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Ionic liquids containing carboxyl acid moieties grafted onto silica: Synthesis and application as heterogeneous catalysts for cycloaddition reactions of epoxide and carbon dioxide

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A series of carboxyl-group-functionalized imidazolium-based ionic liquids (CILs) were synthesized and grafted onto silica gel. The catalytic activity of the resulting heterogeneous catalysts toward the synthesis of cyclic carbonate *via* cycloaddition reactions of epoxide and CO_2 was studied. The effect on the reaction of the grafted ILs' structures and the reaction conditions such as reaction temperature, time, pressure, and the amount of catalyst used, were systematically investigated. For comparison, silica-grafted imidazolium-based ILs with and without hydroxyl groups were also used to catalyze cycloaddition reactions. The carboxylic acid group in the catalyst was demonstrated to have a synergistic effect with halide anions. A high yield of cyclic carbonates and excellent selectivity could be obtained under optimized conditions.

Introduction

Cyclic carbonates have drawn much attention and have been widely used not only as polar aprotic solvents in organic and polymeric synthesis but also as ingredients in pharmaceuticals and fine chemicals in biomedical synthesis.1-3 One of the most effective routes for the synthesis of cyclic carbonates is the cycloaddition of CO_2 with epoxides. Considering the desire for chemical technology that has minimal environmental impact.⁴ some green ionic liquid (IL) catalysts such as 1-butyl-3-imidazolium tetrafluoroborate,5 1-octyl-3-methylimidazolium tetrafluoroborate,6 and pyridinium or ammonium salts7,8 have been developed, and have exhibited excellent catalytic performance toward such reactions. Unfortunately, those reactions were conducted in homogeneous catalytic systems, which suffer from poor catalyst recovery and product separation. Hence, it is crucial to identify more efficient heterogeneous catalysts.

Heterogeneous IL catalysts prepared by grafting ILs onto solid supports retain important physical and chemical features of ILs, such as nonvolatility, nonflammability, and good thermal stability, as well as high catalytic activity and selectivity. Therefore, supported ILs are considered promising as catalysts toward many catalytic reactions. The quaternary ammonium

salts alkali halide9 and imidazolium alkyl halide, immobilized on silica¹⁰⁻¹³ or polymer supports,^{14,15} have been extensively explored for use as heterogeneous catalysts for the synthesis of carbonates. More recently, Sun and co-workers found that hydroxyl groups containing an IL could activate the cycloaddition reaction.¹⁶ Zhu et al. demonstrated that choline chloride/urea could greatly improve catalytic activity for the cycloaddition reaction of CO₂ and epoxide because of the presence of a hydroxyl group in choline chloride.¹⁷ First, the catalyst's OH group and halide anion at the Lewis basic site make a coordinated attack on the epoxide. The coordination of the H and O atoms of the epoxide through a hydrogen bond results in the polarization of C-O bonds, and the halide anion makes a nucleophilic attack on the sterically hindered β -carbon atom of the epoxide. The carboxylic acid group is undoubtedly a stronger Brønsted acid and hydrogen bonding donor than the hydroxyl group.¹⁸ Therefore, the incorporation of carboxylic acid moieties into ILs could provide an effective alternative for improving the catalytic performance of ILs toward the cycloaddition of CO₂ and epoxides.

We synthesized a series of carboxylic-acid-functionalized imidazolium-based ILs bearing different halide anions (CILXes) and grafted them onto a silica gel surface, forming various heterogeneous catalysts for the cycloaddition reaction of CO_2 and epoxides. The effect of anions (Cl⁻, Br⁻, and I⁻) and reaction parameters (temperature, pressure, and time) on the yields and selectivity were investigated. For comparison, we also studied silica grafted non-functionalized IL (IL1-Si) and silica-grafted hydroxyl-group-functionalized IL (IL2-Si) in this work.

