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Original Research

Facile Preparation of Poly(ionic liquid)s-zinc Halide Composite Toward Highly Efficient Conversion of CO_2 into Cyclic Carbonates

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Abstract

A class of novel poly(ionic liquid)s-ZnX_2 complexes ([IMEP]R-ZnX_2 (R = Cl, Br, X = Cl, Br, I) with multi-functional active sites were fabricated by a facile method and initially employed as efficient heterogeneous catalysts for transformation of CO_2 and epoxides into corresponding cyclic carbonates without the aid of any organic solvent and co-catalyst. Therein, the one-pot fabrication of poly(ionic liquid)s was realized using imidazole and epibromohydrin or epichlorohydrin as raw materials. The catalysts revealed pronounced activity and selectivity toward the cycloaddition reaction under the optimal conditions (120ºC, 2.0 MPa and 3 h). The effect parameters of the reaction, such as reaction temperature, duration time, initial CO_2 pressure, amount of catalyst, the counter anions and halide ions of the catalysts were also investigated. The cooperative effect of Lewis acidic Zn sites and hydroxyl group for polarizing the oxygen atom of epoxide, together with the nucleophilic attack of X^- on the adjacent β-carbon atom of epoxide promotes readily the ring-opening, thus leading to the enhanced activity. In addition, the catalytic activity can be retained substantially after five times of recycling test.

Keywords: Poly(ionic liquid)s, zinc bromide, heterogeneous catalysis, CO_2 cycloaddition, cyclic carbonates

Introduction

It is well-known that CO_2 is the major culprit to cause global warming and climate deterioration. However, CO_2 as an ample, facilely available, nontoxic and reproducible C1 feedstock can be converted to various useful fine chemicals [1-3]. Among the alternative approach for CO_2 chemically transformation, the cycloaddition of CO_2 to epoxides has been regarded as one of the most potential strategies at a large scale, due to its 100% atom-economical and green process. Additionally, the product of cyclic carbonates can be extensively employed as valuable polar aprotic solvents, electrolyte for lithium ion batteries, the monomers for synthesis of polycarbonates and intermediates of fine organic compounds [4-7]. However, the CO_2

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cycloaddition reaction does not proceed automatically, owing to the naturally thermodynamical and kinetic stability of CO_2, even though it is highly exothermic [8]. To date, numerous catalytical systems have been proposed to promote the CO_2 cycloaddition procedure, such as alkali metal salts [9], metal oxides [10], molecular sieves [11], polyoxometalate [12, 13], metal-organic frameworks [14], Lewis acids or bases [15, 16], etc.

Furthermore, in recent few decades, ionic liquids (ILs) was proved to be promising efficacious catalysts and have received increasing attention [17, 18], like quaternary ammonium salts [19], quaternary phosphonium salts [20], imidazolium salts [21, 22], guanidinium salts [23, 24], due to their extremely low vapor pressure, thermal and chemical stability, a broad range of liquid temperature as well as low toxicity. Whereas, these ionic liquids frequently exhibited poor activity toward the cycloaddition of CO_2 with epoxides when used as catalyst alone, owing to their insufficient active sites. Therefore, many efforts were devoted to elevate the catalytic performance of ionic liquids. Modifying the ionic liquids with hydrogen bond donor, such as hydroxyl, carboxyl, amino and so on, which benefits to promote the ring-opening of epoxides via the polarization of C-O bond from epoxides, may be an efficient approach for accelerating the CO_2 cycloaddition reaction [25-27]. Additionally, it was demonstrated that ionic liquids in combination with metal halides, especially zinc halides, could dramatically improve the catalytic property. For instance, Kim and co-workers [28] found that imidazolium zinc tetrahalides complexes showed surprisingly high activity at 100ºC and 3.5 MPa toward CO_2 cycloaddition reaction and the TOF was up to 3545 h^{-1} for 1-butyl-3-methylimidazolium bromide-$ZnBr_2$. Sun et al. [29] reported that the conjunction of phosphonium halides and $ZnCl_2$ exhibited excellent catalytic activity and high TOF value could be realized in the presence of $ZnCl_2/PPh_3C_6H_{13}Br$ (molar ratio = 1:6) at 120ºC and 1.5 MPa. Thereafter, varieties of catalytic systems composing of zinc halides and ILs were developed [30-35], which displayed superior activity compared with the ILs moieties due to their bifunctional Lewis acid/base active sites. In most cases, however, these catalytic systems suffered from harsh procedure for separation and purification of products, which may result in the loss of catalytic activity, because of their homogeneous nature. Consequently, many attempts have been made construct heterogeneous catalysts for efficient CO_2 conversion involving multiple active sites.

Recently, plenty of poly(ionic liquid)s, as a typical heterogeneous catalyst, have been employed for the cycloaddition of CO_2 to epoxides [36-39], which revealed preeminent stability and recyclability. Encouraged by previous research, herein, a series of hydroxyl functional poly(ionic liquid)s-zinc halides compositely heterogeneous catalysts were proposed in view of the high activity of catalysts with ionic liquids and zinc halides. The poly(ionic liquid)s were facilely fabricated through one-pot polymerization using imidazole and epichlorohydrin/epibromohydrin as monomers, as illustrated in Scheme 1. Interestingly, both hydroxyl group and available halide ion can be synchronously obtained through such approach. It should be mentioned that even though the catalysts of polymer nanoparticles grafted zinc halides have been reported to catalyze CO_2 cycloaddition in our previous literature [40], the resultant catalysts containing poly(ionic liquid)s in this paper can be prepared much easily and present environmentally benign.

To our delight, such catalytic systems exhibit satisfactory activity, recyclability as well as stability for the cycloaddition of CO_2 and epoxides without any solvent and co-catalyst. Additionally, systematic investigations towards the effect of halide ions and the operation conditions, like reaction temperature, duration time, catalyst dosage and initial CO_2 pressure, on the reaction process were also performed. Furthermore, a tentative reaction mechanism was proposed according to the experimental results.

