Accepted Manuscript

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PII:	\$1381-1169(13)00264-1
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2013.06.024
Reference:	MOLCAA 8803
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	6-4-2013
Revised date:	26-6-2013
Accepted date:	28-6-2013

Please cite this article as: D. Wei-Li, J. Bi, L. Sheng-Lian, L. Xu-Biao, T. Xin-Man, A. Chak-Tong, Novel functionalized guanidinium ionic liquids: Efficient acid-base bifunctional catalysts for CO₂ fixation with epoxides, *Journal of Molecular Catalysis A: Chemical* (2013), http://dx.doi.org/10.1016/j.molcata.2013.06.024

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Novel functionalized guanidinium ionic liquids: Efficient acid-base

bifunctional catalysts for CO₂ fixation with epoxides

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Abstract

A series of functional guanidinium-based ionic liquids (FGBILs) that contain both Lewis acid and basic sites was prepared by a simple method, and used as catalysts for the synthesis of cyclic carbonates through the cycloaddition of CO₂ to epoxides in the absence of co-catalyst and solvent. Propylene oxide conversion was near completion at 130 °C and 2.5 MPa in 2 h when [TMGC₂H₄NH₂]Br was used as catalyst. The effects of functional groups and counter anions on catalytic performance were investigated. The synergistic effect of polarization by hydrogen bonding and the nucleophilic attack by bromide anion account for the facile ring-opening of epoxide. Furthermore, the protocol is applicable to a variety of terminal epoxides, producing the corresponding cyclic carbonates in high yield and selectivity. It is envisaged that the metal- and solvent-free process using a single catalyst has high potential for large-scale fixation of CO₂.

Keywords: carbon dioxide fixation; cycloaddition reaction; guanidinium-based ionic liquid; cyclic carbonate.

1. Introduction

Carbon dioxide is a renewable C1 resource that is abundant, inexpensive and nontoxic. The fixation of CO_2 for the generation of useful compounds has attracted much attention [1]. There are over 20 known chemical reactions that involve CO_2 as starting material, but CO_2 fixation in an industrial scale remains as a challenge [2]. One of the promising processes is the cycloaddition of CO_2 to epoxides for the formation of cyclic carbonates. Cyclic carbonates are valuable compounds that are used as polar solvents, electrolytes in lithium secondary batteries, precursors for synthesizing polycarbonates and polyurethanes, and intermediates for production of pharmaceuticals, fine chemicals, and agricultural chemicals [1-4].

With an atom utilization ratio of 100%, the cycloaddition of CO₂ to epoxides is in accord with the concept of "green chemistry" and "atom economy" [5]. In the past decades, numerous catalysts have been developed for the synthesis of cyclic carbonates. In recent years, ionic liquids (ILs) have received more attention than the other catalysts (such as alkali metal salts [6], metal oxide [7-9], modified molecular sieve [10-11], and organometallic complexes [12-15]) because they are low-cost, good in solvating ability as well as being variable in polarity and adjustable in structure and acid-base properties. So far, imidazolium salts [16-23], quaternary ammonium salts [22,24,25], quaternary phosphonium salts [26-27], pyridinium salts [28], and gunidinium salts [29-31], and other ILs [32-33] have been reported as

efficient catalysts for CO_2 fixation through the synthesis of cyclic carbonates from epoxides. Although the advances are significant, most of the ILs showed shortcomings such as unsatisfactory activity, harsh reaction conditions, being water and/or air sensitive, and the need of a metal salt as co-catalyst. From the viewpoints of industrial production and environment friendliness, it is highly desirable to develop a stable single-component catalyst that functions well under mild reaction conditions.