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Results and discussion

Characterization of catalysts

FT-IR analysis. Imidazolium-based ILs with different functional groups bearing varied anions (Cl⁻, Br⁻, and I⁻) were synthesized and immobilized on the surface of a commercial silica gel. The resulting heterogeneous catalysts (CILX-Si, IL1-Si and IL2-Si) and pure silica were characterized by FT-IR analysis. As shown in Fig. 1, CILX-Si exhibits the characteristic bands of C=O (1730 cm⁻¹) and C-O stretching (1402 cm⁻¹) of carboxylic acid. In comparison with pristine silica, all the IL-grafted silica samples demonstrate newly-appeared C-H stretching (3130, 2950, and 2850 cm⁻¹), and imidazolium ring stretching bands (1560 and 1460 cm⁻¹), characteristic of the presence of IL components in the heterogeneous catalysts. These facts evidenced that the functionalized ILs were successfully grafted onto the silica surface.



Fig. 1 FTIR spectra of pristine silica, CILX-Si, IL1-Si and IL2-Si.

²⁹Si and ¹³C MAS-NMR characterization

To investigate the efficiency of the grafting reaction, a solidstate ²⁹Si MAS-NMR analysis of CILBr-Si was conducted. As shown in Fig. 2, two peaks centered at -103 and -112 ppm can be clearly observed; they are attributed to Q₃ [Si (OSi)₃ (OH)] and Q₄ [Si (OSi)₄] silicon atoms, respectively. The peaks located at -67, -56, and -44 ppm are assigned to T₃ [Si(OSi)₃R], T₂ [Si(OSi)₂R(OH)], and T₁ [Si (OSi)₃R(OH)₂] organosiloxane, respectively. These results indicated the presence of organic functionalization moieties as part of the silica.

Fig. 3 shows the ¹³C MAS-NMR spectrum of CILBr-Si. The chemical shifts at 174 ppm correspond to carbon atoms in the carboxylic acid group; those at 135 and 120 ppm correspond to the three imidazole ring carbon atoms. The signal at 55 ppm is





Fig. 3 ¹³C NMR spectrum of CILBr-Si.

attributed to carbon atoms connected to the imidazole ring, and other carbon atoms show peaks from 5 to 38 ppm.

Catalytic performance of grafted ILs with a functional group

To investigate the effects of molecular composition (functional group and anion type) of grafted ILs on catalytic reactivity, a variety of silica-grafted ILs with functional groups (-COOH, -OH) were employed as heterogeneous catalysts in cycloaddition reactions. All reactions were performed under the same conditions (110 °C, 0.86 MPa, 3 h) using the same amount of catalysts and allyl glycidyl ether (AGE). As shown in Table 1 and 2, the obtained AGE conversions ranged from 65% to 76% of the total available AGE with >93% allyl glycidyl carbonate (AGC) selectivity. The high selectivity indicated negligible creation of byproducts in the cycloaddition reactions. Runs 1–3 in Table 2 demonstrate the effects of halide anions located on the grafted CILX on the catalytic reactivity in the cycloaddition reactions between AGE and CO₂. CILI-Si exhibited the highest catalytic activity. The AGE conversions for CILCI-Si, CILBr-Si, and CILI-Si were 71%, 73%, and 76%, respectively (Table 2, runs 1, 2,

Table 1 Elemental analysis of catalyst

Sample	N (%)	C (%)	H (%)	IL grafting amount/mmol g ⁻¹
CILCI-Si	1.04	6.84	3.14	0.37
CILBr-Si	1.03	6.87	3.62	0.36
CILI-Si	1.00	6.34	3.44	0.35
IL2-Si	1.62	8.11	2.99	0.58
IL1-Si	3.50	9.27	2.88	1.25

 Table 2
 Effect of grafted IL structure on cycloaddition reaction^a

Run	Catalyst ^c	Conversion (%)	Selectivity (%)	TON ^b
1	CILCI-Si	71	93	143
2	CILBr-Si	73	96	156
3	CILI-Si	76	98	170
4	IL2-Si	70	92	89
5	IL1-Si	65	95	40
6 ^d	IL1-Si/H ₂ O	71	92	41
7 ^d	IL1-Si/CH ₃ COOH	77	96	47