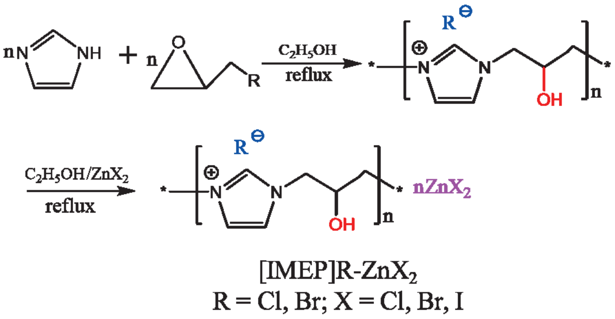
Experimental

Reagents

The CO_2 (99.9% purity) purchased from Nanchang Guoteng Co. was used without any further treatment. Propylene oxide was received from Sinopharm Chemical Reagent Co., Ltd. The other epoxides were obtained from Alfa Aesar China Co., Ltd. Imidazole (99%), zinc chloride, zinc bromide and zinc iodide, epibromohydrin, epichlorohydrin were purchased from Aladdin Chemical Co. All reagents were used without further purification.

Characterization

^1H nuclear magnetic resonance (NMR) spectra were examined at room temperature using a Bruker 400 MHz spectrometer and D_2O was used as a solvent. The Fourier transformed infrared (FT-IR) spectra were collected by a Bruker vertex 70 FT-IR spectrophotometer. The microstructures of samples



Scheme 1. Preparation of [IMEP]R-ZnX_2 catalysts.

and the accompanying Energy dispersive X-ray spectroscopy were observed using a Nova NanoSEM 450 microscope and the accessory INCA 250. The X-ray diffraction (XRD) patterns were recorded by a Bruker AXS-D 8 Advance X-ray diffractometer utilizing Cu Kα radiation (λ = 1.5408 Å) in the 2θ range of 5-80º. Thermogravimetric analysis (TGA) was conducted on a SDT Q600 (TA Instruments-Waters LLC) at a heating rate of 10ºC/min under a nitrogen flow.

Preparation of the Poly(ionic liquid)s

The poly(ionic liquid)s were fabricated as previously reported with a minor modification [41]. In a typical reaction, imidazole (10 mmol) and anhydrous ethanol (60 mL) were added in sequence into a 150 mL three-neck-round flask. Then the mixture was heated to 45ºC and refluxed for 1 h. Epibromohydrin (10 mmol) was slowly added after the completely dissolution of the solid, and then the reaction solution was stirred at 75ºC for 72 h under a nitrogen atmosphere. After reaction, the mixture was cooled to room temperature, and the solid precipitate was obtained by filtration and abstersion with ethanol. The products imidazolium-epibromohydrin copolymers (denoted as [IMEP]Br) were dried at 60ºC for 12 h under vacuum. [IMEP]Br. ^{1}H NMR (400 MHz, D2O): δ = 7.56 (s, 2H), 4.54 (d J = 8.0 Hz, 2H), 4.33 (s, 1H), 4.23(t, J = 12.0 Hz 2H). 13C NMR (100.6 MHz, D2O): δ = 136.80, 123.30, 68.70, 52.22. IR (neat): n = 3480, 3162, 3121, 2967, 2897, 1576, 1468 cm^{-1}. Analogously, the imidazolium-epichlorohydrin copolymers (denoted as [IMEP]Cl) was synthesized via the same method except that using epichlorohydrin rather than epibromohydrin. [IMEP]Cl. ^{1}H NMR (400 MHz, D2O): δ = 7.57 (s, 2H), 4.55 (d, J = 12.0 Hz, 2H), 4.37 (s, 1H), 4.25 (t, J = 8.0 Hz, 2H). 13C NMR (100.6 MHz, D2O): δ = 137.12, 123.30, 68.19, 52.38. IR (neat): n = 3415, 3269, 3143, 2945, 2850, 1566, 1438 cm^{-1}.

Immobilization of Zinc Halides on the Poly(ionic liquid)s

In a typical procedure, [IMEP]Br (0.8 g) and anhydrous zinc bromide (2.5 mmol) were charged in 40 mL anhydrous ethanol, and stirred at 70ºC for 24 h under N_2 atmosphere. After reaction, the obtained solid was filtered out and washed several times with anhydrous ethanol, followed by drying at 60ºC for 6 h under vacuum to give the poly(ionic liquid)s-zinc bromide composite (denoted as [IMEP]Br-$ZnBr_2$.). The synthetic procedure for [IMEP]Cl-$ZnCl_2$, [IMEP]Cl-$ZnBr_2$, [IMEP]Cl-ZnI_2, [IMEP]Br-$ZnCl_2$, [IMEP]Br-ZnI_2 were similar to that of [IMEP]Br-$ZnBr_2$ except that $ZnBr_2$ was substituted with $ZnCl_2$, ZnI_2 or [IMEP]Cl was replaced by [IMEP]Br. [IMEP]Br-$ZnBr_2$. ^{1}H NMR (400 MHz, D2O): δ = 7.56 (s, 2H), 4.55 (d, J = 12.0Hz, 2H), 4.37(s, 1H), 4.23(t, J = 8.0 Hz, 2H). IR (neat): n = 3480, 3162, 3121, 2967, 2897, 1576, 1468, 632 cm^{-1}.

General Procedure for Synthesis of Cyclic Carbonates

In a typical run, epoxide (35.7 mmol), certain catalyst dosage (calculated upon the molar weight of Zn) and a suitable amount of biphenyl (as internal standard for GC analysis) were added to a 50 mL high-pressure stainless-stress autoclave reactor, then the reactor was pressurized with a desired pressure of CO_2 at a selected temperature and stirred for a designated time. After the reaction, the reactor was cooled down to 0ºC in an ice-water bath and the residual CO_2 was slowly exhausted. The products were quantitatively analyzed using Agilent 7890A gas chromatograph equipped with a TCD detector and a DB-WAX capillary column (30 m × 0.53 mm × 1.0 μm).

