The Immobilization of Glycidyl-Group-Containing Ionic Liquids and Its Application in CO_2 Cycloaddition Reactions

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Abstract: Covalent immobilization of glycidyl-group-containing ionic liquids (ILs) on organic and inorganic supports with functional surfaces was achieved, based on the fact that the glycidyl group can actively react with almost all nucleophilic, electrophilic, neutral, and free-radical species. By using polymer spheres with amino- and carboxyl-group-functionalized surfaces as organic supports and silicas (including SBA15 and silica gel) with amino groups attached as inorganic supports, the ionic liquid 1-glycidyl-butylimidazolium chloride was successfully grafted onto these polymer and silica supports, respectively, through reactions between the glycidyl group in the IL and the polar groups on the support surfaces. The resultant samples were examined by transmission electron microscopy, solid-state ^{13}C NMR spectroscopy, IR spectroscopy, and ion chromatography. The activities of these resultant polymer- and silica- based catalysts were investigated for CO_2 cycloaddition reactions with epoxides. It was demonstrated that these catalysts could effectively catalyze CO_2 cycloaddition. In particular, the polymer supports generated synergistic effects with the IL in the coupling reaction of CO_2 with propylene oxide, and the turnover frequency could reach about $1700\ h^{-1}$ when the IL attached to the NH_2-functionalized polymer was used as the catalyst.

Keywords: carbon dioxide · cycloaddition · heterogeneous catalysis · immobilization · ionic liquids

Introduction

Ionic liquids (ILs) have promising applications in various fields due to their unusual properties.[1] In particular, ILs offer opportunities for the development of new catalytic systems and relevant materials.[2] The immobilization of ILs onto suitable solid supports has attracted much attention in recent years, and many catalytic materials with high performances have been prepared.[3] This new class of heterogeneous catalytic materials, that is, the supported IL catalysts, shares the advantages of IL media and solid supports, and new functions are generally generated; thus, these materials have many potential applications in catalysis.

Since the first work to prepare an IL–polymer gel in 1997,[4] several methods to immobilize ILs have been reported, and these can mainly be grouped into two categories: noncovalent and covalent methods.[3,5] The former are mainly based on various intermolecular forces between the ILs and the supports including Van der Waals forces, π-stacking interactions, hydrogen bonding, and Coulomb forces. This method is relatively simple and the loading content of the supported ILs can reach a high level.[6] The inherent drawback of this method is that the loss of the immobilized ILs cannot be avoided if they are used in polar solvent systems. To avoid this shortcoming of the noncovalent method, approaches for chemically grafting IL fragments onto a surface-modified support were developed. For example, ILs were covalently immobilized onto silica supports by a silane coupling agent,[5a] different linkers were designed for grafting imidazolium salts onto polymer supports,[3b] and 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) was anchored onto a divinylbenzene (DVB) cross-linked polymer through copolymerization of [VBIM]Cl and DVB.[3e] However, in the covalent method, the immobilization of ILs typi-

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cally requires specifically designed linkers that rely on different support materials or surface modification. Therefore, the development of a more general approach to immobilize ILs on various supports is still challenging.

CO_2 is a major greenhouse gas, but it is also a nontoxic, abundant, cheap, and recoverable carbon source. The chemical fixation of CO_2 to produce valuable chemicals is becoming more and more important.[7] The synthesis of cyclic carbonates through the cycloaddition of CO_2 and epoxides is one of the promising routes for chemical CO_2 fixation.[8] It has been demonstrated that some ILs with halide anions (for example, Cl^-, Br^-, or I^-) are active for the cycloaddition reaction of CO_2.[9] The development of new catalysts with high efficiency for CO_2 cycloaddition reactions is especially desirable.

