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Fixation and conversion of CO_2 using ionic liquids

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Abstract

Ionic liquids (ILs), a kind of novel green media composed entirely of cations and anions, have recently attracted considerable attention due to their unique properties such as non-volatility, tunable polarity, high stability and so on. In this work, the latest progress on the fixation and conversion of carbon dioxide (CO_2) using ILs as absorbents, catalysts or promoters has been summarized. The absorption performance of conventional ILs and task-specific ILs was systematically investigated, the conversion of CO_2 with epoxides, propargyl alcohols and amines using ILs was critically evaluated, and the significant advantages in the fixation and conversion of CO_2 using the ILs were demonstrated compared to the conventional absorbents and the catalytic systems without ILs. This research progress may finally lead to building of an in situ fixation–conversion process of CO_2 with ILs. If so, we are near an epoch of the fixation and utilization of CO_2, although there is obviously a long way to go for us to achieve such a goal.

Keywords: CO_2; Ionic liquids; Fixation; Conversion; Absorption; Reaction

1. Introduction

Carbon dioxide (CO_2) produced by combustion of fossil fuels is regarded as the most significant greenhouse gas; the increasingly accumulation of CO_2 in the atmosphere has attracted worldwide attention. On the other hand, CO_2 is one of the most naturally abundant, inexpensive, non-flammable and non-toxic C1 resources. Recalling the history of chemical industry, we can find many applications of CO_2 in the production of valuable products and materials such as carbonated drinks, urea, polycarbonates and so on [1–5].

In order to utilize CO_2 as C1 feedstock or sequestrate CO_2 for reduction of greenhouse effect, the investigation of efficient methods for capturing CO_2 from flue gas, in which CO_2 concentration varies from 3 to 14%, is critically important. One of the most commercially applied technologies is the chemical absorption of CO_2 by aqueous amines [6]. This technology, however, has shown serious disadvantages, such as the uptake of water into gas stream requires additional drying process and causes serious corrosion. The loss of volatile amines increases the operation cost and other difficulties and the evaporation of water for the release of CO_2 upon heating requires excessive cost of energy. The amines used for post-combustion CO_2 separation also are known to decompose, causing an environmental problem due to waste. Therefore, a novel solvent that could facilitate the separation of CO_2 from gas mixtures without concurrent loss of the capture solvent into the gas stream is highly required. In this regard, ionic liquids (ILs) show great potential as an alternative for such applications [7].

Ionic liquids are a kind of novel medium composed entirely of ions. Some typical cation/anion combinations comprising the main types of ILs are listed in Scheme 1. In recent years, significant progress has been made in the application of ILs as alternative solvents and catalysts due to their unique properties such as negligible vapor pressure, a broad range of liquid temperatures, excellent thermal and chemical stabilities, tunable physicochemical characteristics and selective dissolution of certain organic and inorganic materials [8–11].

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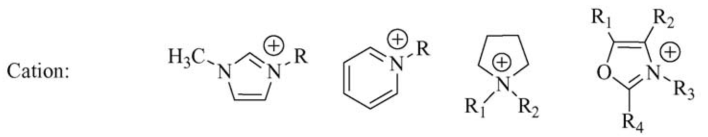
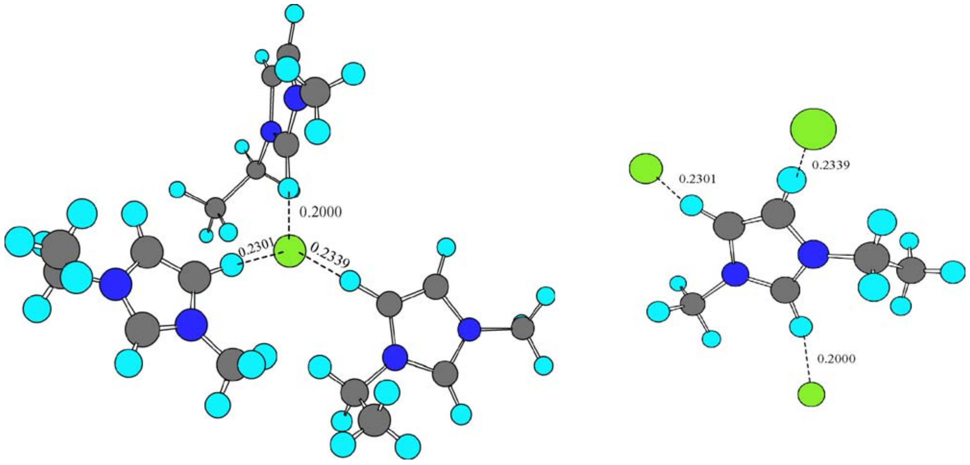


anion: I^-, Br^-, Cl^-, BF_4^-, PF_6^-, SbF_6^-, $ZnCl_3^-$, $CuCl_2^-$, $SnCl_3^-$, $N(SF_3SO_2)_2^-$, $N(C_2F_5SO_2)_2^-$, $N(FSO_2)_2^-$, $CF_3CO_2^-$, $CF_3SO_3^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Fe_2Cl_7^-$, $Sb_2F_{11}^-$