Results and Discussion

Characterization of the Synthesized Catalysts

The chemical structure of the as-prepared samples was testified by FT-IR spectra. As seen in Fig 1a), the spectrums at 2927, 1566 and 1413 cm^{-1} are attributed to N-H, C=C and C-N stretching vibrations of imidazole framework, respectively [42]. Compared with that of imidazole (Fig 1a), the spectrum of [IMEP]Br (Fig 1b) exhibits new peaks at 3450 and 1168 cm^{-1}, attributing to the O-H stretching vibrations of hydroxyl and the C-N$^+$ stretching vibrations of imidazolium. In addition, the peaks at 2927 cm^{-1} disappear, implying that the reaction between imidazole and epibromohydrin successfully occurred. Moreover, upon complexation with $ZnBr_2$, the broad peaks at 3450 cm^{-1} shift to higher frequencies at 3458 cm^{-1} over the spectrum of [IMEP]Br-$ZnBr_2$ (Fig 1c), indicating that the hydrogen bond interaction between hydroxyl and Br$^-$ is weakened by the incorporation of $ZnBr_2$ [31]. All of above results

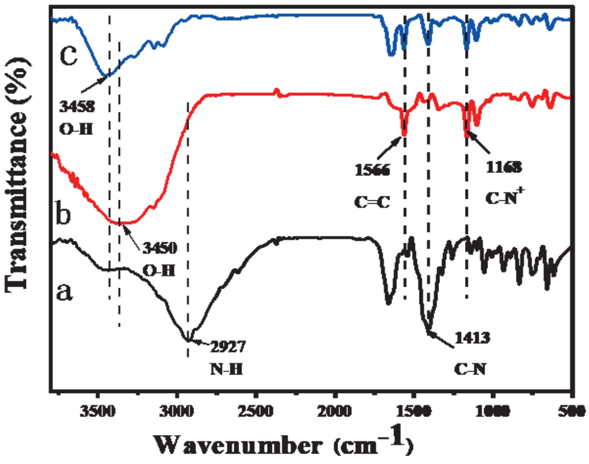


Fig. 1. FT-IR spectrums of a) imidazole, b) [IMEP]Br and c) [IMEP]Br- $ZnBr_2$.

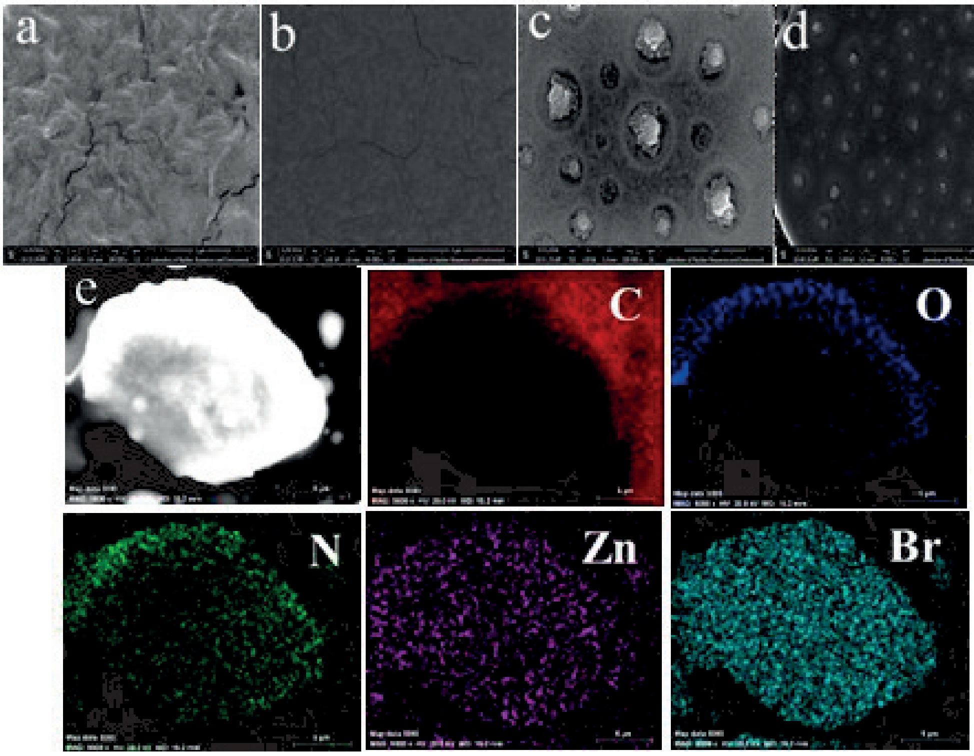


Fig. 2. SEM images of (a, b) [IMEP]Br, (c, d) [IMEP]Br- $ZnBr_2$ and e) EDS mapping images of [IMEP]Br- $ZnBr_2$.

confirmed that the poly(ionic liquid)s-$ZnBr_2$ composites was smoothly prepared.

The morphology of [IMEP]Br and [IMEP]Br-$ZnBr_2$ catalysts were collected by SEM. As presented in Fig 2a) and b), the SEM images of [IMEP]Br exhibit a small number of different sizes of spherical particles on the smooth surface, while after coordination with $ZnBr_2$, [IMEP]Br-$ZnBr_2$ surface becomes to be rough (Fig. 2c and d) and the $ZnBr_2$ particles are well dispersed on the surface of [IMEP]Br. This structure is favorable for the contact of metal halides active sites and PO molecules, which affords these catalysts desired catalytic activity. Furthermore, the concomitant and uniformly distributive C, N, O, Zn and Br element in the complex material can be confirmed by the EDS mapping images (Fig. 2e). The results also validate the successful introduction of the $ZnBr_2$ into the polymer frameworks, which are in accordance with the results of FT-IR. Table 1 summarized the loading contents of ZnX_2 (X = Br, Cl, I) on the [IMEP]R (R = Br, Cl) based on the Zn content.

