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Porous Ionic Polymers as a Robust and Efficient Platform for Capture and Chemical Fixation of Atmospheric CO_2

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Direct use of atmospheric CO_2 as a C_1 source to synthesize high-value chemicals through environmentally benign processes is of great interest, yet challenging. Porous heterogeneous catalysts that are capable of simultaneously capturing and converting CO_2 are promising candidates for such applications. Herein, a family of organic ionic polymers with nanoporous structure, large surface area, strong affinity for CO_2, and very high density of catalytic active sites (halide ions) was synthesized through the free-radical polymerization of vinyl-functionalized quaternary phosphonium salts. The resultant porous ionic polymers (PIPs) exhibit excellent activities in the cycloaddition of epoxides with atmospheric CO_2, outperforming the corresponding soluble phosphonium salt analogues and ranking among the highest of known metal-free catalytic systems. The high CO_2 uptake capacity of the PIPs facilitates the enrichment of CO_2 molecules around the catalytic centers, thereby benefiting its conversion. We have demonstrated for the first time that atmospheric CO_2 can be directly converted to cyclic carbonates at room temperature using a heterogeneous catalytic system under metal-solvent free conditions. Moreover, the catalysts proved to be robust and fully recyclable, demonstrating promising potential for practical utilization for the chemical fixation of CO_2. Our work thereby paves a way to the advance of PIPs as a new type of platform for capture and conversion of CO_2.

Introduction

Accumulation of the primary greenhouse gas CO_2 in the atmosphere is suspected as the main culprit for global climate changes. Reduction of CO_2 emissions is now a matter of genuine public concern and tremendous efforts have been devoted to address this issue.[1] Currently, carbon capture and sequestration (CCS) has been projected as a feasible approach.[2] The captured CO_2 is proposed to be injected into underground reservoirs and stored as waste. Alternatively, catalytic transformation of the captured CO_2 into high-value chemicals would be more desirable.[3] Toward this end, the cycloaddition of CO_2 to an epoxide to produce cyclic carbonates is quite promising because of their wide applications in pharmaceutical and fine chemicals and high atomic efficiency of those transformations.[4] Thus far, a variety of efficient catalytic systems involving metal species from simple alkali salts to classical organometallic complexes as well as related heterogeneous catalysts were developed and studied.[5] Despite of these achievements, the search for more environmentally benign processes, in particular for metal-free catalytic systems, has been an impetus for research in both industry and academia.[6] Organic ionic compounds such as alkyl ammonium or phosphonium halides proved to be extremely effective for high-yield conversion of epoxides with CO_2 to form the corresponding cyclic carbonate.[7]

Nevertheless, the complicated product separation from the catalysts still represents a limitation for large-scale applications.

Organic ionic polymers have recently become a new research focus in the polymer and materials communities because of their potential for applications in numerous areas including carbon precursors, catalysis, ion conductors, and smart stabilizers.[8] Impressively, it has also been suggested that the ionic polymers seem to have intrinsic CO_2 philicity, because of the strong dipole–quadrupole interactions between ionic moieties and CO_2.[9] This property makes them interesting as they are expected to provide a unique benefit in the fields involving CO_2. Furthermore, the introduction of porosity into these materials yields porous ionic polymers (PIPs), which in principle can not only amplify the uptake capacity of CO_2 and accelerate the interfacial mass and energy transport by virtue of the

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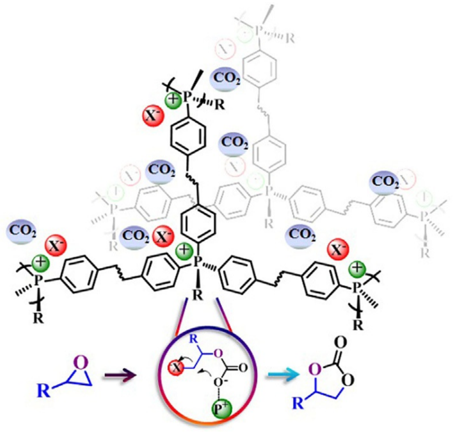
porous structures, but also overcome the issue of catalyst/product separation as encountered for the soluble organic ionic compounds.[10] Thereby, such type of materials is postulated to be promising candidates to catalyze CO_2 transformations by taking advantage of the combination of CO_2 capture and conversion (Scheme 1).



Scheme 1. Illustration of the application of PIPs in CO_2 capture and conversion.

