBr_3$	92	91	523

[a] Reaction conditions: 34.5 mmol PO, 0.04 mmol Cat., $T = 120$ °C, $P(CO_2) = 2.0$ MPa, $t = 1.0$ h. [b] Based on GC analysis. [c] Moles of PC produced per mole of catalyst per hour. [d] $T = 100$ °C. [e] The fourth run. [f] The fifth run, $t = 1.5$ h.

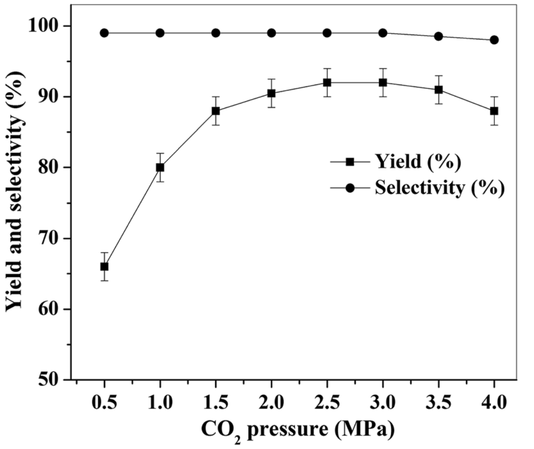


Fig. 1 Effect of CO_2 pressure on the synthesis of PC. Conditions: 34.5 mmol PO, 0.04 mmol [(CH_2CH_2OH)Bim]$ZnBr_3$, $T = 120$ °C, $t = 1.0$ h.

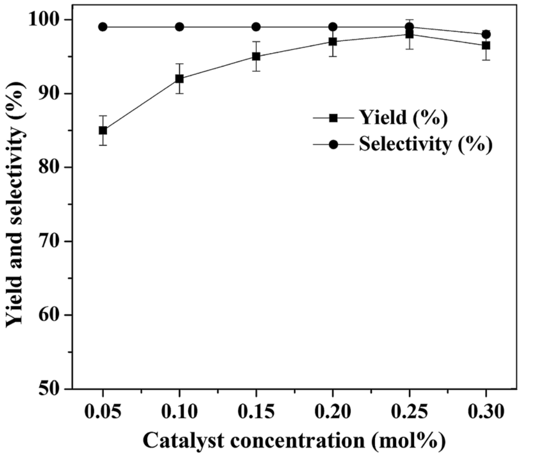
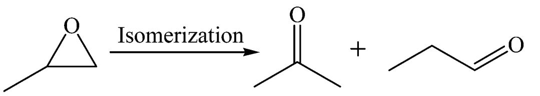


Fig. 2 Dependence of catalyst concentration on the synthesis of PC. Conditions: 34.5 mmol PO, $T = 120$ °C, P (CO_2) $= 2.5$ MPa, $t = 1.0$ h.



Scheme 4 Possible side reactions of PO.

from Aladdin Chemical Co. $ZnBr_2$ (CP) was purchased from Adamas Reagent Co. Ltd. All other chemicals were purchased from Beijing InnoChem Science & Technology Co. Ltd. and were of analytical grade and used without further purification.

FT-IR spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. ^{1}HNMR spectra were detected on a Bruker 400 spectrometer in D_2O (4.79 ppm) at ambient temperature. GC analyses were performed on an Agilent GC-7890A equipped with a capillary column (Agilent 19091J-413), using a flame ionization detector.

2.2. Synthesis of Zn-based task-specific ionic liquids

Four ILs composed of $ZnBr_3^-$ anions and different cations were prepared according to Scheme 3. The detailed synthesis procedures are described in ESI† and characterization results are as follows.

[(CH_2CH_2OH)Mim]$ZnBr_3$: yield: 97%; ^{1}H NMR (400 MHz, D_2O): $\delta = 8.78$ (s, 1H), 7.54 (m, 1H), 7.48 (m, 1H), 4.51–4.21 (m, 2H), 3.99–3.94 (m, 2H), 3.93 (s, 3H). FT-IR: 3497, 3152, 2955, 1619, 1567, 1384, 1165, 1061, 826, 748, 643 cm^{-1}.