^{*a*} Reaction conditions: catalyst, 0.5 g; AGE, 40 mmol; CO₂ pressure, 0.86 MPa; reaction temperature, 110 °C; time, 3 h; without solvent. ^{*b*} Turnover number (TON): number of moles of product per mole of immobilized IL. ^{*c*} The amount of immobilized IL was calculated by EA. ^{*d*} The amount of H₂O and acetic acid is the same as immobilized IL.

and 3). These marked differences may reflect the nucleophilicity of the anions in the immobilized alkyl halides.

The ion radii of Cl⁻, Br⁻, and I⁻ increase and their electronegativity decreases in that order; thus, anion movement away from the imidazolium cation in the order of I⁻ > Br⁻ > Cl⁻ reflects their nucleophilicity order. Generally, anions with higher nucleophilicity are favored for AGE conversion,¹⁹ a finding that is supported by the increases in AGE conversion in the order of I⁻ > Br⁻ > Cl⁻ observed in this study.

The CILI-Si catalyst showed not only the highest AGE conversion (76%) but also the highest selectivity (98%) among the tested CILX-Si catalysts. In addition, all the tested CILX-Si catalysts showed quite high turnover numbers (TONs) ranging from 143 to 170. For example, CILBr-Si had a TON of 156, which was significantly higher than that reported for an IL with no functional group immobilized on commercial silica (TON = 40)¹⁰ and that of silicate MCM-41 (TON = 11.6).¹¹

The grafted IL with an OH group (IL2-Si) exhibited lower activity (70% AGE conversion, run 4 in Table 2) than CILBr-Si. Silica-grafted ILs (IL1-Si) with no functional group exhibited rather lower catalytic activity (65% AGE conversion and a TON of 40; run 5 in Table 2). This indicates that the carboxylic acid group was responsible for the high conversion and selectivity. For comparison, a small amount of water was introduced into the reaction; the AGE conversion increased to 71%, but the selectivity decreased to 92% (run 6 in Table 2). This can be explained by the fact that the presence of water in a catalytic system facilitates the formation of the byproduct 1,2glycol,²⁰ which was confirmed through GC-MS spectrometry (GC-MS; Micromass, UK) by comparing the retention times and fragmentation patterns with those of authentic samples. Surprisingly, when acetic acid was added to the reaction, the catalytic reactivity of IL1-Si was greatly enhanced, yielding a much higher AGE conversion (77%) and selectivity (96%, run 7 in Table 2). Therefore, the involvement of carboxylic acid moieties, either in the free state or fixed by IL catalysts into the catalytic system can greatly enhance the catalytic performance of supported ILs toward the cycloaddition reaction.

Effect of temperature, pressure, and reaction time

Since CILBr-Si showed good catalytic activity, the effects of reaction parameters (temperature, time, and CO_2 pressure) were examined using a CILBr-Si-based catalytic system. First, the relationship between AGE conversion and reaction time was investigated. Fig. 4 shows that AGE conversion increased with reaction duration up to a reaction time of 3 h, after which AGE conversion did not increase and the reaction rate slowed. The results suggest that the fixation of CO_2 onto AGE was completed within 3 h. Thus, the other reaction parameters were assessed using 3 h reaction times.



Fig. 4 Time variant yield for CILBr-Si at 110 $^{\circ}$ C and CO₂ pressure of 1.62 MPa.

The results in Table 3 show that the reaction temperature has a strong effect on AGE conversion (runs 2a, 2b, and 2c). In catalytic reactions conducted at 90 °C, 100 °C, and 110 °C, the AGE conversions were 56%, 66%, and 73%, respectively. This temperature and conversion-rate relationship is attributed to higher reactivity at higher temperatures. However, when the reaction temperature was increased to 120 °C (run 2h), AGE conversion decreased to 70%. Although higher reaction system temperatures increase reactivity, the solubility of the CO₂ gas phase in the reaction system decreases with increasing temperature. Therefore, in reactions performed at temperatures greater than 110 °C, CO₂ solubility affects reactivity, leading to a decrease in AGE conversion.