There is increasing investigation on guanidinium ILs because they are thermally as well chemically stability. With tunable groups on the N atoms, they show excellent catalytic activity for organic reactions [34]. Compared to the use of imidazolium-based ILs for the cycloaddition of CO₂ to epoxides, the use of guanidinium-based ILs (GBILs) is rare. Xie et al. [29]. reported that hexabutylguanidinium chloride showed certain activity for the cycloaddition reaction, but the reaction time was long and large amount of catalyst was needed. Later on, the researchers reported the observation of high activity over a hexabutylguanidinium bromide/ZnBr₂ binary system, but ZnBr₂ is required as a co-catalyst [30]. Furthermore, Dou et al. [31] synthesized PEG that was functionalized with guanidinium salt which showed certain activity for cycloaddition reaction. Recently Sun et al. reported that hydroxyl- and carboxyl-functionalized imidazolium-based ILs showed good catalytic activity for cycloaddition reactions [22-23]. As far as we know, there is no report on the synthesis of functionalized guanidinium-based ILs (FGBILs) and their use as catalysts for the synthesis of cyclic carbonate.



Scheme 1. Structures of FGBILs.

In the present work, a series of FGBILs (Scheme 1) were synthesized, and for the first time used as catalysts for the cycloaddition of CO_2 to epoxides in the absence of solvent and co-catalyst. We studied in detail the roles of functional group attached to the cation as well as the role of the counter anion. Furthermore, a systematic investigation was conducted on the effects of reaction parameters (catalyst loading, temperature, time and initial CO_2 pressure) on the catalytic reaction.

2. Experimental

2.1 Chemicals

The tetramethylguanidine, 2-bromoethanol, 3-bromopropionic aicd, bromoethane, 1-bromopropane, NaBF₄, and KPF₆ were purchased from Shanghai Jingchun Industry Co., Ltd. 2-Bromoethylamine hydrobromide was purchased from Aldrich Chemical Co. Propylene oxide and ethylene oxide were produced by Sinopharm Chemical Reagent Co., Ltd. The other epoxides were purchased from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO₂ (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any further treatment.

2.2 Charaterization

The products were analyzed on a gas chromatograph (Agilent 7890A) that was equipped with a FID and a DB-wax capillary column (30 m \times 0.53 mm \times 1.0 µm).

NMR spectra were recorded on a Bruker 400 spectrometer in DMSO- d_6 . ¹H NMR chemical shifts (δ) in ppm were downfield from tetramethylsilane. Elemental analysis was performed over a Vario EL III analyzer. The FT-IR spectra were recorded using a Bruker vertex 70 FT-IR spectrophotometer. All reagents were used as received. *2.3 Preparation and characterization of Guanidinium-based ILs*

A typical procedure for preparation of [TMGC₂H₄NH₂]Br (**1a**) is as follows: A solution of tetramethylguanidine (TMG) (40 mmol) in MeCN (12 mL) was prepared at 0 °C under N₂ atmosphere in a dry round-bottomed flask equipped with a reflux condenser. Another solution of 2-bromoethylamine hydrobromide (40 mmol) in MeCN (6 mL) was added dropwise to the flask, and the mixture was heated to room temperature and stirred for 24 h. Afterward, the solvent was removed, and the resulted solid was washed three times with triethylamine and ethyl acetate respectively, then dried at 60 °C under vacuum for 12 h to give product **1a** as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.84 (s, 1H), 3.14-3.08 (m, 2H), 2.92 (s, 12H), 1.23 (t, *J* = 7.2 Hz, 2H); Anal. calcd for C₇H₁₉N₄Br: C 35.15, H 8.01, N 23.43, found: C 35.27, H 8.08, N 23.55.

Other guanidinium ILs (**1b-e**) were prepared following the same method but without the procedure of washing with triethylamine. [**TMGC₂H₄COOH]Br** (**1b**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 7.80$ (s, 1H), 3.28 (s, 4H), 2.90 (s, 12H); Anal. calcd for C₈H₁₈N₃O₂Br: C 35.83, H 6.77, N 15.67, found: C 35.72, H 6.72, N 15.51; [**TMGC₂H₄OH]Br** (**1c**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 7.80$ (s,

1H), 3.30 (s, 4H), 2.90 (s, 12H); Anal. calcd for $C_7H_{18}N_3OBr$: C 35.01, H 7.56, N 17.50, found: C 34.96, H 7.50, N 17.64; **[TMGC₂H₄CH₃]Br** (1d): Colorless liquid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.81 (s, 1H), 3.16-3.08 (m, 2H), 2.92 (s, 12H), 1.61-1.52 (m, 2H), 0.90-0.70 (m, 3H); Anal. calcd for C₈H₂₀N₃Br: C 40.34, H 8.46, N 17.64, found: C 40.48, H 8.56, N 17.75; **[TMGC₂H₅]Br** (1e): Colorless liquid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.76 (s, 1H), 3.27-3.15 (m, 2H), 2.92 (s, 12H), 1.13 (dt, *J* = 7.2 Hz, 3H); Anal. calcd for C₇H₁₈N₃Br: C 37.51, H 8.09, N 18.75, found: C 37.78, H 7.92, N 18.91.