The XRD patterns of [IMEP]Br and [IMEP]Br-$ZnBr_2$ were shown in Fig 3. As depicted in Fig. 3a), the XRD pattern of [IMEP]Br reveals a wide peak at $2\theta = 22\text{-}28°$, which may be the result of diffraction at the crystalline region of the polymer moiety [43]. It can be clearly seen that the XRD pattern of [IMEP]Br-$ZnBr_2$ (Fig. 3b) is similar to [IMEP]Br and the diffraction

Table 1. The loading contents of ZnX_2 (X = Br, Cl, I) on the [IMEP]R (R = Br, Cl).

Catalyst	EDS results							Amount of Zn (mmol/g)
	C (wt.%)	N (wt.%)	O (wt.%)	Zn (wt.%)	Br (wt.%)	Cl (wt.%)	I (wt.%)	
[IMEP]Cl	49.6	22.7	13.3	—	—	14.4	—	—
[IMEP]Br	46.5	23.8	14.8	—	14.9	—	—	—
[IMEP]Cl-$ZnCl_2$	45.5	20.9	11.3	3.1	—	19.2	—	0.47
[IMEP]Cl-$ZnBr_2$	45.9	22.1	13.7	1.1	9.3	7.9	—	0.17
[IMEP]Cl-ZnI_2	45.6	21.4	12.6	2.3			18.1	0.35
[IMEP]Br -$ZnCl_2$	45.6	23.3	11.4	4.9	8.4	6.7	—	0.76
[IMEP]Br -$ZnBr_2$	44.3	23.1	18.3	5.6	8.7	—	—	0.86
[IMEP]Br -ZnI_2	40.9	16.9	3.1	5.5	7.1	—	26.6	0.85

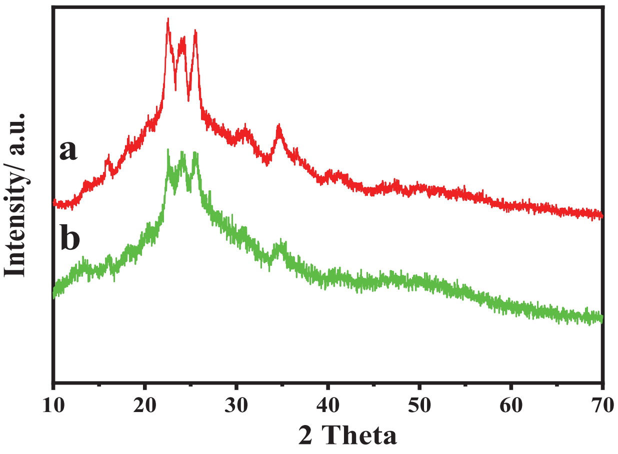


Fig. 3. XRD patterns of a) [IMEP]Br- $ZnBr_2$, b) [IMEP]Br.

peaks of $ZnBr_2$ are not obviously observed, indicating that $ZnBr_2$ are highly dispersed in the [IMEP]Br [44], which is consistent with the SEM images.

In order to describe the electronic state and the superficial element composition of catalytic materials, [IMEP]Br and [IMEP]Br-$ZnBr_2$ were examined by XPS. From Fig. 4a), there exists only C, O, N and Br elements in [IMEP]Br, while additional Zn element can be observed over [IMEP]Br-$ZnBr_2$. These results conform to the chemical ingredient of the resultant catalysts illustrated in Scheme 1. Fig. 4(b-d) showed the high-resolution spectra of the C 1s, N 1s and Br 3d. The high-resolution spectra of C 1s is divided into three peaks at 284.7 (C-C/C-H in alkyl groups), 286.1 (C-N in imidazole ring) and 286.7 eV (Chetero of imidazolium groups) [45], respectively. The N 1s spectra (Fig. 4c) of [IMEP]Br and [IMEP]Br-$ZnBr_2$ exhibit a peak at 401.3 and 401.6 eV, respectively, confirming the presence of nitrogen with positive charge in the imidazole ring [46, 47].

Furthermore, both the Br 3d spectra of [IMEP]Br and [IMEP]Br-$ZnBr_2$ (Fig. 4d) exhibit a peak at ~68.0 eV (Br 3d 3/2), affirming the existence of the negatively charged Br^- [48, 49], which are conducive to the nucleophilic attack on the epoxide. Notably, the binding energy of N and Br elements in [IMEP]Br-$ZnBr_2$ appear a upshift in comparison to that of [IMEP]Br, which are ascribed to the coordinate effect between Zn^{2+} and N/Br elements, therefore leading to the decrease in their electron density. This phenomenon also verifies the strong interaction between [IMEP]Br substrate and $ZnBr_2$.

Moreover, thermal analysis was used to examine the decomposition profiles of [IMEP]Br and [IMEP]Br-$ZnBr_2$, and the results were depicted in Fig. 5. It is apparent that both materials present excellent stability up to 320°C. Unlike [IMEP]Br, the decomposition of [IMEP]Br-$ZnBr_2$ contains two endothermic steps at 362 and 567°C, possibly ascribing to the disintegration of the polymer and the ZnBr2, respectively. It is generally recognized that the CO_2 cycloaddition reaction proceeds below 140°C, far lower than the onset temperature of the catalyst destruction.