The effects of CO₂ pressure were also investigated. As shown in runs 2c and 2d in Table 3, when the reaction CO₂ pressure increased from 0.86 MPa to 1.34 MPa, AGE conversion increased from 73% to 92%. At higher pressures, 1.62 MPa and 1.82 MPa, AGE conversion increased to 98% and 99%, respectively (Table 3, runs 2e and 2f). Similar effects of CO₂ pressure on catalytic activity have been observed in other catalytic systems.^{5,21} During such catalytic reactions, a higher CO₂ pressure can effectively increase the solubility of CO₂ in AGE, enabling the reaction

Table 3 Effect of reaction parameter on catalytic performance^a

Run	<i>T</i> /°C	Pressure/MPa	Conversion (%)	Selectivity (%)
2a	90	0.86	56	94
2b	100	0.86	66	95
2c	110	0.86	73	96
2d	110	1.34	92	98
2e	110	1.62	98	97
2f	110	1.82	99	99
2g	110	2.17	97	99
2h	120	0.86	70	92
^a Reac	tion cond	itions: catalyst C	II Br Si 0.5 a. AGE	5 40 mmol: time

3 h. equilibrium to shift toward a carbonate formation. However,

when the catalytic reaction was conducted at a CO_2 pressure of 2.17 MPa, the AGE conversion dropped slightly (97%; Table 3, run 2 g) compared with that in the reaction carried out at 1.82 MPa (run 2f). The results indicate that AGE conversion does not continue to increase with pressure, suggesting that a high CO₂ pressure may retard the interaction between AGE and the catalyst. Such retardation may be related to a dilution effect occurring when the reaction pressure reaches equilibrium at a specific temperature, which has been reported to result in lower AGE conversion.²¹

The reusability of the grafted IL catalyst was also studied with the catalyst used in Table 2, entry 2. Fig. 5 shows the performance of the catalyst, which did not lose its catalytic abilities significantly after five runs.

 $\begin{array}{c} 80 \\ 60 \\ 60 \\ 20 \\ 20 \\ 0 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ Run \end{array}$

Fig. 5 AGC yield of recycled CILBr-Si.

Synthesis of cyclic carbonate from CO₂ and other epoxides

The above results demonstrate that grafted ILs with a functional group were efficient catalysts for the cycloaddition of AGE and CO_2 in the absence of a solvent. To investigate the applicability of these catalysts to other epoxides, cyclic carbonates were synthesized from different epoxides and CO_2 at the optimized temperature in the presence of the synthesized catalysts. The results are summarized in the Table 4. CILBr-Si was found to be applicable to a variety of epoxides to produce the corresponding



 Table 4
 Different epoxides react with CO2^a

 a Reaction condition: epoxide, 40 mmol; catalyst CILBr-Si, 0.5 g; CO_2 pressure, 1.62 MPa.

cyclic carbonates in high yields with high selectivity. Compared with the other epoxides, when cyclohexene oxide was reacted with CO_2 , the reaction took longer (24 h) and a relatively lower yield (82%) was obtained. This fact was attributed to higher hindrance of the reactant, which was also demonstrated by other authors.^{18,22} When other epoxides were used, the yields ranged from 96% to 99%.