[(CH_2COOH)Mim]$ZnBr_3$: yield: 93%; ^{1}H NMR (400 MHz, D_2O): $\delta = 8.66$ (s, 1H), 7.43–7.22 (m, 2H), 4.66 (s, 2H), 3.87 (s, 3H). FT-IR: 3400, 3134, 2617, 1747, 1593, 1171, 1082, 974, 834, 749, 623 cm^{-1}.

[(CH_2CH_2OH)Bim]$ZnBr_3$: yield: 95%; ^{1}H NMR (400 MHz, D_2O): $\delta = 8.78$ (s, 1H), 7.70–7.11 (m, 2H), 4.35–4.25 (m, 2H), 4.18 (t, $J = 7.2$ Hz, 2H), 3.95–3.84 (m, 2H), 1.92–1.71 (m, 2H), 1.37–1.19 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H). FT-IR: 3449, 3142, 2959, 2871, 1937, 1614, 1562, 1458, 1161, 1057, 947, 832, 749 cm^{-1}.

[(CH_2COOH)Bim]$ZnBr_3$: yield: 90%; ^{1}H NMR (400 MHz, D_2O): $\delta = 8.75$ (s, 1H), 7.54–7.33 (m, 2H), 4.71 (s, 2H), 4.16 (t, $J =$ 7.3 Hz, 2H), 1.93–1.71 (m, 2H), 1.35–1.13 (m, 2H), 0.84 (t, $J = 7.4$ Hz, 3H). FT-IR: 3432, 2959, 2285, 1746, 1616, 1572, 1168, 1081, 838, 751, 621 cm^{-1}.

2.3. General procedure for PC synthesis from PO and CO_2

The cycloaddition reaction of PO and CO_2 was conducted in a 50 mL high pressure stainless-steel reactor equipped with a magnetic stirring bar. In a typical run, the reactor was purged with CO_2 to evacuate air, and then Zn-TSIL catalyst (0.035 mmol, 0.12 mol% of PO) and PO (34.5 mmol) were added successively, then the reactor was heated using an oil bath. At a fixed reaction temperature such as 120 °C, CO_2 was introduced into the reactor and the pressure was adjusted to 2.0 MPa. The autoclave was heated at that temperature for a designated period of time. After the reaction was completed, the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO_2 was released. The product was extracted with ethyl acetate and analyzed by GC and Zn-TSILs were separated by centrifugation, washed with ethyl acetate (3 × 5 mL), dried under vacuum and then reused directly for the next run.

3. Results and discussion

3.1. Catalyst screening for the cycloaddition of CO_2 to PO

The activities of different catalysts were tested on the reaction of PO and CO_2, and the corresponding results are summarized in Table 1. Almost no reaction occurred in the absence of any catalyst or in the presence of only $ZnBr_2$ catalyst (entries 1 and 2). Although the hydroxyl-functionalized (HFILs) and carboxyl-functionalized ionic liquids (CFILs) showed higher catalytic activity (entries 7–10) compared with non-functionalized ionic liquids, such as [Emim]Br (1-ethyl-3-methylimidazolium bromide) and [Bmim]Br (1-butyl-3-methylimidazolium bromide) (entries 3 and 4), the activities were still unsatisfactory. Almost no reactivity was observed in the presence of $BrCH_2CH_2OH$ or $BrCH_2COOH$ (entries 5 and 6). However, the Zn-based task-specific ionic liquids