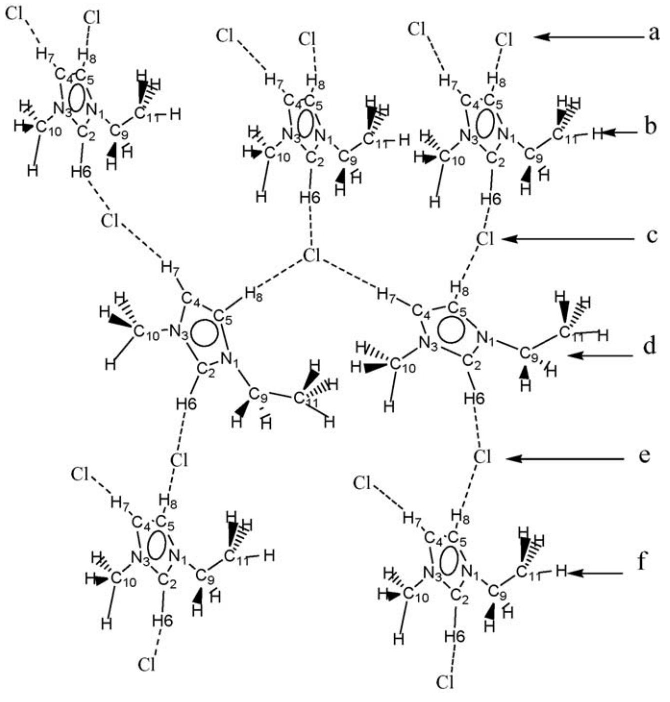
Scheme 1. The constituents of conventionally used ionic liquids.



Scheme 2. Hydrogen bond formed between chloride anion and imidazolium cation.

These unique features of macroscopic properties are essentially determined by the specific microstructures and interactions of ILs. Both spectroscopic investigation and quantum computations discovered the existence of hydrogen bonds between ionic pairs [12–16], and more interesting is the recent work discovering the hydrogen bond network in ILs as shown in Schemes 2 and 3 [17]. Obviously, these studies are helpful for us to understand the structure–property relationship of ILs, and will essentially lead to the rational design of functional ILs. If so, it can be expected that the exponential increase of publications on the fundamental and application studies of ILs will be continued as shown in Fig. 1.

The neglectable volatility of ILs results in a non-contaminated target gas and makes it especially fascinating in absorption of CO_2. More interesting is that CO_2 can significantly dissolve in the ILs as compared to conventional organic solvents even in the case of physical absorption [18,19]. Such higher solubilities show the great potential of ILs as not only good absorbents for CO_2 capture but also good solvents or catalysts for CO_2 reacting with other compounds such as epoxides, because the higher concentration of CO_2 in the ILs phase is a substantially positive factor for promoting the reaction of CO_2. Based on the above-mentioned merits of ILs as both absorbents and reaction media, we can further draw a fascinating picture like Fig. 2, which draws an in situ fixation–conversion coupling process of CO_2 in ILs powered by sunlight. Although there is obviously a long way to go for us to achieve such a dream or goal, the rapid progress on the fixation and conversion of CO_2 using ILs seems to be continuously validating the truth of our dream. In the limited pages of this paper we are trying to summarize these latest research results, especially focusing on the fixation/absorption of CO_2 in two classes of ILs, namely conventional ILs and task-specific ILs, and the conversion of CO_2 to valuable carbonyl-containing compounds via the reaction between CO_2 and epoxides,



Scheme 3. The hydrogen bond network of [emim]Cl ((a, c and e) Cl^- anions; (b, d and f) $[emim]^+$ cations).

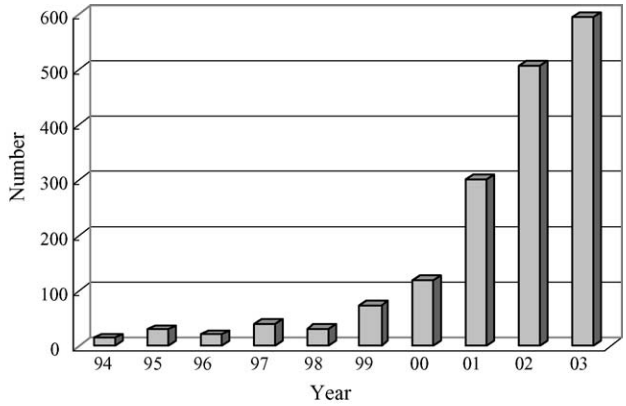


Fig. 1. Publications on the ionic liquids from 1994 to 2003.

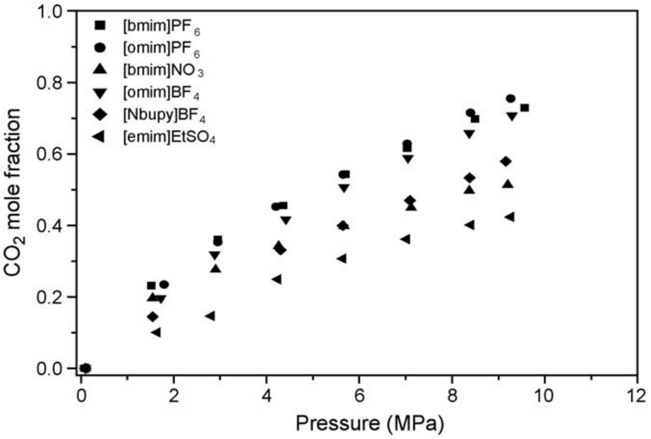


Fig. 3. Relationship between the solubility of CO_2 and pressure in six kinds of ionic liquids [20].

alcohols and amines using ILs as reaction solvents and/or catalysts or promoters.

2. Fixation of CO_2 using ionic liquids

A number of investigations have shown that CO_2 is remarkably soluble in ILs. According to the structural features and fixation/absorption mechanisms, the ILs can be classified into two categories, conventional ILs and task-specific ILs. The conventional ILs could absorb/fix less amount of CO_2 because of the physical interactions between CO_2 and ILs. The task-specific ILs with alkaline groups could sequester larger amount of CO_2 than that of conventional ILs because of the chemical interactions or reactivities between CO_2 and alkaline groups of ILs.