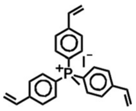
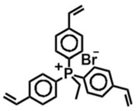
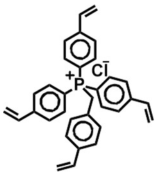
Bearing all those above in mind, herein, a family of organic ionic polymers, featured with nanopores, large surface area, and very high ionic density was synthesized by free-radical polymerization of vinyl-functionalized quaternary phosphonium salts. As a result of the combined contributions of highly accessible active sites and the excellent CO_2 affinity of the resultant PIPs, they demonstrate excellent activities in the cycloaddition of epoxides with atmospheric CO_2 at low temperature in the absence of any solvent, co-catalyst, or other additives, outperforming their corresponding soluble phosphonium salt analogues. Considering the improved performance and diversity of the organic ionic compounds, our work provides a promising direction for the development of highly efficient materials for sustainable conversion of CO_2.

Results and Discussion

Synthesis, characterization, and gas adsorption tests

PIPs were prepared by the free-radical solvothermal polymerization of the vinyl-functionalized quaternary phosphonium salt monomers (Figure S1 in the Supporting Information), which can be readily synthesized from tris(4-vinylphenyl)phosphine and the corresponding alkyl halide (Table 1), to obtain PIP-Me-X, PIP-Et-X, and P-Bn-X (X = Cl, Br, I). N_2-sorption isotherms collected at 77 K reveal that these polymers have relatively high surface areas of 402, 625, and 758 $m^2 g^{-1}$ for PIP-Me-I, PIP-Et-Br, and PIP-Bn-Cl, respectively (Figure 1 a), which should be very beneficial for the mass transfer during the reaction.[11] Correspondingly, they exhibit excellent CO_2 affinity, allowing CO_2 uptake of 1.38, 1.47, and 1.52 $mmol\,g^{-1}$ at 298 K and 1.88, 2.01, and 2.23 $mmol\,g^{-1}$ at 273 K, respectively (Figure 1 b and c), higher than those reported for other PIP materials[12] and about 20 times the values for the nonporous counterparts (Figure S2) as well as about 40 times the values for the corresponding quaternary phosphonium salt moieties obtained by the treatment of triphenylphosphine and the corresponding alkyl halides (homogeneous quaternary phosphonium analogues, QPs, shown in Figure 1 d). In addition, an inferior CO_2 uptake is observed for nonionic porous polymer (polydivinylbenzene) than that for PIP-Bn-Cl, although they possess similar large surface areas (Figure S3). These results suggest that because of the high po-

Table 1. Molecular structures of vinyl-functionalized quaternary phosphonium salts and textural parameters of corresponding PIPs.

Monomer	Polymer	BET surface area $[m^2 g^{-1}]$	Pore volume $[cm^3 g^{-1}]$
	PIP-Me-I	402	0.24
	PIP-Et-Br	625	0.40
	PIP-Bn-Cl	758	0.59

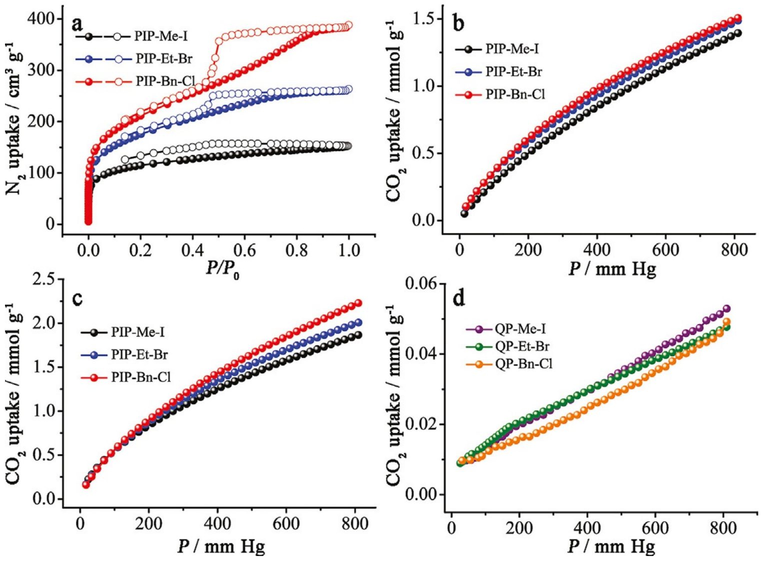


Figure 1. a) N_2-sorption isotherms collected at 77 K, b) CO_2-sorption isotherms collected at 298 K, and c), d) CO_2-sorption isotherms collected at 273 K. Soluble quaternary phosphonium salts of QP-Me-I, QP-Et-Br, and QP-Bn-Cl synthesized from triphenylphosphine with iodomethane, bromoethane, and benzyl chloride, respectively.

rosity and ionic character, there is a sound interaction between the PIP frameworks and CO_2 molecules, which provides these polymers with unique properties, particularly for the transformations involving CO_2.