Herein, we propose a general approach for the covalent immobilization of glycidyl-group-containing ILs on functionalized organic and inorganic supports, based on the fact that the glycidyl group can actively react with almost all nucleophilic, electrophilic, neutral, and free radical species.[10] As an example, 1-glycidyl-butylimidazolium chloride (GlBIMCl) was selected as the supported IL. In this work, we chose polymer spheres functionalized with NH_2 and COOH groups and silica (including SBA15 and silica gel) functionalized with NH_2 groups as supports, and we investigated the grafting of GlBIMCl onto the various supports. To the best of our knowledge, this is the first work to use the glycidyl group as a versatile and effective linker to graft ILs onto both organic and inorganic supports. The catalytic properties of the as-prepared catalysts were tested in the cycloaddition reaction of CO_2 with epoxides, and the effect of the support on the reaction was also investigated.

Results and Discussion

As illustrated in Scheme 1, the glycidyl group in the cation of the IL acts as a versatile linker, which can be grafted onto a wide range of supports functionalized with nucleophiles and electrophiles such as NH_2, COOH and so on.

The morphology of the resultant samples was detected by scanning electron microscopy. It was demonstrated that all of the as-prepared samples exhibited almost the same morphology as their parent supports (see Figure S1 in the Supporting Information). This suggests that the microstructures of the supports were retained during the immobilization of the IL onto the supports. The loading amounts of IL on the different supports were determined by ion chromatography based on the content of the element Cl; the values were 0.0022, 0.0027, 0.093, and 0.102 mmol g^{-1} for P-NH$_2$–IL, P-COOH–IL, SBA15-NH$_2$–IL and silica-NH$_2$–IL, respectively (P represents the polymer support). Solid-state ^{13}C NMR analysis was used to examine whether the IL was covalently immobilized onto the different supports. Figure 1 shows the solid-state ^{13}C NMR spectra of the resultant samples. In general, the peak intensity in solid-state NMR spectroscopy is mainly determined by two factors: the relative amount and
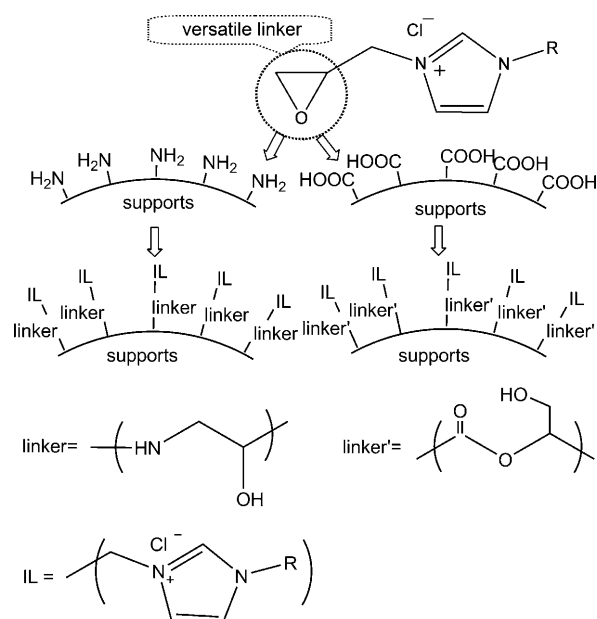
Scheme 1. General approach for the covalent immobilization of a glycidyl-group-containing IL on supports functionalized with active groups through oxirane-ring-opening reactions.
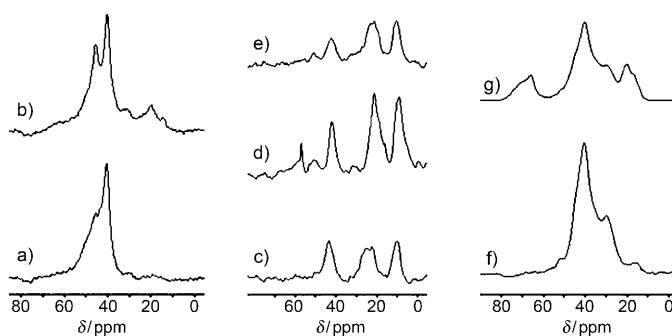