2.1. Fixation of CO_2 using conventional ionic liquids

There are several reported works on the fixation/absorption of CO_2 in conventional imidazolium-type ILs [19–24], which are composed of 1-alkyl-3-methylimidazolium ($[rmim]^+$) cations, and the anions such as BF_4^-, PF_6^-, Tf_2N^-, NO_3^- and $EtSO_4^-$. Blanchard et al. [20] determined the solubility of CO_2 in a series of imidazolium-type ILs including 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim]-PF_6), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([omim]PF_6), 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([omim]BF_4), 1-*n*-butyl-3-methyl imidazolium nitrate ([bmim]NO_3), 1-ethyl-3-methylimidazolium ethyl-sulfate ([emim]$EtSO_4$) and *n*-butylpyridinium tetrafluoroborate ([*N*-bupy]BF_4) in the pressure region from 0.1 to 10 MPa. The solubility data at 313 K are presented in Fig. 3 [20]; it can be seen that the solubility of CO_2 follows the sequence of $[bmim]PF_6/[omim]PF_6 > [omim]BF_4 > [N\text{-}bupy]BF_4 > [bmim]NO_3 > [emim]EtSO_4$. Cadena et al. [22] studied the mechanism of CO_2 dissolution in imidazolium-type ILs by experimental and molecular modeling, and found that the anions have larger impact on the solubility of CO_2. Kazarian

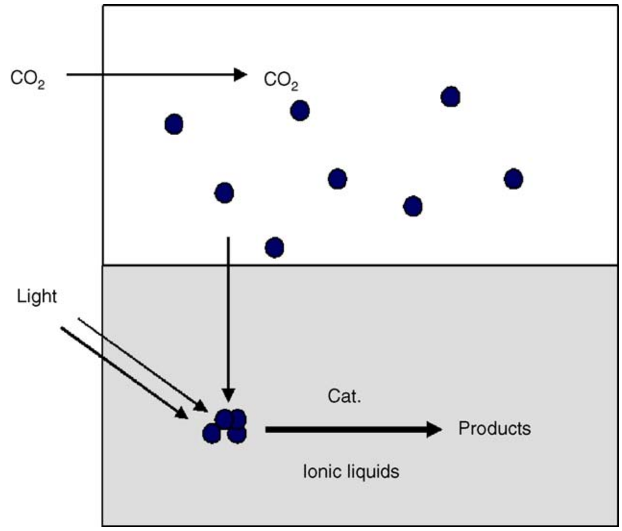


Fig. 2. Proposed integrative fixation–conversion process of CO_2 in ionic liquids.

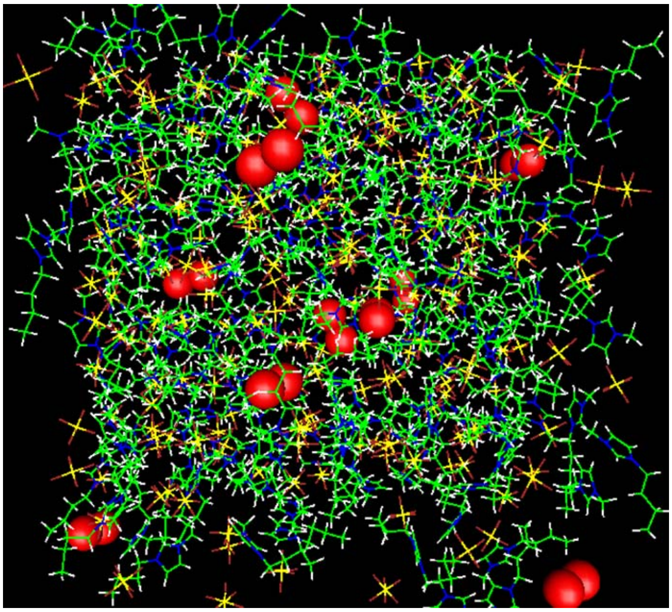


Fig. 4. Image of the equilibrium state of CO_2 in [bmim]PF_6 by molecular dynamic simulation.

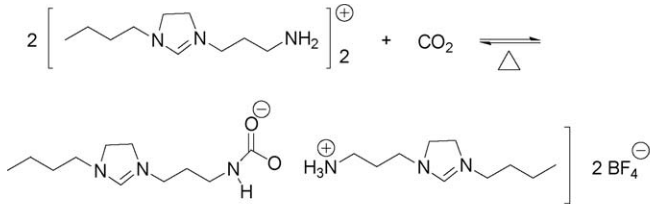
et al. [25] found that there was evidence of a weak Lewis acid–base interaction between CO_2 and PF_6^- or BF_4^- anions using ATR-IR spectroscopy. The image of the equilibrium state of CO_2 in [bmim]PF_6 is shown in Fig. 4 by molecular dynamic simulation carried out in our laboratory. The simulations were performed at 298 K and 1 atm for a system composed of 192 molecules of [bmim]PF_6 and 10 molecules of CO_2 with the standard periodical boundary conditions. In the obtained equilibrium state it can be seen that the molecules of CO_2 disperse well in the [bmim]PF_6 ILs. These microscopic studies provide valuable information for understanding the solubility behavior of CO_2 in the conventional imidazolium-type ILs.