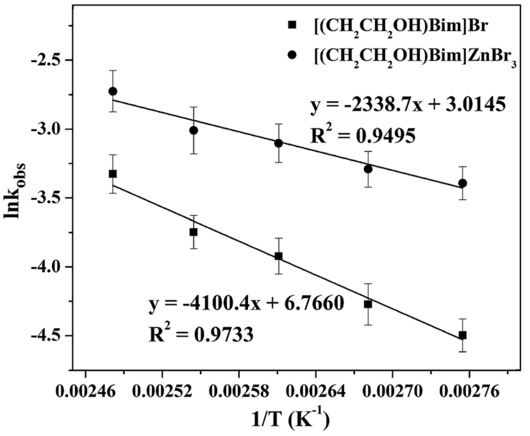


Fig. 3 Arrhenius plots for the CO_2 cycloaddition to PO catalyzed by $[(CH_2CH_2OH)Bim]Br$ (■) and $[(CH_2CH_2OH)Bim]ZnBr_3$ (●). Conditions: 34.5 mmol PO, 0.25 mol% Cat., P (CO_2) = 2.5 MPa. The average and standard deviation of ln k_{obs} were obtained from the experiments at each temperature.

Table 2 Kinetic parameters of CO_2 cycloaddition to PO over different catalysts[a]

	Kinetic parameters		
Catalyst	Ea (kJ mol^{-1})	A (min^{-1})	R^2
$[(CH_2CH_2OH)Bim]Br$	34.1	867.8	0.9733
$[(CH_2CH_2OH)Bim]ZnBr_3$	19.4	20.4	0.9495

[a] The values of kinetic parameters obtained from the linear Arrhenius plot of ln k_{obs} against $1/T$.

realized the obvious enhancements in catalytic activity in comparison with the former non Zn-based ILs, indicating the necessary cooperative effects between Zn and IL, which stabilized intermediates through hydrogen bonds and Zn–O bonds for accelerating the reaction (entries 11–14). Notably, the $[(CH_2CH_2OH)Bim]ZnBr_3$ catalyst showed the best activity and PO conversion approached 93% with 92% PC yield under cocatalyst and solvent free conditions of 120 °C and 2.0 MPa CO_2 for 1.0 h (entry 13), and the high turnover frequency (TOF) value was up to 794 h^{-1}. The catalytic activity decreased in the order of $[(CH_2CH_2OH)Bim]ZnBr_3$ > $[(CH_2CH_2OH)Mim]ZnBr_3$ > $[(CH_2COOH)Bim]ZnBr_3$ > $[(CH_2COOH)Mim]ZnBr_3$. As hydrogen-bond donors, the –OH and –COOH played the same roles of interacting with epoxides to polarize the C–O ring bond and facilitate the nucleophilic attack by the halide anion for subsequent ring opening. The OH-containing Zn-TSILs showed better activities than the COOH-containing Zn-TSILs (entries 11 and 13 *vs.* entries 12 and 14), which were accordant with the effects of HFILs and CFILs (entries 7 and 9 *vs.* entries 8 and 10). The different activities presumably were attributed to the carbonyl oxygen in COOH-containing Zn-TSILs forming intramolecular hydrogen bonds, thus competing with the hydrogen bonds formed between Zn-TSILs and PO, thereby lowering the product yield.[24] Besides, it was detected that a slight increase in PC yield resulted from increasing the alkyl chain length of the imidazolium cation with the same functional groups, due to the higher solubility of CO_2 and PO in the IL phase.[23] Compared with the imidazolium zinc tetrahalides catalyst reported by Kim *et al.*,[34] the same reaction temperature of 100 °C was used and the PC yield reached 86% with TOF of 742 h^{-1} under a lower reaction pressure of 2.0 MPa (entry 15) for 1.0 h, proving that $[(CH_2CH_2OH)Bim]ZnBr_3$ possessed excellent catalytic performance.