Figure 1. Solid-state ^{13}C NMR spectra of a) amino-functionalized polymer, b) P-NH$_2$–IL, c) amino-functionalized silica substrate, d) SBA15-NH$_2$–IL, e) silica-NH$_2$–IL, f) carboxyl-functionalized polymer, and g) P-COOH–IL.

the cross-polarization efficiency of the detected sample.[11] Whereas the amount of IL grafted onto the substrates was very low, the high relative cross-polarization efficiency made the grafted IL generate clear new peaks. By comparison with the NMR spectrum of the polymer support (Figure 1, spectrum a), the enhanced signal at around 20 ppm and a new peak at 15 ppm in the spectrum of P-NH$_2$–IL (Figure 1, spectrum b) could be assigned to the butyl carbon atom of GlBIMCl. The resonance signal at around 62 ppm was unconspicuous and hidden by the strong peak of the polymer substrate at around 50 ppm; it could possibly be assigned to a methine attachment to a hydroxy group, which would suggest that the IL was covalently grafted onto the polymer support. From a comparison with the spectrum of an amino-functionalized silica substrate (Figure 1, spectrum c), the enhanced resonance signals at around 50 ppm in the ^{13}C NMR

spectra of SBA15-NH2–IL and silica-NH2–IL (Figure 1, spectra d and e, respectively) may be attributed to a methylene carbon atom that originates from the glycidyl group of GlBIMCl and is grafted onto the amino group of the substrates. The new peak at 57 ppm in spectrum d in Figure 1 could also be assigned to a methine group attached to a hydroxy group after the ring-opening reaction. From a comparison with the spectrum of the carboxyl-functionalized polymer (Figure 1, spectrum f), two new resonance peaks centered at 67 and 20 ppm were identified in the spectrum of P-COOH–IL (Figure 1, spectrum g); this provided direct evidence of the covalent immobilization of IL onto the polymer spheres. Therefore, it can be concluded that the glycidyl-containing IL, GlBIMCl, was successfully grafted onto both organic (polymer spheres) and inorganic (SBA15 and silica) substrates through oxirane-ring-opening reactions between the glycidyl noiety and the NH2 and COOH groups, respectively.

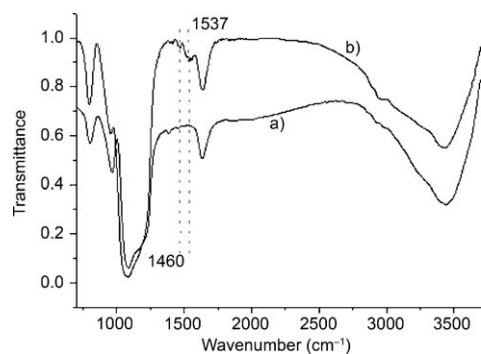We also examined the resultant samples through IR analysis. As shown in Figure 2, new absorption peaks at around

Figure 2. FTIR spectra of a) the SBA15-NH2 support and b) the SBA15-NH2–IL catalyst.

1460 and 1537 cm^{-1} appeared in the IR spectrum of SBA15-NH2 grafted with IL, which could be attributed to the C=N and C=C vibrations of the imidazole ring, a result indicating that the IL was grafted onto the surface of the SBA15-NH2 support. The IR results are in agreement with the NMR analysis. Both of them indicate that the IL was chemically immobilized onto the supports.

It has been reported that some ILs with halide anions (for example, Cl^{-}, Br^{-}, or I^{-}) are active for catalyzing the cycloaddition reaction of CO_2 with epoxides.[9] In this work, the cycloaddition of CO_2 with propylene oxide (PO) was performed by using GlBIMCl as a catalyst, and it was demonstrated that GlBIMCl was effective for catalyzing this reaction (Table 1, entry 1). However, the catalytic activity of GlBIMCl was low, probably due to the poor miscibility of GlBIMCl with PO. When the cycloaddition reaction was carried out in DMF, the GlBIMCl showed high catalytic activity (Table 1, entry 2). From the above experiments, it can be deduced that GlBIMCl may be used as a catalyst for CO_2 cycloaddition with epoxides. Therefore, the materials