The Henry's constants show higher solubilities of CO_2 in the ILs compared to conventional organic solvents, for example, the Henry's constant at 298.15 K is 5.34 MPa in [bmim]PF_6 [19], while it is 8.43 MPa in heptane, 13.33 MPa in cyclohexane, 10.41 MPa in benzene and 15.92 MPa in ethanol, respectively [26]. The relatively higher solubility of CO_2 in imidazolium-type ILs is due to the activity of 2-H in imidazolium ring [22,27]. More interesting are the very small excess volumes for CO_2 dissolution in the ILs compared to that in conventional organic solvents, although there is a relatively larger solubility of CO_2 in the ILs than that in conventional organic solvents. For example, the liquid phase composition of 0.69 mole fraction CO_2 in [bmim]PF_6 produces a mere 18% volume increase over the pure IL, whereas a liquid phase composition of 0.740 mole fraction CO_2 in toluene gives a 134% volume increase over the pure solvent.

Brennecke and co-workers looked for insight into the solubility of CO_2 in a series of imidazolium-type ionic liquids [19,21,28]. According to the different solubilities of CO_2 and methane, ILs have potential to be utilized in separation of CO_2 from natural gas. Anthony et al. [20] found that CO_2 solubility in [rmim]PF_6 is much higher than other gases such as CO, CH_4, H_2, N_2 and CH_3CH_3, which suggested that [rmim]PF_6 might be potentially applied as absorbent from separation of CO_2 from a coal steam gas mixture.

Recently there are some reported works on the solubility of CO_2 in sulfonate ILs. Zhang et al. [29] determined the solubility of CO_2 in trihexyl (tetradecyl) phosphonium dodecylbenzenesulfonate ([$P_{666,14}$]$C_{12}H_{25}PhSO_3$) and trihexyl (tetradecyl) phosphonium methylsulfonate ([$P_{666,14}$]$MeSO_3$) at temperatures ranging from 305 to 325 K and the pressures ranging from 2 to 9 MPa. At a given temperature, the magnitude of Henry's constants for CO_2 follows the sequence of [$P_{666,14}$]$MePhSO_3$ > [$P_{666,14}$]$MeSO_3$ > [bmim]BF_4, which indicates that the solubility of CO_2 in sulfonate ILs is generally lower than that in imidazolium-type ILs.

In general, the absorption/fixation of CO_2 in the conventional ILs such as imidazolium-type ILs and sulfonate ILs is very limited because of its physical nature of interactions, although it is relatively higher than the solubility of CO_2 in the conventional organic solvents such as heptane, ethanol, benzene and so on. The equilibrium solubility of CO_2 in these conventional ILs is about 0.10–0.15 wt% at room temperature and atmospheric pressure, which is obviously too low for industrial application for CO_2 capture.



Scheme 4. Proposed reaction mechanism between [pabim]BF_4 and CO_2.

2.2. Fixation of CO_2 using task-specific ionic liquids

Considering the very limited capability of the conventional ILs in the absorption/fixation of CO_2, it is essentially necessary to explore novel ILs with the specific function for absorption/fixation of CO_2. Due to the unique "self-designable" characteristics of ILs, alkaline group such as $-NH_2$ can be attached to the structure of cations or anions of ILs while still keeping the merits of the ILs [30]. The designed task-specific ILs obviously can break the limitation of the conventional ILs and tackle the disadvantages of the commercially applied absorbents such as aqueous amines.

Bates et al. [30] reported a task-specific IL, 1-*n*-propylamine-3-butylimidazolium tetrafluoroborate ([pabim]BF_4), for CO_2 capture, the saturated concentration of CO_2 in [pabim]BF_4 reaches a level of 7.4 wt%. The proposed reaction mechanism is shown in Scheme 4 [30], which is basically the same as that for the amines currently used as CO_2 absorbents. CO_2 molecule attacks the free electron-pair of N atom and forms a new COO^- group, simultaneously the NH_2 group of another [pabim]$^+$ accepts one H^+ and becomes $-NH_3^+$ group, which accounts for the saturation molar ratio of 1:2 between CO_2 and [pabim]BF_4.

Recently, Zhang et al. [31] reported a new kind of task-specific ILs, tetrabutylphosphonium amino acids ([$P(C_4)_4$]AA). Tetrabutylphosphonium bromide [$P(C_4)_4$]Br was transformed into tetrabutylphosphonium hydroxide [$P(C_4)_4$]OH by anion exchange resin and neutralized by amino acids such as glycine, L-alatine, L-β-alatine, L-serine and L-lysine to produce [$P(C_4)_4$]AA. The photographic image of the synthesized 20 kinds of [$P(C_4)_4$]AA ILs is presented in Fig. 5. To increase the

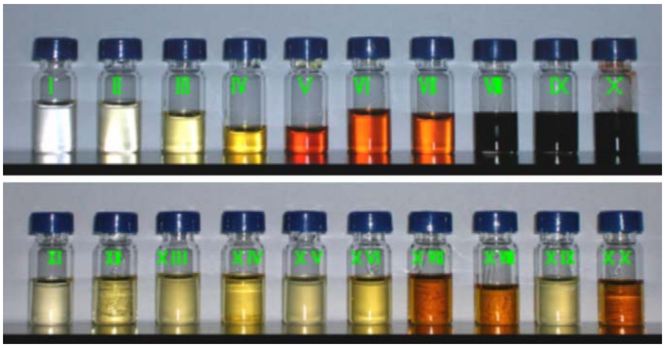
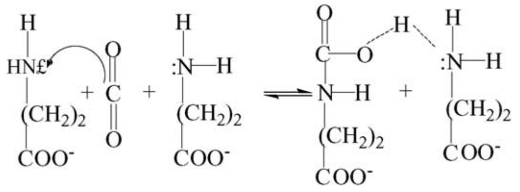