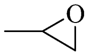
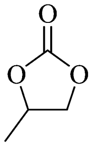
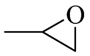
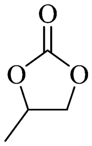
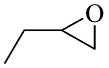
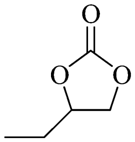
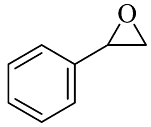
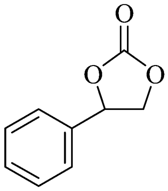
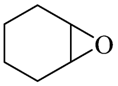
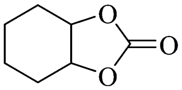
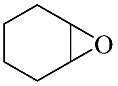
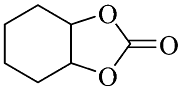
For a potential application in a green and economic process, the recyclability of the catalyst plays an important role. Fig. S1 in ESI† displays the recyclability of $[(CH_2CH_2OH)Bim]ZnBr_3$ at 120 °C and 2.0 MPa CO_2 pressure. No significant decrease in PC yields was observed after four cycles (entry 16), and in the 5th reuse, the catalyst still exhibited high PO conversion and PC yield with reaction time of 1.5 h (entry 17). Further reuse of the spent catalyst could still achieve a high PO conversion and PC yield, but at the expense of a little longer reaction time because of the washing loss of the IL catalyst, demonstrating a very feasible and reusable catalyst for the CO_2 cycloaddition reaction.

3.2. Effects of reaction parameters

The influence of CO_2 pressure on the PC yield was investigated at 120 °C for 1.0 h with $[(CH_2CH_2OH)Bim]ZnBr_3$ catalyst. As shown in Fig. 1, the reaction pressure had a significant effect on PC yield. With the increase of CO_2 pressure from 0.5–1.5 MPa, the PC yield increased rapidly. In the range of 1.5–2.5 MPa, there was a moderate increase in yield and in the range of 2.5–3.0 MPa, the PC yield was almost constant, but decreased initially when the CO_2 pressure was above 3.0 MPa. To our delight, there were no obvious changes in PC selectivity. A similar influence of CO_2 pressure on catalytic activity was observed in other catalytic systems in the literature.[15,40,41] The reason for this could be ascribed to the phase behavior of the CO_2–PO system. There appeared two phases; a CO_2-rich gas phase and a PO-rich liquid phase in the system under experimental conditions, and the reaction mainly took place in the liquid phase, which dispersed the catalyst. The concentration of CO_2 in the liquid phase rose remarkably with increasing pressure when the reaction was carried out in the low-pressure region, thus significantly promoting the reaction. However, too high a CO_2 pressure would decrease PC yield because of the lower concentration of PO in the liquid phase because more PO was extracted into the vapor phase. Therefore, 2.5 MPa was chosen as the most suitable pressure for PC synthesis.

Additionally, the effects of the catalyst concentration on the reaction were investigated with the molar percentage of $[(CH_2CH_2OH)Bim]ZnBr_3$ to PO in the range 0.05–0.30 mol% (Fig. 2). It is worth mentioning that only 0.05 mol% of catalyst showed good catalytic performance at 85% PC yield. The PC yield increased smoothly from 85% to around 98% with catalyst concentration increasing from 0.05 to 0.25 mol%, and no obvious changes in PC selectivities. Further increase in the catalyst concentration caused a slight decrease in PC yield, presumably due to side reactions such as isomerization of PO as

Table 3 Coupling reaction of CO_2 with various epoxides catalyzed by $[(CH_2CH_2OH)Bim]ZnBr_3$[a]

					Reaction results[b]	
Entry	Epoxide	Product	T (°C)	t (h)	Y_{PC} (%)	S_{PC} (%)
1			90	4.0	96	≥99
2			120	2.0	99	≥99
3			120	2.0	97	≥99
4			120	4.0	94	≥98
5			120	12.0	68	≥99
6			120	16.0	85	≥98

[a] Reaction conditions: 34.5 mmol epoxide, 0.25 mol% Cat., $P\,(CO_2) = 2.5$ MPa. [b] Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analysis.

shown in Scheme 4. As a consequence, 0.25 mol% was chosen as the most suitable catalyst concentration.