The ionic liquid **2a** and **3a** were synthesized by anion exchange between ionic liquid **1a** and the corresponding inorganic salt. A typical synthesis route to $[TMGC_2H_4NH_2]BF_4$ (**2a**) is as follows: Solid NaBF₄ (2 mmol) was added to a solution of **1a** (2 mmol) in H₂O (10 mL), and the mixture was stirred vigorously at room temperature for 10 h. The solution was extracted with CH₂Cl₂ (3 × 10 mL), and the organic phase was collected and dried with anhydrous Na₂SO₄ for 24 h. The organic solution was subject to evaporation for solvent removal, and the resulted product was dried at 60 °C under vacuum for 12 h to give product **2a** as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.77 (s, 1H), 3.13-3.07 (m, 2H), 2.90 (s, 12H), 1.20 (t, *J* = 7.0 Hz, 2H); Anal. calcd for C₇H₁₉N₄BF₄: C 34.17, H 7.78, N 22.77, found: C 34.35, H 7.72, N 22.94.

The ionic liquid $[TMGC_2H_4NH_2]PF_6$ (**3a**) was prepared by the same method but using KPF₆ rather than NaBF₄. **[TMGC_2H_4NH_2]PF_6** (**3a**): White solid; ¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.76 (s, 1H), 3.13-3.07 (m, 2H), 2.90 (s, 12H), 1.19 (t, *J* = 7.2

Hz, 2H); Anal. calcd for C₇H₁₉N₄PF₆: C 27.64, H 6.30, N 18.42, found: C 27.92, H 6.41, N 18.57.

The imidazolium IL (1-(2-hdyroxyl-ethyl)-3-methyl-imidazolium, [MImC₂H₄OH]Br) and quaternary ammonium IL (hydroxyl-ethyl-triethylammonium bromide, [TEAC₂H₄OH]Br) were prepared according to the procedures reported in ref [22]. [**MImC₂H₄OH]Br:** White solid; ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 9.24$ (s 1H), 7.79 (d, 2H), 5.17 (s, 1H), 4.26 (t, J = 8.2 Hz, 2H), 3.89 (s, 3H), 3.72 (t, J = 6.6Hz, 2H); Anal. calcd for C₆H₁₁N₂OBr: C 34.38, H 6.89, N 16.70, found: C 34.26, H 6.81, N 16.87; [**TEAC₂H₄OH]Br:** White solid; ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 5.27$ (s, 1H), 3.77 (t, J = 4.8 Hz, 2H), 3.34 (q, J = 7.55 Hz, 6H), 3.31 (t, J = 4.8 Hz, 6H), 1.18 (t, J = 14.4 Hz, 9H); Anal. calcd for C₈H₂₀NOBr: C 42.49, H 8.91, N 6.19, found: C 42.63, H 8.85, N 6.37.

2.4 Procedure for cyclic carbonate formation from epoxides and CO₂

The cycloaddition reactions were carried out in a 50 mL high-pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, the reactor was charged with epoxide (35.7 mmol), and certain amount of catalyst. After the reactor was fed with CO_2 to a desired pressure, the autoclave with its contents was heated to a designated temperature and stirred for a designated period of time. Then the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO_2 was released. The resulting mixture was analyzed using a GC-mass spectrometer. The products were quantitatively analyzed using GC with a flame ionization detector.

3. Results and discussion

3.1 Effect of catalyts

The synthesis of propylene carbonate (PC) through the cycloaddition of CO_2 to propylene oxide (PO) was chosen as model reaction to evaluate the catalytic activity of the as-synthesized acid-base FGBILs, and the results are depicted in Table 1.