Fig. 5. Phosphonium-amino acids ionic liquids: (I) [$P(C_4)_4$]-L-Gln; (II) [$P(C_4)_4$]-L-Asn; (III) [$P(C_4)_4$]-L-β-Ala; (IV) [$P(C_4)_4$]-Gly; (V) [$P(C_4)_4$]-L-Ser; (VI) [$P(C_4)_4$]-L-Ala; (VII) [$P(C_4)_4$]-L-Lys; (VIII) [$P(C_4)_4$]-L-Trp; (IX) [$P(C_4)_4$]-L-Tyr; (X) [$P(C_4)_4$]-L-Thr; (XI) [$P(C_4)_4$]-L-Val; (XII) [$P(C_4)_4$]-L-Pro; (XIII) [$P(C_4)_4$]$_4$-L-Arg; (XIV) [$P(C_4)_4$]-L-His; (XV) [$P(C_4)_4$]-L-Glu; (XVI) [$P(C_4)_4$]-L-Ile; (XVII) [$P(C_4)_4$]-L-Met; (XVIII) [$P(C_4)_4$]-L-Cys; (XIX) [$P(C_4)_4$]-L-Leu; (XX) [$P(C_4)_4$]-L-Phe.

$[H_2N\text{-}CH_2\text{-}COO^-][P(C_4)_4]^+ + CO_2 + H_2O \rightarrow {}^+H_3NCH_2COO^- + [HCO_3]^-[P(C_4)_4]^+$

Scheme 5. Proposed adsorption mechanism between $[P(C_4)_4]$Gly and CO_2 in the presence of water.



Scheme 6. Proposed adsorption mechanism between $[P(C_4)_4]$β-Ala and CO_2 without water.

absorption/fixation rate of CO_2 in these highly viscous ILs, the $[P(C_4)_4]$AA ILs were coated on porous silica gel to form a thin film, four cycles of sorption–desorption proved their stable, fast and reversible behavior comparing to bubbling CO_2 through bulk ILs which usually takes more than 3 h. The saturated molar ratio between CO_2 and $[P(C_4)_4]$AA reached a level of 1:2 at room temperature and atmospheric pressure. Interestingly, in the presence of small amount of water, the $[P(C_4)_4]$AA ILs could adsorb equal molar amounts of CO_2, i.e., the absorption/fixation capability of these ILs was double that in the case of no water. Spectroscopic investigations suggested differences in the absorption mechanism with or without water as shown in Schemes 5 and 6, respectively. As shown in Scheme 6, in the case of no water, CO_2 molecule attacks the free electron-pair of N atom and forms a new COOH group which constructs a hydrogen bond O···H···N with the NH_2 group of another AA^-. The hydrogen bond partly occupies the free electron-pair of the N atom and makes it inert to reaction with CO_2; therefore, the saturated molar ratio is 1:2 between CO_2 and $–NH_2$ groups. However, in the presence of small amount of water, the reaction between CO_2 and H_2O is very complex. For example, the $–NH_2$ group can catalyze the formation of bicarbonate. CO_2 and H_2O react to form H_2CO_3 and HCO_3^- and the H^+ proton resourced from the deprotonation of H_2CO_3 to HCO_3^- attacks the free electron-pair of NH_2 group and forms $–NH_3^+$ group as shown in Scheme 5. Therefore, one molecule of $[P(C_4)_4]$AA can absorb one CO_2 molecule, which accounts for the absorption molar ratio of 1:1 between CO_2 and $[P(C_4)_4]$AA in the presence of water.

It is worthwhile to notice that not all the ILs containing $–NH_2$ group can absorb/fix CO_2 effectively. Our experimental studies [32] showed the guanidine ILs, e.g., 1,1,3,3-tetramethylguanidium lactate (TMGL), can only absorb/fix 0.25 wt% CO_2, which is much lower than the expected amount according to the absorption molar ratio of 1:2 between CO_2 and $–NH_2$ group if it follows the same mechanism as $[pabim]BF_4$ and $[P(C_4)_4]$AA. The underlying reason is the large FMO energy gap (9.53 eV) between HOMO-5 of TMGL and LUMO of CO_2, which is much larger than the energy gap (6.07 eV) between HOMO of $[pabim]BF_4$ and LUMO of CO_2 as shown in Fig. 6. It is the carbocation that lowers the HOMO-5 energy of TMGL and weakens its nucleophilicity; as a result, TMGL cannot effectively interact with CO_2.

3. Conversion of CO_2 using ILs

3.1. Conversion of CO_2 with epoxides using ILs as catalysts

One of the most promising technologies in the utilization of CO_2 is the cycloaddition between epoxides and CO_2 to produce five-membered cyclic carbonates as shown in Scheme 7, which are excellent aprotic polar solvents and intermediates extensively applied in the production of a variety of indispensable products such as pharmaceuticals, fine chemicals and so on (Scheme 8).