Proposed mechanism of coupling reaction

Previous research suggested that Brønsted acids can accelerate the ring-opening reaction of epoxides by forming hydrogen bonds.²³ In our current study, grafted ILs with carboxyl and hydroxyl functional groups demonstrated better catalytic activities than grafted ILs with no functional group (Table 2, entries 2, 4, 7). It can be deduced that the carboxylic acid group and hydroxyl group can efficiently promote the cycloaddition reaction. Furthermore, when acetic acid was introduced into the coupling reaction, the AGC yield is 77% which is much higher than that obtained by grafted IL with no functional group. This further proves that the carboxylic acid group is favorable to the cycloaddition reaction. The proposed mechanism is shown in Scheme 1: the X anion (Lewis base) of the catalyst opens the epoxy ring, which was activated by the carboxylic acid group and electronic interaction with the imidazolium cation, to give the intermediate. Then the intermediate further reacts with CO₂ to form the corresponding cyclic carbonate and regenerates the catalyst. Thus, in our current catalysis systems, the coexistence of hydrogen bond donors (-COOH) and the imidazolium cation and halide anion showed the synergistic effect of promoting the



Scheme 1 The proposed reaction mechanism for cycloaddition of epoxide and CO₂ catalyzed by CILX-Si.

coupling reaction. This effect might be the main contribution to their high catalytic activity and selectivity.

Conclusions

Silica-grafted imidazolium-based ILs with carboxylic acid and hydroxyl groups and with no functional group, have been demonstrated as effective catalysts for the synthesis of cyclic carbonates *via* the cycloaddition of epoxides with CO₂. Carboxylic acid-functionalized imidazolium-based ILs immobilized on silica (CILX-Si) show the highest activity and selectivity, since the -COOH group in the IL cation can greatly accelerate the reactions and showed a synergistic effect with the halide anions. We also found that the involvement of acetic acid can significantly improve catalytic performance more efficiently than water. These heterogeneous catalysts can be easily separated from the products and reused.

Experimental

Material

The following reagents were purchased from Aldrich and used as-received: 3-chloropropionic acid, 3-bromopropionic acid, 3-iodopropionic acid, bromoacetic acid, (3-chloropropyl) triethoxysilane, dichloromethane, diethyl ether, allyl glycidyl ether (AGE), and other epoxides. Silica gel (500 m² g⁻¹, 60 Å) was commercially obtained from Aldrich and purified with hot piranha solution (H_2O_2 and H_2SO_4) before use.

Preparation of CILXes

CILXes were synthesized according to the procedures shown in Scheme 2. In a typical reaction, imidazole (3.4 g) and (3chloropropyl) triethoxysilane (12 mL) were poured in sequence into a flask containing 50 mL of dry toluene with vigorous stirring under an argon atmosphere. After the reaction proceeded under reflux conditions for 10 h, 8 g of 3-bromopropionic acid were added to the flask. The mixture was held for another 24 h. Subsequently, CILBr was obtained after the solvent was removed. Following a similar procedure, the other



Scheme 2 Synthesis of IL with or without functional group.

CILXes and IL2 were synthesized by using 3-chloropropionic acid, 3-iodopropionic acid, and 2-bromoethanol, respectively, instead of 3-bromopropionic acid. An IL with no functional group, 1-ethyl-3-(3-triethoxysilypropyl) imidazolium bromide (IL1), was synthesized according to the reported procedure.¹⁰

The NMR data are as follows:

1-Propionic acid-3-(3-triethoxysilypropyl) imidazolium bromide (CILBr): ¹H NMR (300 MHz, DMSO-*d*₆): δ 0.52 (m, 2H), 1.05 (t, 9H), 1.82 (m, 2H), 2.95 (t, 2H), 3.45 (q, 6H), 4.35 (m, 4H), 7.68 (s, 1H), 7.82 (s, 1H), 9.36 (s, 1H), 9.65 ppm (br, 1H); ¹³C (75 MHz, DMSO-*d*₆); δ 7.8, 18.2, 24.3, 34.2, 43.8, 45.9, 47.8, 118.7, 121.1, 136.2, 172.3 ppm.