Entry	Catalyst	Catalytic results		
Entry	Catalyst	Yield [%]	Sel. [%]	
1	TMG	1.8	88.5	
2	[TMGC ₂ H ₄ NH ₂]Br (1a)	94.6	99.8	
3	[TMGC ₂ H ₄ COOH]Br(1b)	90.8	99.9	
4	[TMGC ₂ H ₄ OH]Br (1c)	88.3	99.8	
5	[TMGC ₂ H ₄ CH ₃]Br (1d)	71.6	99.8	
6	[TMGC ₂ H ₅]Br (1e)	62.8	99.7	
7	[TMGC ₂ H ₅]Br/CH ₃ (CH ₂) ₂ NH ₂ ^b	80.3	99.6	
8	[TMGC ₂ H ₅]Br/CH ₃ COOH ^b	78.0	99.7	
9	[TMGC ₂ H ₅]Br/CH ₃ CH ₂ OH ^b	78.8	99.7	
10	CH ₃ CH ₂ CH ₂ NH ₂	6.0	99.0	
11	CH ₃ COOH	1.6	98.6	
12	CH ₃ CH ₂ OH	1.9	99.1	
13	$[TMGC_2H_4NH_2]BF_4(\mathbf{2a})$	3.1	99.1	
14	$[TMGC_2H_4NH_2]PF_6(\textbf{3a})$	2.7	99.0	
15	[MImC ₂ H ₄ OH]Br ^c	58.1	99.6	

Table 1. Performance of various catalysts^a

16	[TEAC ₂ H ₄ OH]Br ^c	49.6	99.6
17	KBr	3.4	99.3
18	TMG/KBr ^b	48.5	99.0

^a Reaction conditions: PO 35.7 mmol, Cat. 0.5 mol%, initial CO₂ pressure 2.0 MPa, Temp. 130 °C, time 2 h.

^b Equal catalyst amount (0.179 mmol).

^c [MImC₂H₄OH]Br (1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide) and [TEAC₂H₄OH]Br (2-hydroxyl-ethyl-triethylammonium bromide) were prepared according to ref [22].

One can see that the organic base tetramethylguanidine (TMG) shows almost no activity for the synthesis of PC (entry 1) whereas the FGBILs ([TMGC₂H₄NH₂]Br (**1a**), [TMGC₂H₄COOH]Br (**1b**) and [TMGC₂H₄OH]Br (**1c**)) prepared from TMG exhibit high catalytic activity and selectivity (entries 2-4). In comparison, the traditional ILs [TMGC₂H₄CH₃]Br (**1d**) and [TMGC₂H₅]Br (**1e**) are less efficient for the cycloaddition reaction (entries 5, 6). Nevertheless, in the presence of alkyl compounds containing NH₂, COOH or OH group, the activity of **1e** is greatly enhanced (entries 7-9), regardless that the alkyl compounds by themselves are almost inactive (entries 10-12). The results indicate that the functional groups play an important role in the promotion of the reaction. However, the species used to functionalize the guanidinium cation has distinct effect on the catalytic activity. One can see that the activity order of FGBILs is **1a** (NH₂) > **1b** (COOH) > **1c** (OH) (entries 2-4). While adding certain compounds containing NH₂, COOH, or OH to **1e**

(entries 7-9), the order of activity enhancement is *n*-propylamine > acetic acid \approx ethanol, in consistent with the sequence of the FGBILs. Recently, it was reported that carboxyl- or hydroxyl-functionalized imidazolium-based ILs exhibited good catalytic activity for the cycloaddition reaction, a result of hydrogen bonding between the carboxyl or hydroxyl hydrogen atom and the oxygen atom of epoxide [22-23, 35-36]. In the CO₂-capture procedure, it is regarded that the primary amine (R-NH₂) first reacts directly with CO₂ to form carbamic acid (R-NHCOOH), then the carbamic acid reacts with other base or water to form carbamate or carbonic acid [37-39]. However, because the epoxide is weakly basic, the carbamic acid may interact with epoxide through hydrogen bonding, which has a positive effect on the opening of epoxide ring. Due to the inductive effect of amine group, the hydrogen bonding between carbamic acid and epoxide is stronger than that between carboxylic acid and epoxide [40]. Furthermore, the hydrogen bonding between carboxylic acid and epoxide is also stronger than that between hydroxyl and epoxide. Hence, with the influence of hydrogen bonding on the opening of epoxide ring, the activity sequence of FGBILs $(1a (NH_2) > 1b (COOH) > 1c (OH))$ may be correlated to the strength of hydrogen bonding between FGBILs and epoxide.