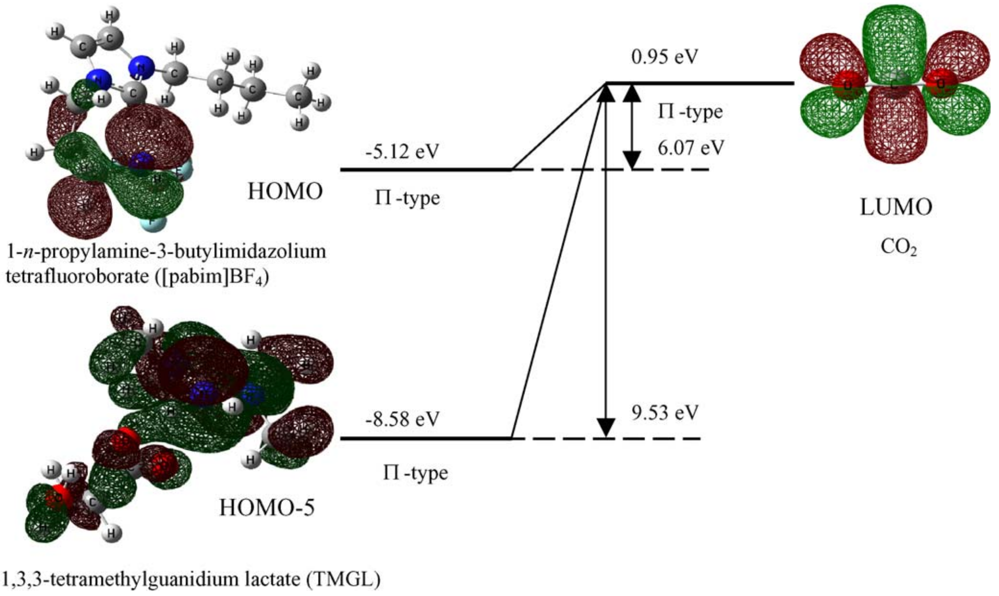
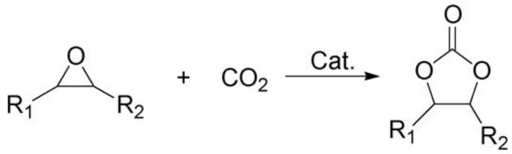
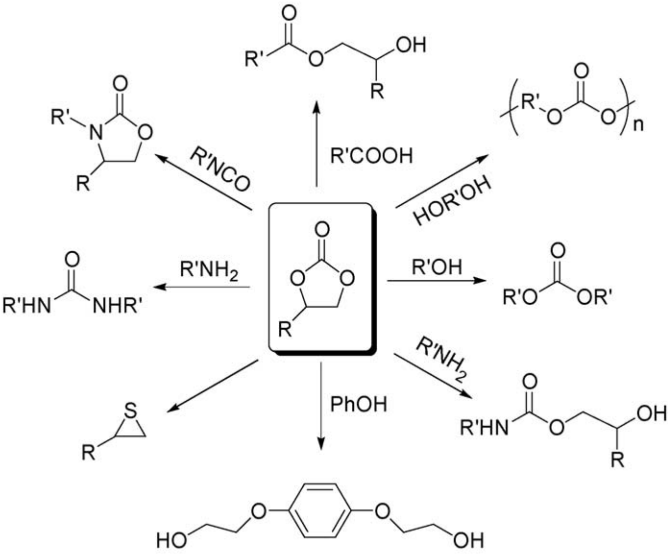


Fig. 6. Comparison of the HOMO and LUMO energies for $[pabim]BF_4$, GTML and CO_2 at $B_3LYP/6\text{-}31G^{**}$ theory of level.



Scheme 7.



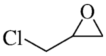
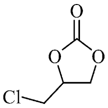
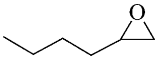
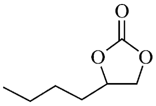
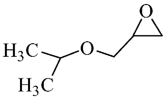
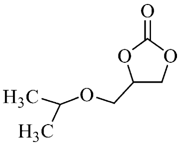
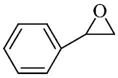
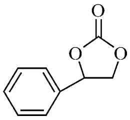
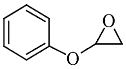
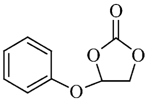
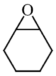
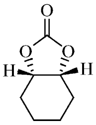
Scheme 8. Some applications of cyclic carbonate in organic synthesis.

A variety of catalysts such as alkali metal halides [33–36], metal oxides [37–39] and metal complexes [40–44] have been intensively studied for this kind of reaction; there are however a number of disadvantages such as low catalytic activity, severe reaction conditions, difficult recycling of the catalysts and so on. As one of the alternative approaches for tackling these problems, ILs have been investigated as the catalysts or promoters for this kind of reaction. Herein we present some typical examples to demonstrate the performance of ILs in the cycloaddition reactions.

In Table 1, a comparison of the ILs catalytic systems and the conventional catalyst systems for synthesis of propylene carbonate are presented. It can be seen that the ILs catalytic systems such as $ZnCl_2$/[bmim]Br, SalenAl/TBAI and $Ni(PPh_3)_2Cl_2$/Zn/TABA (Ni/Zn/TABA) show significant advantages over the conventional catalysts such as high catalytic efficiency (TOF), mild reaction conditions, non-toxic reagents and recycling of the ILs catalysts, although the cylcoaddition between propylene oxide and CO_2 could not be effectively catalyzed by using [bmim]BF_4 solely [45].

The catalytic system comprised of zinc chloride ($ZnCl_2$) and 1-butyl-3-methylimidazolium bromide ([bmim]Br) achieved 95% yield, >98% selectivity and 5410 h^{-1} TOF under mild reaction conditions without any cosolvents [46], and it could be reused for five times with a little loss of catalytic activity. Also, the $ZnCl_2$/[bmim]Br catalyst showed excellent activity and selectivity for a variety of other epoxides listed in Table 2 [46]. Interestingly, the *cis*-stereochemistry cyclic carbonate was

Table 2
The yield and efficiency of the reaction between CO_2 and various epoxides reactions catalyzed by $ZnCl_2$/[bmim]Br

Substrate	Product	Yield (%)	TOF (h^{-1})
		95	4887
		95	3332
		100	3165
		90	3155
		99	2919
		36	1276

$ZnCl_2$ (0.05 mmol), [bmim]Br (0.30 mmol), epoxides (20 ml), CO_2 pressure 1.5 MPa, temperature 373 K, time 1 h, the selectivity to carbonate >98%.