3.3. The activation energy and kinetic equation for PC synthesis

In order to illustrate the unique features of $ZnBr_2$, the synthesis of PC using the respective $[(CH_2CH_2OH)Bim]Br$ and $[(CH_2CH_2OH)Bim]ZnBr_3$ catalysts was undertaken as a function of temperature and the contrast calculations of the activation energies were provided. The kinetic parameters were studied over a temperature range from 90 to 130 °C and the rate laws for this process were fitted to eqn (1).[20,42,43]

$$\text{Rate} = k[\text{epoxide}]^a[CO_2]^b[\text{Cat}]^c \tag{1}$$

where k represents the rate constant; [epoxide], $[CO_2]$, [Cat] represents propylene oxide, carbon dioxide and catalyst concentration, respectively; a, b, c is the reaction order of corresponding substrates.

As the reaction was carried out in a constant volume reactor, CO_2 was present in large excess, and the concentrations of CO_2 and catalyst would be effectively constant during the reaction, then eqn (1) could be simplified to eqn (2):

$$\text{Rate} = k_{\text{obs}}[\text{epoxide}]^a,\ \text{where}\ k_{\text{obs}} = k[CO_2]^b[\text{Cat}]^c \tag{2}$$

The reaction was assumed to follow first-order kinetics and the observed pseudo-first-order rate constant (k_{obs}) could be calculated from eqn (3):

$$\text{Rate} = \frac{-\text{d}[\text{epoxide}]}{\text{d}t} = k_{\text{obs}}[\text{epoxide}] \tag{3}$$

Integrating eqn (3) as a function of time yielded eqn (4)

$$-\ln[\text{epoxide}] = k_{\text{obs}}t \tag{4}$$

where t is time and k_{obs} is the observed pseudo-first-order rate constant for PO conversion.

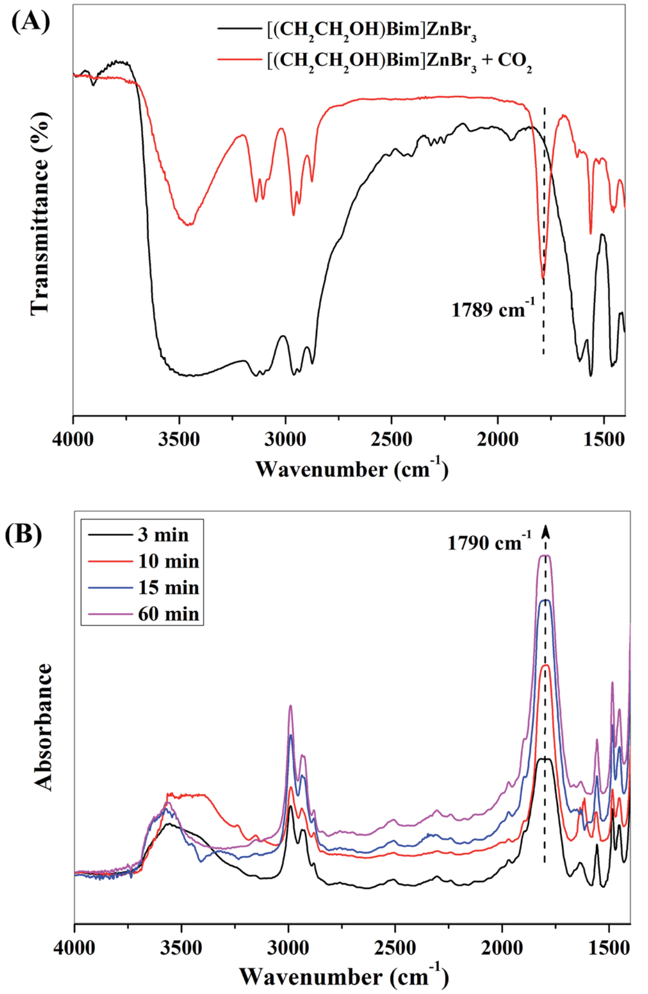


Fig. 4 (A) FT-IR spectra monitoring the interaction between the catalyst and CO$_2$. Reaction conditions: n (cat.) = 0.08 mmol, P (CO$_2$) = 2.5 MPa, T = 120 °C, t = 30 min; (B) FT-IR spectra monitoring the PC synthesis at various reaction times. Reaction conditions: 34.5 mmol PO, 0.25 mol% Cat., P (CO$_2$) = 2.5 MPa, T = 120 °C.