Table 1. Activities of various catalysts for the cycloaddition reaction of CO_2 with PO.[a]

Entry	Catalyst	Molar ratio PO/IL	t [h]	Yield of PC [%]	TOF[b] [h^{-1}]
1	GlBIMCl	333	8	54	–
2	GlBIMCl in DMF[c]	333	8	97	40.4
3	P-NH2–IL	14258	8	95	1693
4	P-COOH–IL	16667	22	78	591
5	SBA15-NH2–IL	333	11	95	28.8
6	silica-NH2–IL	333	11	82	24.8

[a] Reaction conditions: 6.2 mmol of PO, initial pressure of CO_2 at 6 MPa, 403 K, and either 200 mg of P-NH2–IL, 200 mg of SBA15-NH2–IL, 183 mg of silica-NH2–IL, or 139 mg of P-COOH–IL as the catalyst. [b] Turnover frequency (TOF), defined as moles of PO consumed per mole of supported IL per hour. [c] With N,N-dimethylformamide (DMF; 3 mL) as the solvent.

prepared in this work, that is, P-NH2–IL, P-COOH–IL, SBA15-NH2–IL, and silica-NH2–IL, were expected to be useful as heterogeneous catalysts for CO_2 cycloddition with epoxides. The dispersibility of these samples was examined in PO, and it was shown that all four samples could be easily dispersed in PO to form relatively stable suspensions; this is beneficial for the reaction of CO_2 with PO.

The catalytic activity of P-NH2–IL was first examined in the cycloaddition of CO_2 with PO to produce propylene carbonate (PC). Figure 3 illustrates the dependence of the PC
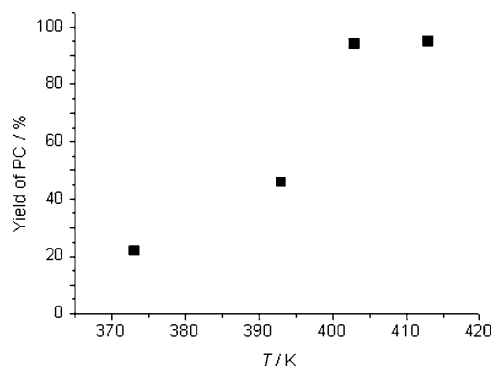

Figure 3. Influence of the reaction temperature on the PC yield. Reaction conditions: 6.2 mmol of PO, 200 mg of P-NH2–IL, initial pressure of CO_2 at 6 MPa, reaction time of 8 h.

yield on the reaction temperature; the PC yield was strongly affected by the reaction temperature and increased with the temperature in the range from 373 to 403 K. However, further increase in the reaction temperature did not enhance the PC yield, which may be due to side reactions occurring at higher temperature. Therefore, the reaction temperature was fixed at 403 K to perform the cycloadditions of CO_2 in the subsequent studies.

Although the loading content of IL on the NH2-functionalized polymer support was very low (0.0022 mmol g^{-1}), P-NH2–IL was demonstrated to have very high activity for the coupling of CO_2 with PO (Table 1, entry 3). This may result

from good contact between the PO and the catalyst. As described above, IL, as the catalytically active component, was chemically immobilized on the surface of the polymer spheres and the polymer catalyst could be uniformly dispersed in PO, which would provide good contact between the IL and the reactant molecules. Figure 4 shows the influ-
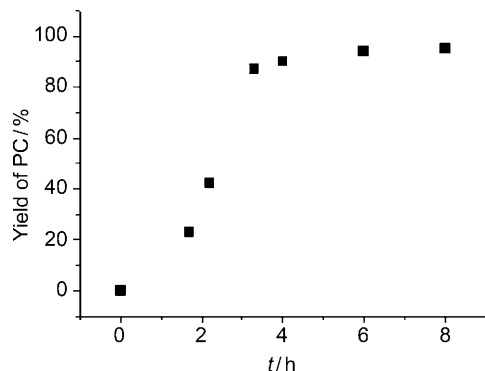