Evaluation of catalytic performance

Given the high density of catalytically active sites and their capability to adsorb a substantial amount of CO_2, we set out to evaluate their performance in the cycloaddition of epoxides with CO_2 to form cyclic carbonates. Control experiments were conducted for homogeneous quaternary phosphonium salts and nonporous ionic polymer. In a typical experiment, the reactions were conducted in a Schlenk tube using epichlorohydrin (1.0 g, 10.9 mmol) purged with atmospheric CO_2 and the catalyst (0.05 mmol, based upon the quaternary phosphonium salt) under solvent-free conditions at 323 K. As shown in Figure 2, all tested PIPs demonstrate higher catalytic activities for cycloaddition of epichlorohydrin with CO_2 than those of the corresponding QPs. In addition, as a representative catalyst PIP-Bn-Cl exhibits higher activity than the nonporous polytriphenyl(4-vinylbenzyl)phosphonium chloride, affording chloropropene carbonate yields of 92.8 and 34.6%, respectively. These observed catalytic activities could be attributed to the following reasons: i) the integration of CO_2 philicity and porous structures of these frameworks render the CO_2 molecules concentrated near the catalytic sites, thus promoting the cycloaddition of epichlorohydrin and CO_2; ii) the 3D nanochannels of these PIPs allow the reactions not to be diffusion controlled.

The catalytic activities of the synthesized PIPs have the following order: PIP-Me-I < PIP-Et-Br < PIP-Bn-Cl. Given the great differences in catalytic performance of these PIPs, the effect of the halogen anions and quaternary phosphonium cations on the catalytic activity was examined. Because of their ionic nature, anion exchanges can be readily carried out on PIPs, yielding PIP-Me-X, PIP-Et-X, and PIP-Bn-X (X = Cl, Br, I), respectively. Notably, the catalytic efficiency of PIPs with the same cations decreased in the order $Cl^- > Br^- > I^-$, which is different form the catalytic systems that involved metal species (such as metal–organic framework (MOF)-based catalysts with the assistance of organic ionic compounds), where the order is $Br^- > Cl^- > I^-$. These results can be explained as follows: in the absence of the Lewis acid, nucleophilic attack of I^- or Br^- on the epoxide was slower than that of Cl^- because I^- and Br^- are intrinsically less nucleophilic than Cl^-. On the other hand, the catalytic efficiency of the PIPs bearing the same X^- anions decrease in the order: PIP-Bn^+ > PIP-Et^+ > PIP-Me^+, which is likely a result of the less tight ion pairing between bulkier cations in PIP-Bn-X with X^- than those in PIP-Me-X and PIP-Et-X with less bulkier cations, thus increasing their nucleophilicity. As a consequence, the combined contributions of the high nucleophilicity and easy availability of Cl^- in the PIP-Bn-Cl catalyst leads to its enhanced catalytic performance. These interpretations are in good agreement with mechanisms proposed previously, which suggest that the rate-determining step of this reaction is the ring opening of the epoxide, which occurs through the attack by anions.[13]

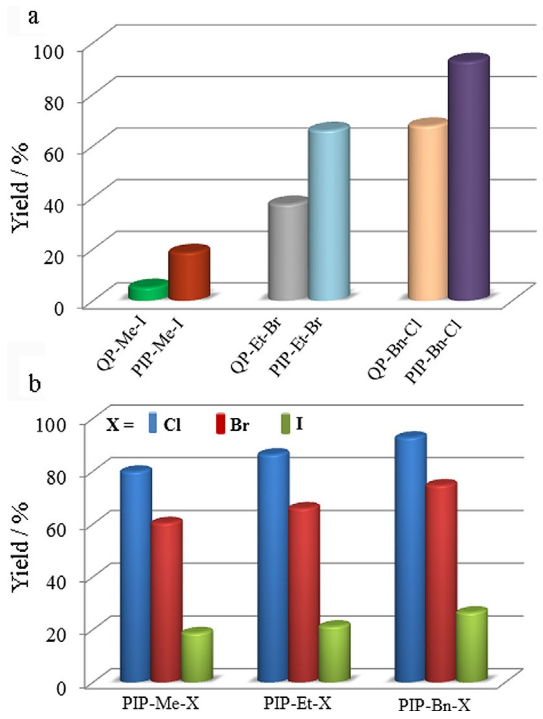
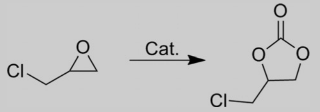