After CO$_2$ was introduced into the reaction system containing [(CH$_2$CH$_2$OH)Bim]Br or [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$ catalyst at different temperatures, the PO concentrations decreased with reaction time as shown in Fig. S2 and S3.† The k_{obs} could be determined from the slope of the natural logarithm of remaining PO concentration *versus* time at different temperatures based on eqn (4). The plots were linear as shown in Fig. S4.† The kinetic equations, correlation coefficient R and observed pseudo-first-order rate constant (k_{obs}) are listed in Table S1.†

According to the Arrhenius equation, the activation energies with respect to the CO$_2$ cycloaddition to PO catalyzed by [(CH$_2$CH$_2$OH)Bim]Br and [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$ could be calculated as shown in Fig. 3. The derived data are summarized in Table 2.

The activation energies were 34.1 kJ mol^{-1} and 19.4 kJ mol^{-1} for [(CH$_2$CH$_2$OH)Bim]Br and [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$, respectively, indicating that ZnBr$_2$ played the main role in reducing the activation energy. This was specifically attributable to the synergistic effects of the zinc halides, which acted as Lewis acids to form the zinc-epoxide adduct, cooperating with hydroxyl groups and bromide anions to facilitate the ring-opening reaction of PO, which was the rate-limiting step of CO$_2$ cycloaddition to PO.

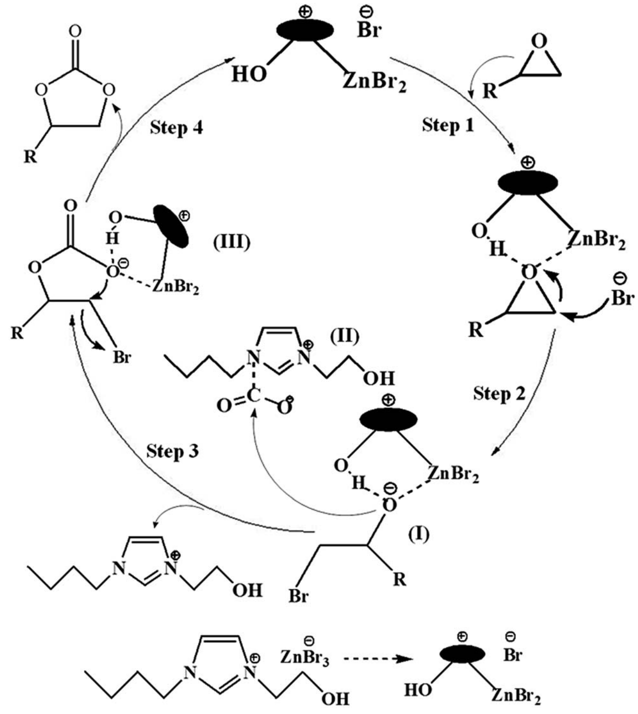
3.4. Catalytic activity towards CO$_2$ cycloaddition to other epoxides

In order to show the potential and general applicability of the novel Zn-TSILs catalysts, the coupling reactions of CO$_2$ with various epoxides were carried out over [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$ in Table 3. [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$ was an efficient catalyst for the conversions of a variety of substrates to the corresponding cyclic carbonates with high yields and selectivities. It is worth mentioning that although the catalytic reaction was impeded by the increase in the steric hindrance from the side chains of the substrates, the activities of styrene oxide and cyclohexene oxide were still excellent under longer reaction times at 120 °C and 2.5 MPa CO$_2$ pressure (entries 4 and 6). Especially for cyclohexene oxide, a much longer reaction time was needed to complete the conversion due to the higher steric hindrance originating from the two rings, which obstructed the nucleophilic attack by Br$^-$, causing a decreased ring-opening rate.[27,44] Hence, the extension to various epoxides reflected the outstanding efficiency of the Zn-TSILs catalysts.