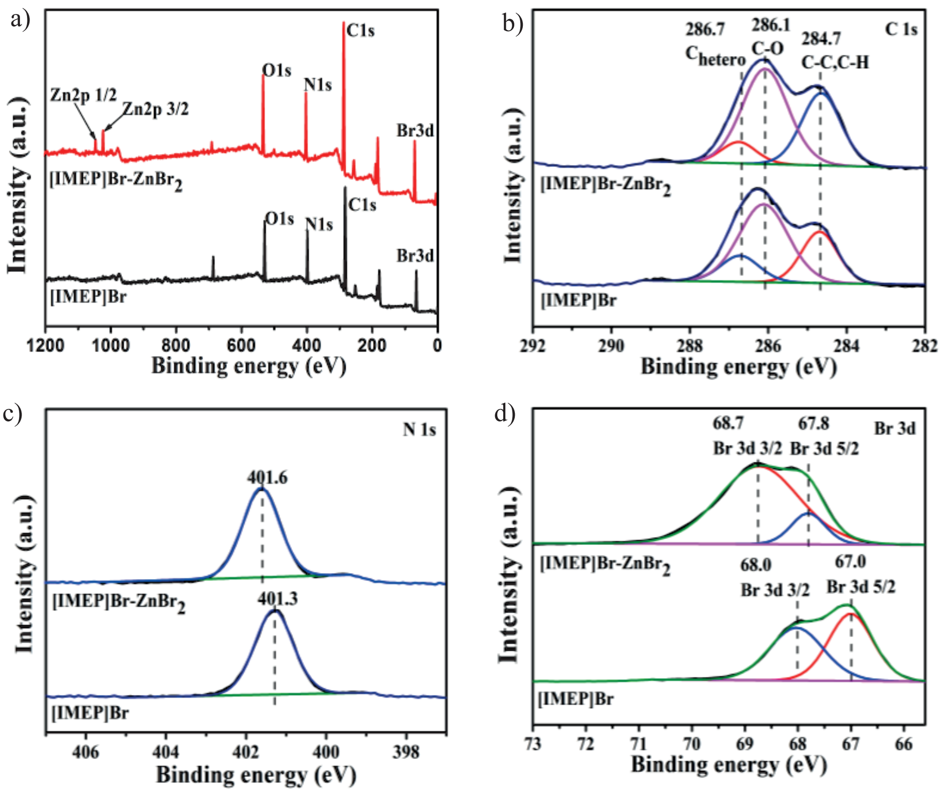


Fig. 4. a) The survey XPS spectra of [IMEP]Br and [IMEP]Br-$ZnBr_2$; b) C 1s, c) N 1s and d) Br 3d of [IMEP]Br and [IMEP]Br-$ZnBr_2$.

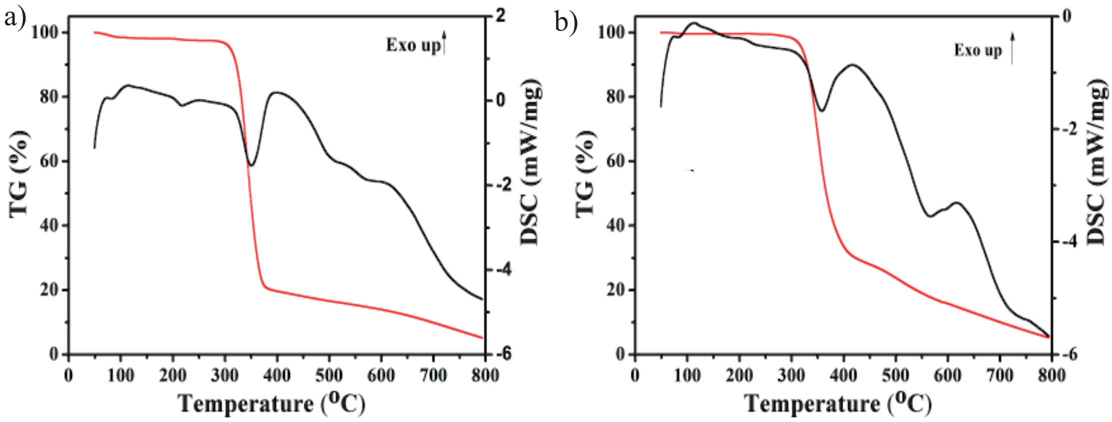


Fig. 5. TG and DSC curves of a) [IMEP]Br, and b) [IMEP]Br- ZnBr$_2$.

Catalytic Performance

The cycloaddition reaction of PO with CO$_2$ was assigned as the model reaction to assess the catalytic performance of the complex materials, and the results were listed in Table 2. Almost no conversion was gained in the case of catalyst-free (Table 2, entry 1), and the PC yields were very low (<16.4%) (Table 2, entries 2-4) when either ZnCl$_2$, ZnBr$_2$ or ZnI$_2$ used as catalyst alone. As expected, with separate 0.25 mol% of [IMEP]Cl or [IMEP]Br as catalyst for the reaction, PC yield of 35.6%, 53.7% were obtained, respectively (Table 2, entries 5 and 6), which probably due to the acceleration of the epoxy ring-opening, resulting from the polarization of C-O bond induced by hydrogen bonds between hydroxyl groups and epoxides [50, 51]. In addition, the [IMEP]Br exhibits higher catalytic activity than [IMEP]Cl (Table 2, entries 6 vs 5), ascribing to the nucleophilicity of the anions decrease in the sequence of Br^->Cl^-, which was in conformity to the previously reports [52, 53]. Delightedly, the Zn-containing materials reveal outstanding catalytic activity. When combined [IMEP]R and ZnX$_2$ (Table 2, entries 7 to 11), the catalytic activities were significantly improved in comparison with [IMEP]R moieties (Table 2, entries 5 and 6), and the catalytic activities decreased in the sequence of [IMEP]Cl-ZnI$_2$>[IMEP]Cl-ZnBr$_2$>[IMEP]Cl-ZnCl$_2$ (Table 2, entries 7 to 9) and [IMEP]Br-ZnI$_2$>[IMEP]Br-ZnBr$_2$>[IMEP]Br-ZnCl$_2$ (Table 2, entries 10 to 12), which were in accordance with the effect of ZnI$_2$, ZnBr$_2$, ZnCl$_2$ (Table 2, entries 2 to 4). Besides, it was detected that the catalytic activity of different [IMEP]R-ZnX$_2$ decreased in the following order of (Br^-+ ZnBr$_2$) ≈ (Cl^-+ ZnI$_2$) ≈ (Br^-+ ZnI$_2$)>(Cl^-+ ZnBr$_2$)>(Br^-+ ZnCl$_2$)>(Cl^-+ ZnCl$_2$) (Table 2, entries 7 to 12), demonstrating that the counter anions and halide ions both play an important role in the cycloaddition. This order might be attributed to the balance of leaving ability and nucleophilicity of halide ions (Cl^-, Br^-, and I^-) [54]. Even when used [IMEP]Br-ZnI$_2$ as catalyst for the reaction, the PC yield can reach 87.6% within only 1.5 h (Table 2, entry 13). Additionally, it presents an interior activity for the case of simple mechanical mixture of [IMEP]Br and ZnBr$_2$ upon the molar ratio of 1:1 (Table 1, entry 14) in comparison to [IMEP]Br-ZnBr$_2$ complex catalyst, due to their relative isolation between the active sites. Collectively, it can be concluded that the [IMEP]R-ZnX$_2$ composites possess enhanced catalytic activity for the CO$_2$ cycloaddition.