Figure 4. Dependence of the PC yield on reaction time. Reaction conditions: 403 K, 6.2 mmol of PO, 200 mg of P-NH$_2$–IL, initial CO$_2$ pressure at 6 MPa.

ence of reaction time on the PC yield with P-NH$_2$–IL as the catalyst for the cycloaddition of CO$_2$ with PO. It is obvious that the reaction proceeded rapidly within the first 4 h and that the PO could be converted completely within 8 h. The turnover frequency (TOF), defined as moles of PO consumed per mole of supported IL per hour, could reach about 1700 h^{-1}, which was much higher than that (21 h^{-1}) obtained over the copolymer of [BVIM]Cl and DVB.[3e] This suggests that the amino-polymer-supported GlBIMCl (P-NH$_2$–IL) was very active for the cycloaddition of CO$_2$ with PO.

The activity of the other supports and the resultant samples for the coupling of CO$_2$ and PO was also examined under similar reaction conditions. All of the parent supports displayed little activity for this reaction, even when the reaction was performed at 403 K for 24 h. All of the immobilized-GlBIMCl catalysts were active for catalyzing the coupling reaction of CO$_2$ with PO, as shown in Table 1. From entries 1–4 of Table 1, it can be seen that the polymer-supported GlBIMCl (P-NH$_2$–IL and P-COOH–IL) was much more active than the pure GlBIMCl catalyst for the reaction performed either under solvent-free conditions or in DMF. This suggests that the polymer support produced a synergistic effect with GlBIMCl in the cycloaddition of CO$_2$ with PO. However, from a comparison of the results in entries 2, 5, and 6 of Table 1, it is indicated that the IL supported on both the SBA15 and the silica gel displayed comparable activity to that of the pure GlBIMCl catalyst. This indicates that the SBA15 and silica gel only acted as supports and had no activity for the reaction. The activity differences between the polymer- and silica-supported catalysts may stem from the differences in the interactions between the support and the reactant. It has been reported that CO$_2$ can swell poly-

mer substrates considerably.[12] In this work, the mixture of PO and CO$_2$ could swell the polymer catalyst to some extent under the experimental conditions, which could render more reactant molecules available to interact with the active species (that is, the immobilized IL) and could finally result in enhanced activity of the catalyst.

Although the IL contents in P-NH$_2$–IL (0.0022 mmol g^{-1}) and P-COOH–IL (0.0027 mmol g^{-1}) were similar, P-NH$_2$–IL was much more active than P-COOH–IL under similar experimental conditions (Table 1, entries 3 and 4). A possible reason is that CO$_2$ could be activated by the amino group on the support, which would be beneficial for the insertion of CO$_2$ into the C–O bond of PO through nucleophilic attack.[13] This indicates that the IL and the amino group generated a synergistic effect for CO$_2$ cycloaddition. SBA15-NH$_2$–IL and silica-NH$_2$–IL also displayed different efficiencies for this reaction (Table 1, entries 5 and 6). The catalytic activity of SBA15-NH$_2$–IL was higher than that of silica-NH$_2$–IL. A plausible reason for this is that SBA15-NH$_2$–IL has more silanol groups than silica-NH$_2$–IL, as confirmed by the IR spectra in which the relative intensity of the Si–OH bending band at around 960 cm^{-1} is stronger for SBA15-NH$_2$–IL than for silica-NH$_2$–IL (not shown). Silanol on the support surface is most likely involved in the activation of PO through H-bond formation,[14] which would lead to the higher activity of SBA15-NH$_2$–IL relative to that of silica-NH$_2$–IL.