Furthermore, the effect of counter anions on the catalytic performance was also evaluated. One can see that individually TMG and KBr show very poor activity for the cycloaddition reaction (entries 1, 17) whereas using a mixture of TMG and KBr as catalyst, there is large rise of PC yield (entry 18). The results suggest that because of excellent nucleophilic attack on the epoxide, Br^- is crucial for the synthesis of PC.

Compared with Br^- , BF_4^- and PF_6^- as counter anions showed lower activity (entries 13, 14), probably due to their poorer leaving ability and nucleophilicity.

Furthermore, Sun et al. [22] reported that hydroxyl functionalized imidazolium-based and quaternary ammonium ILs exhibited good activity for the cycloaddition reaction. In order to make a direct comparison, we evaluated the $[MImC_2H_4OH]Br$ and $[TEAC_2H_4OH]Br$ ILs reported by Sun et al. under the conditions adopted in this study, and the PC yields observed were 58.1% and 49.6%, respectively (entries 15, 16). It is noted that the yields are lower than those observed when **1a**, **1b** and **1c** were used as catalysts (94.6%, 90.8% and 88.3%, respectively, entries 2-4). It is noted that using FGBILs as catalyst, the selectivity to PC is always above 99.8%, and only a minute amount of 1,2-propanediol generated due to PO hydrolysis is detected as by-product. It is apparent that the FGBILs show much better performance, and have great potential for industrial application as a single-component catalyst for the cycloaddition of CO₂ to epoxides.

3.2 Effect of reaction parameters

We adopted $[TMGC_2H_4NH_2]Br$ (1a) for further investigation because of its good activity in the cycloaddition reaction. The influence of catalyst loading on PC synthesis was investigated under identical reaction conditions. As shown in Figure 1, with increase of 1a to PO molar ratio from 0.1 to 0.5 mol%, there is a sharp increase of PC yield from 12.9 to 94.6%. Further increase of 1a loading to 1.0 mol% does not result in significant rise of PC yield. Obviously, even at a low loading of 1a (0.5 mol%), excellent PC yield (94.6%) and selectivity (99.8%) can be obtained, indicating

the high activity of the catalyst. Furthermore, the PC selectivity remains almost unaffected (> 97.0%) upon a change of catalyst loading from 0.2 to 1.0 mol%.



Figure 1. Influence of catalyst loading on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, initial CO₂ pressure 2.0 MPa, 130 °C, 2 h)

The dependence of PC yield and selectivity on reaction temperature is illustrated in Figure 2. It is obvious that the reaction is temperature-sensitive. With increase of temperature from 110 to 130 °C, PC yield rapidly increased from 55.1% to 94.6%. Further rise of temperature to 150 °C would cause only a slight increase of PC yield (to 97.3%). Striking a balance between energy consumption and PC yield, we chose 130 °C as the reaction temperature for PC synthesis. It is noted that the selectivity to PC is almost independent of temperature change within the 110-150 °C range: always above 99.7%. It was reported that using hydroxyl- [35, 41] and carboxyl- [23] functionalized imidazolium ILs as catalyst, temperature higher than 130 °C would cause a decrease of PC selectivity. Moreover, Yang et al. [33] reported that when amidinium-based ILs (1,8-diazabicylo [5.4.0]undec-7-enium chloride) were used as

catalysts, a lowering of temperature below 140 °C would result in a decline of PC selectivity. From the results, it can be seen that the as-synthesized **1a** catalyst shows superior performance.