Figure 2. Yields of chloropropene carbonate from the cycloaddition of epichlorohydrin and CO_2 catalyzed by a) PIPs with corresponding QPs and b) PIP-Me-X, PIP-Et-X, and PIP-Bn-X (X = Cl, Br, and I). Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), catalyst (0.05 mmol, based upon the quaternary phosphonium salt), 323 K, CO_2 (ambient pressure), and 24 h.

Consequently, PIP-Bn-Cl was used as a representative sample in further studies. Table 2 shows the PIP-Bn-Cl-catalyzed cycloaddition of CO_2 with epichlorohydrin under various temperatures and CO_2 pressures. Unprecedentedly, CO_2 is converted efficiently by PIP-Bn-Cl under very mild conditions (i.e., ambient conditions) as well as with very low catalyst dosage (0.46 mol%), giving rise to 91.4% chloropropene carbonate yield after 80 h. As far as we know, no report has appeared for a heterogeneous catalyst to promote the cycloaddition of CO_2 to epoxides under atmospheric CO_2 pressure and room temperature without solvent, metal species, and the addition of an external homogeneous co-catalyst. Heterogeneous catalysts such as MOFs or metal-coordinated porous polymers are active under ambient conditions only with the assistance of external homogeneous co-catalysts. In general, the reaction rate increases sharply in the temperature range 298–373 K. For example, a full conversion can be reached within 3 h when the reaction is performed at 373 K. In contrast, the pressure of CO_2 has relatively little influence on the reaction. Only a slightly increased epichlorohydrin conversion from 63.3 to 71.4% was observed when the CO_2 pressure was increased from 0.1 to 1.0 MPa. However, further increase in CO_2 pressure from 1.0–4.0 MPa does not provide fruitful results, which might be because of the strong affinity of PIP-Bn-Cl to CO_2 that guarantees the presence of sufficient CO_2 molecules in the vicinity of the catalytic sites.

Table 2. Dependence on reaction conditions of the PIP-Bn-C-catalyzed cycloaddition of epichlorohydrin.[a]



Entry	T [K]	CO_2 pressure [MPa]	t [h]	Yields [%]
1	298	0.1	80	94.7
2	298	0.1	48	63.3
3	313	0.1	40	72.7
4	323	0.1	24	92.8
5	333	0.1	18	$>$99.0
6	373	0.1	3	$>$99.0
7	298	0.1	48	71.4
8	298	2	48	73.2
9	298	3	48	72.9
10	298	4	48	73.5

[a] Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), catalyst (25 mg, 0.05 mmol, based upon the quaternary phosphonium salt).

Recyclability and stability tests

Catalyst recyclability and long-term stability under harsh conditions are essential features of any catalysts considered for use in large-scale applications. As a solid catalyst, the PIP-Bn-Cl can be recovered by filtration after the reaction and reused for the next run. The yields of chloropropene carbonate for ten repeated runs are shown in Figure 3, and no considerable decrease in the yield is observed. These results confirm the excellent stability and recyclability of the catalyst.

To further illustrate the robustness of the catalyst, long-term catalytic tests were performed under high temperature (423 K) and high pressure (2–3 MPa) using PIP-Bn-Cl (25 mg) and a large amount of epichlorohydrin (1.0 mol, 92.5 g) in a 200 mL autoclave and by maintaining the pressure of the system by adding CO_2. The conversion of the reagent increased steadily with increasing time. After reaction for 100 h, a 97.1 % chloropropene carbonate yield and a turnover number (TON) value as high as 19420 were achieved, thus indicating the stability of the catalyst. On the other hand, such a high value of TON further suggests that the PIP-Bn-Cl has broad applicability in industry for cycloaddition of CO_2 to cyclic carbonates. After using for 100 h, the chemical structure of PIP-Bn-Cl is well maintained and the surface area does not change considerably (from 758 to 593 m^2g^{-1},) as revealed by IR spectra and N_2-sorption isotherms (Figures S4 and S5), respectively, thus confirming the robustness of the catalyst.