1-Ethyl-3-(3-triethoxysilypropyl) imidazolium bromide (IL1): ¹H NMR (300 MHz, DMSO- d_6): δ 0.50 (m, 2H), 1.03 (t, 9H), 1.39 (t, 3H), 1.84 (m, 2H), 3.68 (q, 6H), 4.22 (m, 4H), 7.67 (s, 1H), 7.85 (s, 1H), 9.46 ppm (s, 1H); ¹³C (75 MHz, DMSO- d_6); δ 7.5, 15.3, 18.4, 23.8, 43.8, 51.0, 56.0, 119.7, 122.1, 134.3 ppm.¹⁰

1-Hydroxyethyl-3-(3-triethoxysilypropyl) imidazolium bromide (IL2): ¹H NMR (300 MHz, DMSO- d_6): δ 0.53 (m, 2H), 1.02 (t, 9H), 1.84 (m, 2H), 3.42 (q, 6H), 3.72 (t, 2H), 4.25 (m, 4H), 7.70 (s, 1H), 7.78 (s, 1H), 9.19 (s, 1H), 9.52 ppm (br, 1H); ¹³C (75 MHz, DMSO- d_6); δ 8.1, 17.8, 24.5, 50.1, 52.2, 54.5, 59.9, 118.9, 121.8, 136.8 ppm.

Synthesis of CILX-Si

Before immobilization, silica gel was purified with hot piranha solution followed by rinsing with water and drying under a stream of nitrogen. The pretreated silica and the IL were co-dispersed in a flask containing a solution of dehydrated toluene and methanol. The mixture was refluxed for 24 h under a nitrogen atmosphere. The resulting product was filtered and washed with dichloromethane to remove excess IL. After evaporating the residual solvent in a vacuum oven, CILBr-Si was obtained. Following a similar procedure, a series of CILX-Si, IL2-Si, and IL1-Si were also synthesized. The preparation process of CILX-Si is shown in Scheme 3.



IL1-Si: R=-CH₂CH₃,X=Br; IL2-Si: R=-CH₂CH₂, R'=-OH, X=Br; CILX-Si: R=-CH₂CH₂, R'=-COOH, X=CI.Br, or I.

Scheme 3 Synthesis of CILX-Si, IL2-Si and IL1-Si.

Cycloaddition reaction

Allyl glycidyl carbonate (AGC) was synthesized by a coupling reaction between AGE and CO_2 in the presence of CILX-Si, as illustrated in Scheme 4. All the reactions were carried out in a 55 mL stainless-steel reactor with a magnetic stirrer. In a typical reaction process, 0.5 g of catalyst was introduced into the reactor containing 40 mmol of AGE. The reactions were conducted under a preset carbon dioxide pressure at different temperatures. After a reaction was complete, the reactor was cooled to ambient temperature, and the products were analyzed on a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 µm) using a flameionized detector. The purity and structure of products obtained at certain experimental conditions were also confirmed by ¹H NMR and gas chromatography/mass spectrometry (GC-MS, Micromass, UK) analysis.



Scheme 4 Synthesis of cyclic carbonate from epoxide and CO₂.

Characterization

Elemental analysis (EA) was performed using a Vario EL III instrument. 2 mg of each sample was subjected to 1100 °C, while sulfanilic acid acted as a standard. ¹H NMR and ¹³C NMR analysis were performed on Varian 300 MHz and 75 MHz spectrometers, respectively, using DMSO as a solvent. Solid-state NMR analysis was conducted at ²⁹Si and ¹³C frequencies of 79.5 and 100.6 MHz, respectively, on an INOVA-400 WB MAS probe. ²⁹Si MAS spectra were measured at room temperature under the following conditions: MAS at 5 kHz; $\pi/2$ pulse, 6.5 µs and a repetition delay of 60 s; 3928 scans referenced to tetramethylsilane. ¹³C cross-polarization spectra were measured with a recycle delay of 5 s under the following conditions: MAS at 5 kHz; $\pi/2$ pulse, 7 µs; 1024 scans referenced to tetramethylsilane. Fourier transformation infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm⁻¹. Thermal gravimetric analysis (TGA) was performed on a Netzsch STA

449 instrument with a heating rate of $10 \degree C \min^{-1}$ at temperatures ranging from 40 °C to 800 °C under a nitrogen atmosphere.

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