Table 1
Comparison of catalytic performance in the cycloaddition between CO_2 and propylene oxide

Entry	Catalyst	Solvent	Temperature (K)	Pressure (MPa)	Time (h)	TOF (h^{-1})	Ref.
1	SalenCr/DMAP	CH_2Cl_2	373	0.69	1	916	[40]
2	SalenZn/Et_3N	CH_2Cl_2	373	3.45	2	457	[41]
3	SalenAl/TBAI	CO_2	383	16	1	2360	[43]
4	BipyZn	CH_2Cl_2	373	3.4	1	851	[43]
5	Ni/Zn/TBAB	No	393	2.5	1	3544	[44]
6	[bmim]BF_4	No	383	2.5	6	15	[45]
7	$ZnCl_2$/[bmim]Br	No	373	1.5	1	5410	[46]

Table 3
Effect of different ILs catalytic activity of reaction between CO_2 and propylene oxide

Entry	Catalyst	Yield (%)	TOF (h^{-1})
1	$ZnCl_2$/[bmim]Br	95	5410
2	$ZnCl_2$/[bmim]Cl	38	1564
3	$ZnCl_2$/[bmim]BF_4	7	–
4	$ZnCl_2$/[bmim]PF_6	4	–
5	$ZnCl_2$/[bpy]Br	85	4800

Zinc salts (0.05 mmol), ionic liquid (0.30 mmol), the other conditions are the same as Table 2.

exclusively synthesized from the cycloaddition of cyclohexene oxide and CO_2.

We have systematically investigated the effects of various 1-butyl-3-methylimidazolium salts ([bmim]X) and *n*-butylpyridinium bromide ([bpy]Br) on the synthesis of propylene carbonate under the same reaction conditions. The experimental results are presented in Table 3 [47] and it can be found that the type of anions and cations has decisive effects on the catalytic performance. The activity increases in the order of imidazolium > pyridinium and of $Br^- > Cl^- > BF_4^- > PF_6^-$. Similarly, we have investigated the effects of various zinc salts with [bmim]Br on the synthesis of propylene carbonate; it can be found that the reaction activity follows an order of $ZnBr_2 > ZnCl_2 > Zn(OAc)_2 > ZnSO_4$ (Table 4) [47].

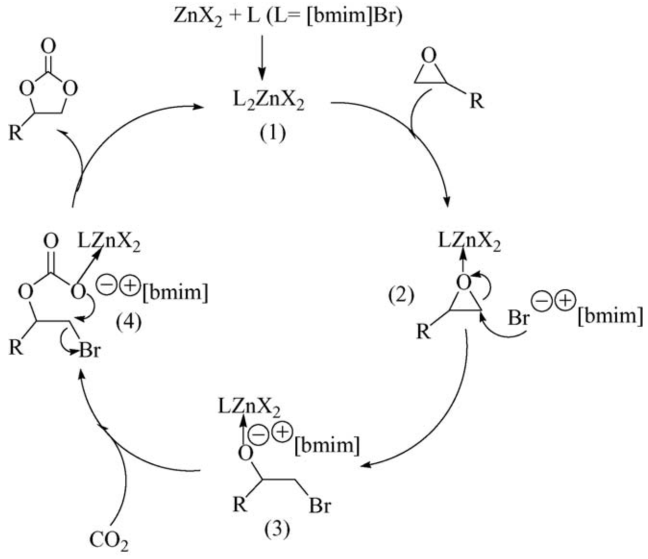
Based on the above experimental results and spectroscopic investigations, the reaction mechanism of CO_2 and propylene oxide with ZnX_2/[bmim]Br may be proposed same as previous paper (Scheme 9) [46]. $ZnCl_2$ and [bmim]Br react to synthesize the zinc imidazolium complex (1), which coordinates the epoxide by replacing one of the 1-butyl-3-methylimidazole bromide ligand first. At the same time, nucleophilic attack of the dissociated [bmim]Br on the less sterically hindered carbon atom of the coordinated epoxide occurs (2) to form the active species (3). The insertion of CO_2 into the Zn–O bond of (3) would give a zinc carbonate active species (4), which eventually forms the cyclic carbonate.

Quaternary ammonium salts can also catalyze the conversion of CO_2 into cyclic carbonate. Caló et al. [48] found that the reaction activity was effectively promoted by *tert*-butylammonium bromide (TBAB) and tetra-butylammonium iodide (TBAI) as co-catalyst. TBAI showed higher activity than TBAB because of their difference in the nucleophilicity of the halide ions. Similarly, Lewis acid metal salts could improve the activity of ammonium salt in the cylcoaddition between CO_2 and epoxides. Same synergistic effects have been also observed by combination of metal complex and ammonium salts. Lu et al. [42] reported that a catalytic system of tetradentate Schiff base aluminium complex (SalenAlCl) with TBAI showed higher activity than that of SalenAlCl or TBAI alone [42]. Recently we found that Ni/Zn/TBAB showed excellent selectivity and catalytic efficiency (TOF) without using organic solvents in the reaction of CO_2 and propylene oxide [44]. It is the cooperative effect between the metal catalyst and quaternary salts that results in higher activity.