Scope and limitation evaluation

Furthermore, we also studied the scope of the PIP-Bn-Cl catalyst for the cycloaddition of various epoxides with atmospheric CO_2 and found that it has a broad substrate scope (Table 3). All tested epoxides can be converted into carbonates with excellent yields. Moreover, despite its high steric hindrance and low-reactivity (owing to the strong chemical bond caused by the conjugation between the benzene ring and epoxy group), styrene oxide can also be smoothly converted under relatively low temperatures (Table 3, entries 5 and 6).

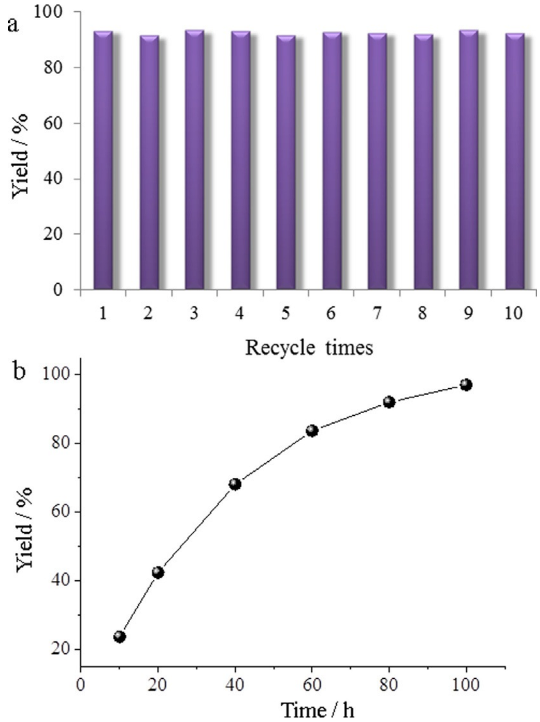


Figure 3. a) Recycling test of PIP-Bn-Cl catalyst in the cycloaddition of epichlorohydrin and CO_2. Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), catalyst (25 mg, 0.05 mmol, based upon the quaternary phosphonium salt), 323 K, CO_2 (ambient pressure), and 24 h; b) yields of chloropropene carbonate versus time under harsh reaction conditions: epichlorohydrin (1.0 mol, 92.5 g), PIP-Bn-Cl (25 mg), 423 K, CO_2 (2–3 MPa).

Conclusions

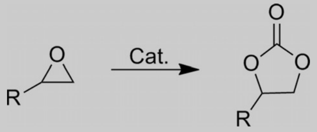
A family of robust, phosphonium-based porous ionic polymers (PIPs) is developed as adsorbents of CO_2 and heterogeneous catalysts for the cycloaddition of epoxides with atmospheric CO_2 at low temperature ($>$100 °C) even at room temperature. Control experiments based on homogeneous catalysts of the quaternary phosphonium salts and nonporous ionic polymer reveal the enhancement achieved by the introduction of the porous structure in the catalytic cycloaddition, which not only amplifies the adsorption capacity of CO_2 but also facilitates the mass transfer, thus leading to high activities. Because of the excellent stability, activity, and recyclability, the PIPs emerge as efficient materials for capture and conversion of CO_2 and, therefore, can have broad prospects for their practical applications in the chemical industry.

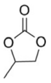
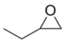
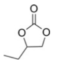
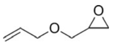
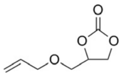
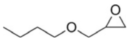
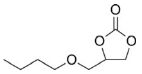
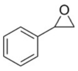
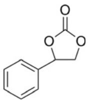
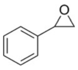
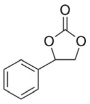
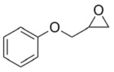
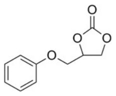
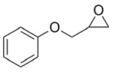
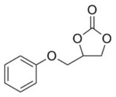
Experimental Section

Chemicals and materials

Solvents were purified according to standard laboratory methods. THF was distilled over $LiAlH_4$. 4-Bromostyrene was distilled over CaH_2. Other commercially available reagents were purchased in high purity and used without further purification.