To explore the stability of the catalysts, a series of catalytic cycles of the reaction of CO$_2$ with PO were carried out. In each cycle, the catalyst was easily recovered through simple centrifugation, followed by washing three times with ethyl acetate. After being dried, the catalyst was reused for the next run. The results illustrated in Figure 5 show that
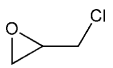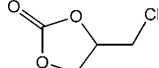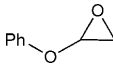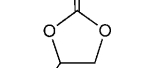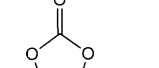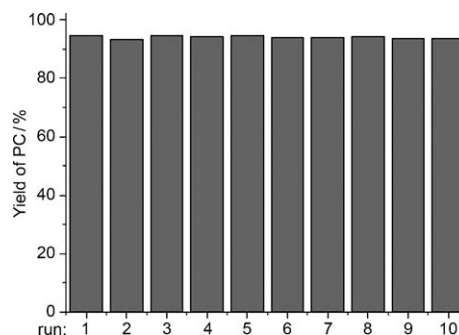

Figure 5. Reuse of the P-NH$_2$–IL catalyst. Reaction conditions: 6.2 mmol of PO, 200 mg of P-NH$_2$–IL, initial pressure of CO$_2$ at 6 MPa, 403 K, 8 h.

the catalyst P-NH$_2$–IL could be reused at least 10 times without noticeable loss of activity, which indicates that the catalyst was very stable. This is reasonable because the active component for catalyzing the reaction was the IL and it was chemically grafted onto the polymer support. Not until the catalyst was reused for 16 cycles, was a slight decrease in the PC yield observed. Solid-state ^{13}C NMR analysis (see Figure S2 in the Supporting Information) was used

to identify the structure of the used catalyst. In comparison with the NMR spectrum of the fresh P-NH$_2$–IL catalyst (spectrum a in Figure S2 in the Supporting Information), the signal at around 20 ppm was enhanced and a new peak appeared at 68 ppm in the spectrum of the reused catalyst P-NH$_2$–IL (spectrum b in Figure S2 in the Supporting Information). This suggests that the IL was not removed from the catalyst. Instead, PO might react with the hydroxy group in the catalyst that was formed during the grafting of the IL onto the polymer substrate, which would cause the catalyst to exhibit less activity for the reaction of PO with CO$_2$. The stability of the catalyst SBA15-NH$_2$–IL was also studied. Similarly, no activity loss was observed if SBA15-NH$_2$–IL was reused five times. This is also attributed to the covalent immobilization of the IL on the SBA15 support. Therefore, it can be concluded that both the polymer- and silica-supported ILs were very active and stable for the CO$_2$ cycloaddition reaction.

From the above results, it can be concluded that the IL supported on an NH$_2$-functionalized polymer (that is, P-NH$_2$–IL) was the most active catalyst for the cycloaddition reaction of CO$_2$ and PO under the experimental conditions. The scope of the P-NH$_2$–IL catalyst was established by using a range of epoxides as substrates, and the results are listed in Table 2. Obviously, this catalyst was very active for the tested cycloaddition of CO$_2$ with epoxides. In particular, glycidyl phenyl ether and styrene oxide were more active, and high yields of the carbonates were achieved within 6 h.

Table 2. Catalytic activity of P-NH$_2$–IL in the reactions of various epoxides with CO$_2$.[a]

Entry	Epoxide	Carbonate	t [h]	Yield [%]
1			8	84
2			5	89
3			6	91

[a] Reaction conditions: 6.2 mmol of epoxide, 200 mg of P-NH$_2$–IL as the catalyst, initial pressure of CO$_2$ at 6MPa, 403 K.

Conclusion

In conclusion, we have developed a general approach for the covalent immobilization of glycidyl-group-containing ILs onto various supports. By using the glycidyl group in the IL GlBIMCl as a versatile and effective linker, the IL was successfully grafted onto inorganic (SBA15 and silica gel) and organic (polymer) substrates. All of the resultant supported-IL catalysts were active for the cycloaddition reaction of CO$_2$ and PO. In particular, the polymer supports generated synergistic effects with the IL in the coupling reaction of CO$_2$ and PO, and P-NH$_2$–IL was the most active catalyst and produced cyclic carbonates with high efficiency. We believe that this method can be applied to immobilize glycidyl-containing ILs on various functional surfaces for the preparation of highly efficient catalysts.