Figure 2. Influence of reaction temperature on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa, 2 h)

It was observed that the PC yield is strongly affected by the initial CO₂ pressure. As shown in Figure 3, an increase of initial CO₂ pressure would result in a rapid rise of PC yield in the low-pressure range (1.5-2.5 MPa), but there was a moderate decrease of yield in the high-pressure range (2.5-4.0 MPa). At an initial CO₂ pressure of 2.5 MPa, PC yield was the highest (96.7%) under the reaction conditions of 130 °C and 2 h. Such an effect of CO₂ pressure on catalytic activity was observed in other catalytic systems [27, 42, 43]. The phenomenon can be explained based on the concepts of reaction equilibrium and mass transfer of reactant. PC is in its liquid form under the adopted reaction conditions and an increase of CO₂ pressure should be a positive factor for PO conversion. It is well known that acidic CO₂ could dissolve in basic

epoxide and liquefies due to CO_2 -epoxide complexing [43, 44]. In the low-pressure range, an increase of CO_2 pressure leads to moderate CO_2 -PO complexing in the liquid phase, and there is enhancement of PC yield. However, in the high-pressure range, rather than promoting interaction among CO_2 , PO and catalyst, heavy CO_2 -PO complexing becomes a negative factor because it is getting difficult to separate CO_2 and PO. Thus the competition between these opposite factors results in a decline of catalytic activity in the high-pressure range. It is noted that PC selectivity is always above 99.6% and can be consider as independent of CO_2 initial pressure.



Figure 3. Influence of initial CO_2 pressure on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, 130 °C, 2 h)

The influence of reaction time on PC synthesis is depicted in Figure 4. One can see that the cycloaddition reaction proceeds rapidly in the first 2 h, reaching a PC yield of 94.6%. After that, the increase of PC yield becomes gradual. Hence, 2 h was chosen as the reaction time in this study. Furthermore, the selectivity to PC stays above 99.8% throughout.



Figure 4. Influence of reaction time on PC yield and selectivity. (Reaction conditions:

PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa, 130 °C)

3.3 Catalytic activity towards other epoxides

In order to investigate the generality of [TMGC₂H₄NH₂]Br (**1a**), the cycloaddition of CO₂ to different epoxides was examined at 130 °C and 2.0 MPa, and the results are summarized in Table 2. As shown, the catalyst **1a** exhibits high activity and selectivity across a variety of terminal epoxides (**4a-f**) (entries 1-6). Within 3 h, the corresponding cyclic carbonates (**5a-f**) were formed quantitatively. However, epoxide **4g** showed poor reactivity, and the yield of the corresponding cyclic carbonate (**5g**) was just 83.3% after a prolonged reaction period of 20 h. It is probably due to the fact that the two rings of cyclohexene oxide hinder the nucleophilic attack of Br⁻, causing the rate of ring-opening to decrease. It is well known that the epoxides with an electron-withdrawing group are able to stabilize the intermediate structure formed after ring-opening of epoxides, thus enhancing the reactivity [32]. Hence, epoxides **4a**, **4c** and **4f** are preferred substrates for the cycloaddition reaction (entries 1, 3, 6) due to

			Time	Catalytic results	
Entry	Epoxide	Product	(h)	Yield	Sel.
			(11)	(%)	(%)
1	^O (4a)	0 ↓ (5a)	1	99.8	99.8
2	СН ₃ (4b)	о СН ₃ (5b)	3	94.6	99.8
3	Cl (4c)		2	99.2	99.7
4	CH ₃ (4d)	CH ₃ (5d)	5	99.0	99.5
5	<u>(4e)</u>	(5e)	3	99.4	99.7
6	Ph ⁻⁰ (4f)	Ph ⁻⁰ , (5f)	4	98.9	98.9
7	(4g)	(5g)	20	83.3	99.7

Table 2. Cycloaddition of CO_2 to different epoxides catalyzed by $\mathbf{1a}^a$

^a Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa,

Temp. 130 °C.

the less sterical hindrance (4a) or the strong electron with-drawing groups (4c, 4f). In these cases, reactions could complete within 1 h. Moreover, the sequence of reactivity of the other epoxides (4b \approx 4e > 4d, entries 2, 4, 5) is understandable based on similar concepts.