Effect of Reaction Conditions

It is generally suggested that reaction conditions such as catalyst dosage, reaction temperature, onset

Table 2. Catalytic performance of various catalysts [a].

Entry	Catalyst	Catalytic results	
		Yield (%)	Sel. (%)
1	None	Trace	Trace
2	ZnCl$_2$	1.2	73.5
3	ZnBr$_2$	13.2	99.3
4	ZnI$_2$	16.4	99.8
5	[IMEP]Cl	37.6	92.9
6	[IMEP]Br	53.7	97.7
7	[IMEP]Cl-ZnCl$_2$	64.4	98.8
8	[IMEP]Cl-ZnBr$_2$	71.8	96.6
9	[IMEP]Cl-ZnI$_2$	97.3	99.4
10	[IMEP]Br-ZnCl$_2$	67.8	99.4
11	[IMEP]Br-ZnBr$_2$	97.7	97.2
12	[IMEP]Br-ZnI$_2$	97.2	98.6
13	[b][IMEP]Br-ZnI$_2$	87.6	99.2
14	[c][IMEP]Br/ZnBr$_2$	82.8	99.3

[a] Reaction conditions: PO 35.7 mmol, catalyst 0.25 mol%, CO$_2$ pressure 2 MPa, temperature 120ºC, time 3 h

[b] Time 1.5 h

[c] Equal catalyst amount (0.86 mmol)

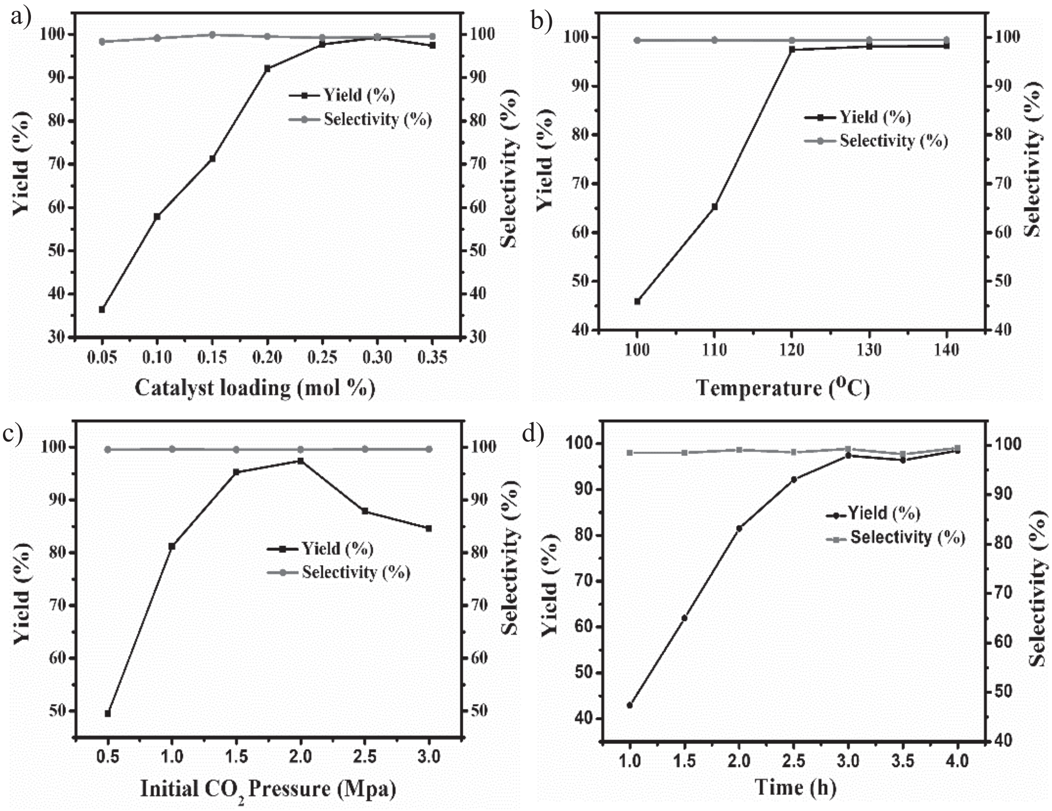


Fig. 6. The effect of reaction factors on the yield and selectivity of propylene carbonate. a) catalyst amount; b) reaction temperature; c) CO_2 pressure; d) reaction time.

CO_2 pressure and duration time have a significant influence on product yield. In this study, we adopted [IMEP]Br-$ZnBr_2$ for further investigation on account of its superior activity. Fig. 6a) presents the dependence of catalyst loading on the PC yield and selectivity at 120ºC, 2 MPa CO_2 pressure and 3 h. It is noted that catalyst dosage remarkably affects the yield of the PC. The PC yield rises from 36.4% to 97.7% as the loading of catalyst increased from 0.05 to 0.25 mol%, owing to the incremental number of active sites accessible. However, the yield remains almost constant as catalyst loading further increased. Gratifyingly, the selectivity of PC remains unchanged (>99%). Therefore, 0.25 mol% was selected as the optimal amount of [IMEP]Br-$ZnBr_2$.