Table 4
Effect of different zinc salt catalysts on the reaction of propylene oxide and CO_2

Entry	Catalyst	Yield (%)	TOF (h^{-1})
1	$ZnCl_2$	95	5410
2	$ZnBr_2$	98	5586
3	$Zn(OAc)_2$	64	3648
4	$ZnSO_4$	60	3420

Zinc salts (0.05 mmol), [bmim]Br (0.30 mmol), propylene oxide (0.285 mol), the other conditions are the same as Table 2.

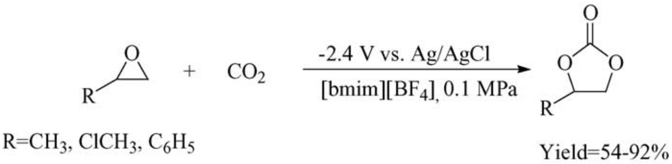


Scheme 9. Proposed mechanism for the reaction of epoxides and CO_2 catalyzed by ZnX_2/[bmim]Br.

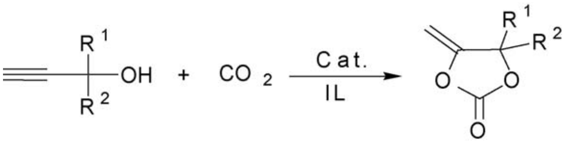
The electrochemical synthesis of cyclic carbonate from epoxides and CO_2 was also reported in the ILs with 54–92% yield (Scheme 10) [49]. It was found that both cation and anion of the ILs have a great effect on the reaction activity, which is similar to that in the thermal reaction catalyzed by the ILs.

3.2. Conversion of CO_2 with propargyl alcohols using ILs as promoters

ILs can be used in the synthesis of alkylidene carbonates from CO_2 and propargyl alcohols by combining with metal



Scheme 10. Electrochemical conversion of CO_2 with epoxide in [bmim]BF_4.

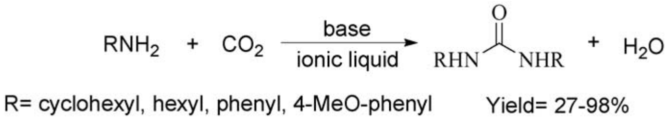


Scheme 11.

Table 5
The reaction between CO_2 and 2-methyl-3-butyn-2-ol catalyzed by CuCl in different solvents

Entry	Ionic liquid	Conversion (%)	Selectivity (%)	Yield (%)
1	[bmim]$PhSO_3$	99	~100	97
2	[bmim]BF_4	65	99	62
3	[bmim]PF_6	100	0	–
4	[bmim]NO_3	50	95	46
5	[bpy]BF_4	44	99	41
6	[bpy]$PhSO_3$	80	99	78
7	CH_2Cl_2	8	98	–
8	Toluene	2	~100	–
9	THF	8	~100	–
10	Dioxane	3	98	–
11	DMSO	0	0	–
12	Sulfolane	0	0	–
13	Nitromethane	41	99	40
14	DMF	62	~100	60
15	DMAc	34	~100	30
16	–	0	0	–

Ionic liquids or solvents 10 mmol, 2-methyl-3-butyn-2-ol 1.68 g (20 mmol), CuCl 0.04 g (0.4 mmol), CO_2 1.0 MPa, temperature 393 K, reaction time 8 h.



Scheme 12.

catalyst (Scheme 11). One example is the synthesis of methylene cyclic carbonate catalyzed by CuCl with [bmim]$PhSO_3$ [50], the high yield and enhanced rate have been achieved with ILs compared to conventional organic solvents, a large amount of tertiary amines has been avoided in this reaction (Table 5) [50]. Moreover, [bmim]$PhSO_3$ could be effectively recycled.

3.3. *Conversion of CO_2 with amines using ILs as promoters*

ILs can be applied as solvents or promoters in the conversion of CO_2 with amines to synthesize symmetric urea derivatives. Compared to the conventional synthetic methods carried out in organic solvents, the ILs can not only improve the catalytic activity and product selectivity but also avoid the use of stoichiometric quantities of dehydrating agent [51,52]. Shi et al. [51] reported a direct synthesis and separation method for producing symmetric urea derivatives with good yield by using CsOH/IL catalytic system (Scheme 12).

4. Prospective

The fixation and utilization of CO_2 is a challenging task that has been intensively investigated but not been solved yet. The ILs, either as absorbents or catalysts, have demonstrated many advantages in the fixation and conversion of CO_2 compared to the conventional organic solvents and catalytic systems without the ILs. For example, the task-specific ILs with $-NH_2$ group could absorb/fix a quite large amount of CO_2, about 7–8 wt% CO_2 at the room temperature and atmospheric pressure, the conversion of CO_2 with epoxides, propargyl alcohols and amines have demonstrated high activity, high yield and mild reaction conditions by using the ILs as catalysts or promoters. We believe that this substantial progress will definitely stimulate research on the utilization of CO_2 using the ILs, and hopefully lead to building an in situ fixation–conversion process of CO_2 with the ILs in the near future.

As a novel approach for the fixation and conversion of CO_2 using the ILs, there are obviously a number of deficiencies in the knowledge of fundamental understanding and industrial applications of the ILs. A systematic approach rather than try-and-error is critically important. We are now developing a DPPAI platform including molecular design, structure-properties, large-scale preparation, industrial applications and green integration, which constitutes an indispensable knowledge base for the industrial applications of the ILs in the fixation and conversion of CO_2.

Acknowledgments

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