3.4 Catalyt recycling



Figure 5. Reusability of catalyst **1a**. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa, 130 °C, 2 h)

Catalyst **1a** shows excellent activity towards the synthesis of cyclic carbonates. It is well known that stability and reusability of a catalyst are key factors that determine whether it is industrially applicable. We studied the reusability of **1a** using PO as model substrate in a series of runs. In the test, the catalyst was separated from the reaction mixture by distillation under reduced pressure and then used for the next run under the same conditions. As shown in Figure 5, there is no significant change of PC yield and selectivity across the five runs. The results indicate that the catalyst **1a** can be reused with stable performance.

3.5 Possible Mechanism



Figure 6. FT-IR spectra of (a) **1a**/CO₂, and (b) **1a**.

In the case of using carboxyl or hydroxyl functionalized imidazolium-based ILs, it was regarded that hydrogen bonding between the hydrogen atom of carboxyl (or hydroxyl) and the oxygen atom of epoxide would result in polarization of C-O bond, which could facilitate the ring open of epoxide [22, 35-36].

Among the FGBILs (**1a**, **1b** and **1c**), the amino-functionalized IL (**1a**) exhibits the best catalytic activity. In order to illustrate the role of amino group, we obtained the ¹HNMR spectrum of **1a** as well as that of **1a** and PO mixture (molar ratio 1:10) using DMSO- d_6 as solvent. We observe no change of chemical shift of H atom of amino group in both cases. We hence deduce that there is no significant interaction between the amino group and epoxide. In general, primary amine (R-NH₂) can react directly with CO₂ to form carbamic acid species (R-NHCOOH) [37-39]. To clarify the interaction between amino group and CO₂, we carried out FT-IR analysis of **1a** and



Scheme 2. Proposed mechanism for the cycloaddition reaction.

1a/CO₂ (keeping **1a** in 4 MPa of CO₂ for 4 h). As shown in Figure 6, the spectra of **1a**/CO₂ exhibits the characteristic bands of C=O (1776 cm⁻¹) and C-O stretching (1240 cm⁻¹), which indicates the formation of carbamic acid species. In cycloaddition reaction, because of the weak basicity of epoxide, the carbamic acid may interact with epoxide through hydrogen bonding; such an interaction has a positive effect on the opening of epoxide ring. Based on such an understanding, a plausible mechanism is proposed as shown in Scheme 2. First, coordination of the central C atom of cation and the H atom of carbamic acid species with the O atom of epoxide results in polarization of epoxide C-O bond and formation of intermediate **I**. Then, nucleophilic attack of bromide ion on the less sterically hindered β-carbon atom of epoxide furnishes ring opening and the formation of intermediate **II**. Second, the oxygen of

intermediate II interacts with CO_2 to form halocarbonate III that transforms to cyclic carbonate through intermolecular displacement of the bromide ion.

4. Conclusions

We developed a facile, reliable, and highly selective catalytic protocol for the synthesis of cyclic carbonate using a type of novel FGBILs as acid-base bifunctional catalysts under solvent- and metal-free conditions. The FGBILs are easily synthesized, air-stable, cheap and environment-benign. They perform well as catalysts in the cycloaddition of CO_2 to epoxides, especially the NH₂-functionalized one. The interaction of functional groups with epoxide through hydrogen bonding and Lewis acid activation strengthens the polarization of epoxide C-O bond, facilitating ring-opening of epoxide as a result. The bromide anion also plays an important role in the ring-opening process through nucleophilic attack of epoxide. With excellent performance, the FGBILs are potentially applicable for chemical fixation of CO_2 in an industrial scale. It is envisaged that the scientific findings are useful for the design of new and efficient catalysts for cycloaddition reaction of epoxides.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 51104089, 51238002, and 51272099), Jiangxi Province Science and Technology Project (Grant Nos. 2010AIB00400); Jiangxi Province Science and Technology Support Program (Grant Nos. 20111BBG70003-4); and Natural Science Foundation of Jiangxi Province (Grant Nos. 20122BAB213013).