The influence of reaction temperature on the reaction was shown in Fig. 6b). According to Fig. 6b), the yield of PC notably elevates from 45.9% to 97.4% when the temperature varies from 100ºC to 120ºC. With further increase of temperature (130ºC to 140ºC), the yield almost retains unchanged. According to previous reports, high temperature (>130 or 140ºC) could arise a distinct decay of PC selectivity regarding to ILs as catalysts, resulting from the occurrence of side reactions, like isomerization of acetone, hydrolysis to diol, and/or thermal polymerization [55-57]. Delightedly, almost 100% PC selectivity was retained even under high reaction temperature. Thus, 120ºC was suggested to be the optimal temperature for the reaction.

In addition, the correlation of initial CO_2 pressure with the reaction process was also investigated. As shown in Fig. 6c), initial CO_2 pressure has a great influence on the PC yield. There exists a rapid increase of PC yield (from 49.5% to 97.4%) in the low-pressure range (from 0.5 to 2.0 MPa), whereas, further promotion of pressure up to 3.0 MPa gives rise to moderate reduction of PC yield (from 97.4% to 84.6%). A similar influence of onset CO_2 pressure on the reaction was also discerned over other catalytic

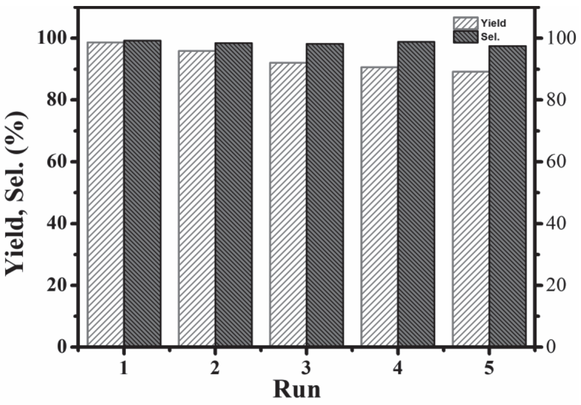
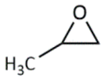
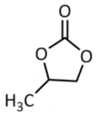
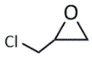
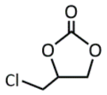
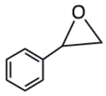
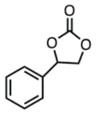
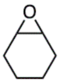
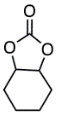


Fig. 7. Recycle of catalyst for cycloaddition reaction. (reaction condition: PO 35.7 mmol, CO_2 pressure 2 MPa, catalyst 0.25 mol%, 120ºC, 3 h).

Table 3. Cycloaddition of CO_2 to different epoxides catalyzed by [IMEP]Br-$ZnBr_2$ [a].

Entry	Epoxide	Cyclic carbonate	Time (h)	Catalytic results	
				Yield (%)	Sel. (%)
1			3	97.7	97.9
2			2	96.4	98.1
3			4	98.2	99.4
4			24	36.3	99.1

[a] Reaction conditions: epoxides 35.7 mmol, catalyst 0.25 mol%, temperature 120ºC, CO_2 pressure 2.0 MPa

systems [58-60], which can be explained upon the concepts of reaction equilibrium and mass transfer of reactant. As the reaction proceeded in the low-pressure area, the acidic CO_2 dissolved in basic epoxide to form CO_2-PO complexes, leading to an enhancement in the PC yield [20, 61]. Nevertheless, CO_2-PO complexes turned into much tightened as the initial CO_2 pressure further increased, resulting in the difficulty in separation of CO_2 and PO, which is inconducive to the cycloaddition reaction catalyzed by [IMEP]Br-$ZnBr_2$. Therefore, 2.0 MPa was regarded as the most appropriate reaction pressure for this catalytic system.

Moreover, the relationship between reaction time and PC yield as well as selectivity was presented in Fig. 6d). The results suggest that the yield of PC closely relates to the reaction time. The yield of PC increases rapidly from 2.9% to 97.4% with the rise of duration time from 1.0 h to 3.0 h in the presence of 0.25 mol% [IMEP]Br-$ZnBr_2$ at 120ºC and 2.0 MPa. Prolonging time from 3.0 h to 4.0 h, the PC yield elevates subtly, while the selectivity of PC remains at 99 % throughout. Therefore, 3 h was considered as the most suitable reaction time for this reaction.

Catalyst Recycling

The stability and reusability are the primal interest for the application of heterogeneous catalyst in the practical operation. To demonstrate the stability of [IMEP]Br-$ZnBr_2$ catalyst, several catalytic recycles were conducted under the optimized conditions. Typically, in each operation, the catalyst was recycled through facile filtration, followed by reused for next run. As displayed in Fig. 7, the catalyst could be reused five runs with only a minor loss in the yield and selectivity of PC. Furthermore, the chemical structure and heat