3.5. Plausible reaction mechanism

In order to gain a deeper insight into the reaction mechanism, FT-IR spectra were employed to identify the possible intermediate under CO$_2$ pressure during the reaction. As shown in Fig. 4, after the reaction of CO$_2$ with the [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$ catalyst, there appeared a new band at 1789 cm^{-1} (Fig. 4A), which corresponded to the new asymmetric (C=O) vibration of the carbamate salt, presumably implying the activation of CO$_2$ by the alkaline nitrogen from [(CH$_2$CH$_2$OH)Bim]ZnBr$_3$.[45,46] Similarly, tracking the change and reaction degree during the process, the absorption peak at 1790 cm^{-1} ascribed to the carbonyl group of the PC product increased gradually along with the reaction time (Fig. 4B), proving the efficient proceeding of the cycloaddition reaction of PO and CO$_2$.

Based on the above results and previous literature,[47] we proposed a plausible mechanism for the CO$_2$ cycloaddition to epoxides in the presence of Zn mediated hydroxyl-functionalized ionic liquids (Scheme 5). It has been proved that epoxides can be activated by zinc halides through the formation of zinc-epoxide adducts.[15,38,39] Meanwhile, the hydroxyl groups in (CH$_2$CH$_2$OH)Bim$^+$ coordinated with the oxygen of PO through hydrogen bonds, also resulting in the activation of the PO molecule (step 1). Simultaneously, the bromide anion as a Lewis base nucleophilically attacked the less sterically hindered β-carbon atom of the epoxide, facilitating the ring-opening of PO (step 2). The cooperative interactions between cation and anion stabilized the intermediate oxyanion (I) before the insertion of CO$_2$. In parallel, the tertiary nitrogen from the IL cation reacted reversibly with CO$_2$ to form the



Scheme 5 A plausible mechanism for the cycloaddition of CO_2 and PO catalyzed by $[(CH_2CH_2OH)Bim]ZnBr_3$.

carbamate salt (II) as the activated species of CO_2.[45,46,48] Thereafter, the intermediate (I) made a nucleophilic attack on the carbamate salt (II) producing the new alkyl carbonate compound (III) (step 3), which eventually afforded the cyclic carbonate PC and regenerated the catalyst by the subsequent intramolecular ring-closure (step 4). Hence, the synergetic effects from the hydrogen bond donor (–OH), ionic liquid cation, and $ZnBr_3^-$ anion in this catalytic system promoted the reaction smoothly.

4. Conclusions

In conclusion, the novel Zn-based task-specific ionic liquids (Zn-TSILs) were developed, and exhibited highly catalytic activity toward the cycloaddition of CO_2 with various epoxides without using additional cocatalyst and solvent. Due to the synergetic effects of hydrogen bond donors (–OH), ionic liquid cations, and $ZnBr_3^-$ anions in this catalytic system, excellent yields of carbonates and high TOF values up to 794 h^{-1} were achieved in the presence of Zn-TSILs, and the catalyst could be reused at least four times without significant loss of reactivity. Further, comparative studies showed that the $[(CH_2CH_2OH)Bim]ZnBr_3$ catalyst reduced the activation energy by 14.7 kJ mol^{-1} compared with the $[(CH_2CH_2OH)Bim]Br$ catalyst, displaying the unique feature of $ZnBr_2$. The facile synthesis and good catalytic property of Zn-TSILs make them good candidates for further developments and applications in sustainable processes concerned with CO_2 fixation.

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