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Figure Captions

Figure 1. Influence of catalyst loading on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, initial CO₂ pressure 2.0 MPa, 130 °C, 2 h)

Figure 2. Influence of reaction temperature on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa, 2 h)

Figure 3. Influence of initial CO₂ pressure on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, 130 °C, 2 h)

Figure 4. Influence of reaction time on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa, 130 °C)

Figure 5. Reusability of catalyst 1a. (Reaction conditions: PO 35.7 mmol, 1a 0.5 mol%, initial CO₂ pressure 2.0 MPa, 130 $^{\circ}$ C, 2 h)

Figure 6. FT-IR spectra of (a) **1a**/CO₂, and (b) **1a**.

Scheme 1. Structures of FGBILs.

Scheme 2. Proposed mechanism for the cycloaddition reaction.

Entry	Catalyst	Catalytic res	ults
Entry	Catalyst	Yield [%]	Sel. [%]
1	TMG	1.8	88.5
2	$[TMGC_2H_4NH_2]Br(1a)$	94.6	99.8
3	[TMGC ₂ H ₄ COOH]Br(1b)	90.8	99.9
4	[TMGC ₂ H ₄ OH]Br (1c)	88.3	99.8
5	[TMGC ₂ H ₄ CH ₃]Br (1d)	71.6	99.8
6	[TMGC ₂ H ₅]Br (1e)	62.8	99.7
7	[TMGC ₂ H ₅]Br/CH ₃ (CH ₂) ₂ NH ₂ ^b	80.3	99.6
8	[TMGC ₂ H ₅]Br/CH ₃ COOH ^b	78.0	99.7
9	[TMGC ₂ H ₅]Br/CH ₃ CH ₂ OH ^b	78.8	99.7
10	CH ₃ CH ₂ CH ₂ NH ₂	6.0	99.0
11	СН₃СООН	1.6	98.6
12	CH ₃ CH ₂ OH	1.9	99.1
13	$[TMGC_2H_4NH_2]BF_4(2a)$	3.1	99.1
14	$[TMGC_2H_4NH_2]PF_6(\mathbf{3a})$	2.7	99.0
15	[MImC ₂ H ₄ OH]Br ^c	58.1	99.6
16	[TEAC ₂ H ₄ OH]Br ^c	49.6	99.6
17	KBr	3.4	99.3
18	TMG/KBr ^b	48.5	99.0

Table 1. Performance of various catalysts^a

^a Reaction conditions: PO 35.7 mmol, Cat. 0.5 mol%, initial CO₂ pressure 2.0

MPa, Temp. 130 °C, time 2 h.

^b Equal catalyst amount (0.179 mmol).

^c [MImC₂H₄OH]Br (1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide) and

[TEAC2H4OH]Br (2-hydroxyl-ethyl-triethylammonium bromide) were

prepared according to ref [22].

			T.	Catalytic results	
Entry	Epoxide	Product	(h)	Yield	Sel.
				(%)	(%)
1	^O (4a)	(5a)	1	99.8	99.8
2	СН ₃ (4b)	о СН ₃ (5b)	3	94.6	99.8
3	Cl (4c)		2	99.2	99.7
4	CH ₃ (4d)	CH ₃ (5d)	5	99.0	99.5
5	<u>(4e)</u>	(5e)	3	99.4	99.7
6	Ph ⁻⁰ (4f)	Ph ⁻⁰ , (5f)	4	98.9	98.9
7	(4g)	(5 g) (5g)	20	83.3	99.7

Table 2. Cycloaddition of CO_2 to different epoxides catalyzed by $\mathbf{1a}^a$

^a Reaction conditions: PO 35.7 mmol, **1a** 0.5 mol%, initial CO₂ pressure 2.0 MPa,

Temp. 130 °C.





Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Scheme 1



Scheme 2





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- A series of novel FGBILs was synthesized by a simple method.
- The FGBILs was firstly used as catalysts for the cycloaddition reaction.
- The FGBILs show high catalytic activity and selectivity under mild conditions.
- Effects of the structure on the catalytic activity of FGBILs were investigated.
- A plausible mechanism for cycloaddition reaction over FGBILs was proposed.

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