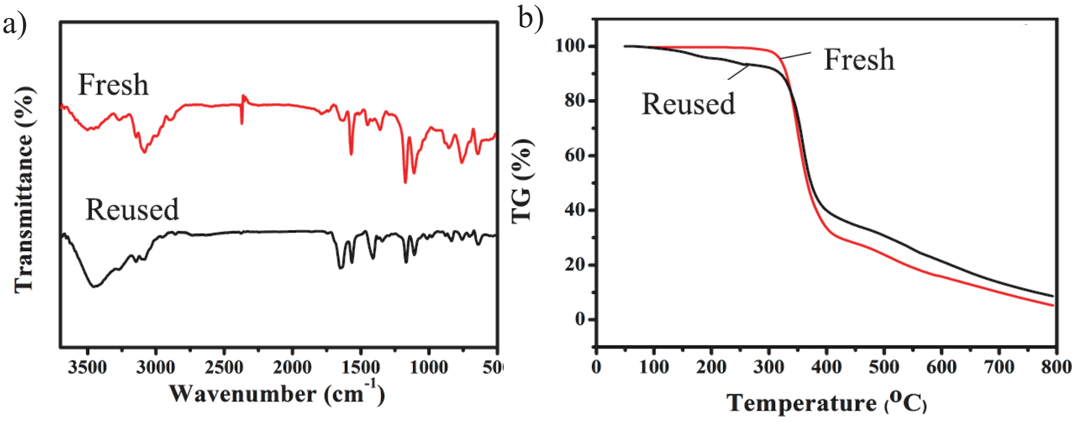
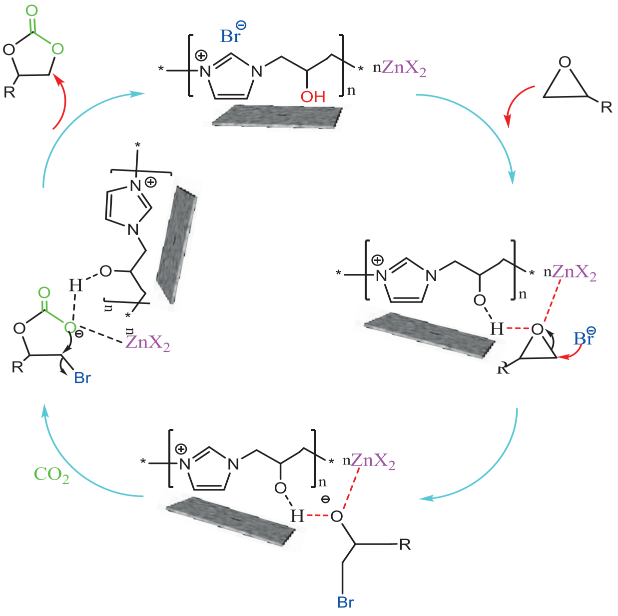


Fig. 8. FT-IR profiles a) and TGA curves b) of fresh and reused [IMEP]Br- $ZnBr_2$.



Scheme 2. Plausible mechanism for the cycloaddition of CO_2 and epoxide catalyzed by [IMEP]Br-$ZnBr_2$.

resistance of [IMEP]Br-$ZnBr_2$ catalyst after recycling experiments were examined by FT-IR, and TGA analysis. In comparison to the FT-IR spectra of the fresh catalyst (Fig. 8a), the recycled catalyst exhibits all the characteristic peaks with the merely slight attenuation in intensity. In addition, TGA curves (Fig. 8b) present that the reused catalyst occurs a diminutive degradation before the collapse of integrated frameworks compared with the fresh one. The above results may be responsible for the minor decline in activity over recycled catalyst after five runs.

Cycloaddition of CO_2 to Various Epoxides

In order to examine the potential application of [IMEP]Br-$ZnBr_2$ catalyst, the cycloaddition of CO_2 with varied epoxide substrates were investigated, and the results were shown in Table 3. Under the adopted condition, all reactions run smoothly and the corresponding cyclic carbonates can be obtained. It is well-known that the epoxides with an electro-withdrawing group are conducive to ring-opening of epoxides [62]. Hence, the 96.4% yield of corresponding product can be gained within only 2 h (Table 3, entry 2) when the epichlorohydrin is employed as reaction substrate. The reactivity of styrene oxide (Table 3, entry 3) is somewhat lower compared with PO and epichlorohydrin, owing to the greater steric hindrance that impedes nucleophilic attack of Br- on the epoxy ring [63]. Because of the larger restraint stemmed from the double rings, the cyclohexene oxide (Table 3, entry 4) reveals the most inferior yield of the corresponding cyclic carbonate. Furthermore, the reaction reveals outstanding selectivity regardless of the electro-withdrawing or steric effect of substrates.

Plausible Reaction Mechanism

DFT calculations showed that the procedure of catalyzing CO_2 and epoxides to synthesis of cyclic carbonates is composed of three steps, that is, ring-opening of epoxide, insertion of CO_2 and intermolecular ring closure to cyclic carbonate. The ring-opening of epoxide was regarded as the rate-determining step [21, 50]. Therefore, the catalyst that accelerates the ring-opening of the epoxide can speed up the reaction proceed. The excellent catalytic performance of the [IMEP]Br-$ZnBr_2$ catalyst in this study may be mainly ascribe to the cooperative effect of Lewis acidic Zn sites and hydroxyl groups for epoxide excitation and the nucleophilic attack of Br^-. Based on the experimental results and predecessors' research, we proposed a plausible mechanism for the CO_2 cycloaddition to epoxides in the presence of Zn mediated hydroxyl-functionalized poly(ionic liquid)s. In the initial step, the C-O bond of epoxide was activated by the hydroxyl groups through forming hydrogen bond and by the Lewis acidic Zn sites via formation of a Zn-O coordination bond. Simultaneously, the less sterically hindered β-carbon atom of the epoxide was attacked by the nucleophilic Br^- (as Lewis base), facilitating the cleavage of C-O bond. Subsequently, CO_2 was inserted in the ring-open intermediate followed by the formation of cyclic carbonate through the subsequent intramolecular ring-closure with release of Br^- and recovery of the catalyst.

Conclusions

Overall, a class of novel poly(ionic liquid)s-supported zinc halides complex catalysts containing hydroxyl groups as heterogeneous catalysts were developed for the CO_2 cycloaddition in the absence of any additional co-catalyst and organic solvent. The [IMEP]Br-$ZnBr_2$ catalyst exhibited excellent catalytic activity with considerable yield (>97%) and approximately 100% selectivity toward the CO_2 cycloaddition reaction due to the cooperative effect of Lewis acidic zinc sites and the hydroxyl groups as well as nucleophilic Br^-. Furthermore, [IMEP]Br-$ZnBr_2$ as heterogeneous catalyst can be easily recycled and reused five runs with a minor decay in catalytic activity due to its slight deterioration of framework structure. Consequently, it is necessary to enhance the structure strength of such catalyst through improving the polymerization degree of poly(ionic liquid)s for further study. In this case, such catalyst will be a good candidate for CO_2 chemically fixation in practical application.

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Conflict of Interest

The authors declare no conflict of interest.

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