Experimental Section

Materials: CO$_2$ ($\geq 99.95\%$) was obtained from Beijing Analytical Instrument Factory. Propylene oxide (PO), methyl alcohol, ethyl acetate, toluene, dichloromethane, DMF, ethyl silicate, n-octanol, 3-aminopropyltriethoxysilane, and epichlorohydrin were analytical-reagent grade, provided by Beijing Beihua Fine Chemical Company and used as received. Silica gel (200–300 mesh) was commercially supplied by Yantai Chemical Institute. The amino- and carboxyl-group-functionalized polymer spheres with a size of around 400 nm were supplied by the State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences.[15] GlBIMCl was synthesized by the direct alkylation of N-butylimidazole with epichlorohydrin in acetonitrile for 12 h with heating to reflux, based on the method described in the literature.[16] The SBA15, rich in silanol groups, was prepared by microwave-assisted template removal based on the procedures reported by Zhao and co-workers.[17] The as-obtained SBA15 and silica gel were amino-functionalized according to the reported procedures.[18]

Grafting of IL onto amino-group-functionalized supports: In a typical experiment, excess amounts of GlBIMCl were dissolved in methanol (50 mL). Amino-functionalized support (that is, amino-functionalized SBA15 or amino-functionalized polymer spheres; 1 g) was then dispersed into the above solution with vigorous stirring. The suspension was stirred at 75°C under an Ar atmosphere for 36 h. The IL-grafted powder was separated by centrifugation and thoroughly washed with ethanol, water, and ethyl acetate at least five times. The obtained samples were vacuum dried at 60°C for 12 h. Based on the supports used, the resultant materials were designated as P-NH$_2$–IL, SBA15-NH$_2$–IL and silica-NH$_2$–IL, respectively.

Grafting of IL onto carboxyl-group-functionalized polymer spheres: According to a modified method,[10a] excess amounts of GlBIMCl and anhydrous FeCl$_3$ (0.018 g) were dissolved in dichloromethane (200 g). The carboxyl-group-functionalized polymer spheres (2.3 g) were then dispersed into the above solution under vigorous stirring. The suspension was heated to reflux at 70°C under an argon atmosphere for 72 h. The obtained product was washed at least five times with water and was finally vacuum dried at 60°C for 12 h. The resultant sample was designated as P-COOH–IL.

Sample characterization: The morphology of the as-prepared samples was observed by scanning electron microscopy (Hitachi-S4300; operated at 15.0 kV) and transmission electron microscopy (JEM 1011; operated at 100 kV), respectively. Solid-state ^{13}C NMR analysis was performed on a Bruker AVANCE III 400 instrument. The loading amounts of IL on different supports were determined by ion chromatography (761 Compact, Metrohm) based on the amount of elemental Cl. IR analysis was carried out on a Bruker Tensor 27 spectrometer.

Cycloaddition reactions of CO$_2$ with epoxides: All of the cycloaddition reactions of CO$_2$ with epoxides were carried out in a 6 mL stainless autoclave with a magnetic stirrer. In a typical experiment, the catalyst (for example, P-NH$_2$–IL, 200 mg) and PO (6.2 mmol) were loaded into the autoclave, which was then heated in an air bath at the reaction temperature. After thermal equilibrium, CO$_2$ was slowly introduced into the reactor with a high-pressure pump (DB-80, Beijing Weixing Factory) up to a pressure of 6 MPa. After the reaction, the autoclave was cooled in an ice bath, and the gas was slowly released and passed through a cold trap containing ethyl acetate (2 mL). After the catalyst was separated by high-

speed centrifugation, the products were analyzed by gas chromatography (Agilent 4890D) with *n*-octanol as an internal standard.

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