Table 3. PIP-Bn-Cl-catalyzed cycloaddition reactions of epoxides with atmospheric CO_2 to cyclic carbonates.[a]



Entry	Epoxides	Products	T [°C]	Yields [%][b]
1			50	93.2
2			50	94.5
3			80	92.8
4			80	94.7
5[c]			80	67.4
6			100	87.6
7[d]			80	89.6
8			100	96.9

[a] Reaction conditions: epoxide (1.0 g), CO_2 (ambient pressure, PIP-Bn-Cl (25 mg), and 24 h. [b] Yields were determined by GC. [c] 72 h. [d] 48 h.

Synthesis of methyltris(4-vinylphenyl)phosphonium iodide

Iodomethane (0.85 g, 6 mmol) and tris-(4-vinylphenyl)-phosphine[14] (1.7 g, 5 mmol) were dissolved in acetone (10 mL), while stirring at 333 K under N_2 atmosphere for 48 h. After cooling to room temperature, the solid was filtrated, washed with diethyl ether, and dried under vacuum. The product was obtained as a white solid in quantitative yield.

Synthesis of ethyltris(4-vinylphenyl)phosphonium bromide

Bromoethane (0.65 g, 6 mmol) and tris-(4-vinylphenyl)-phosphine (1.7 g, 5 mmol) were dissolved in acetone (10 mL), while stirring at 333 K under N_2 atmosphere for 48 h. After the reaction, the mixture was cooled to room temperature, followed by filtrating, washing with diethyl ether, and drying under vacuum. The product was obtained as a white solid in quantitative yield.

Synthesis of (4-vinylbenzyl)-tris-(4-vinylphenyl)-phosphonium chloride.

4-Vinylbenzyl chloride (0.91 g, 6 mmol) and tris-(4-vinylphenyl)-phosphine (1.7 g, 5 mmol) were dissolved in acetone (10 mL), while stirring at 333 K under N_2 atmosphere for 48 h. After the reaction, the mixture was cooled to room temperature, followed by filtrating, washing with diethyl ether, and drying under vacuum overnight. The product was obtained as a white solid (2.2 g, 91 %).

Synthesis of PIPs

As a typical run, 1 g of vinyl-functionalized quaternary phosphonium salt [methyltris(4-vinylphenyl)phosphonium iodide, ethyltris-(4-vinylphenyl)phosphonium bromide, or (4-vinylbenzyl)-tris-(4-vinylphenyl)phosphonium chloride] monomer was dissolved in DMF (10 mL), followed by the addition of azobisisobutyronitrile (AIBN, 25 mg). After stirring at room temperature for 3 h, the mixture was transferred into an autoclave at 373 K for 24 h. After extraction of DMF with ethanol and drying in vacuum, white solid products were obtained and designated as PIP-Me-I, PIP-Et-Br, or PIP-Bn-Cl, respectively.

Synthesis of PIPs with different anions

PIPs with different anions ($X=I^-$, Cl^-, and Br^-) can be readily obtained by anion exchange with NaI, NaCl, and NaBr aqueous solutions.

Catalytic tests

Typical procedure for the cycloaddition at ambient CO_2 pressure

The reactions were carried out in a 25 mL Schlenk tube with a magnetic stirrer. As a typical run, the epoxide (1.0 g) and PIPs (25 mg) were transferred into the reactor. After sealing and purging with CO_2 using a balloon, the tube was placed in a preheated oil bath and stirred for a desired time. After the reaction, the catalyst was removedfrom the system by centrifugation and the product was analyzed by gas chromatography (GC-1690 Kexiao Co. equipped with a flame ionization detector and a HP-INNOWax capillary column) using dodecane as internal standard.

Typical procedure for the cycloaddition reactions at high CO_2 pressure

The reactions were carried out in a stainless steel reactor with a magnetic stirrer. As a typical run, the epoxide (1.0 g) and PIPs (25 mg) were transferred into the reactor. After sealing and purging with CO_2 to a desired pressure, the autoclave was placed in a preheated oil bath and stirred for a desired time. After the reaction, the reactor was cooled to below 273 K by using a cold ethanol bath and CO_2 was released and passed through a cold trap with *N,N*-dimethylformamide as absorbent. After the catalyst was as removed from the system by centrifugation, the product was analyzed by GC using dodecane as internal standard.

Characterizations

N_2-sorption isotherms at the temperature of liquid N_2 were measured using Micromeritics ASAP 2020 M and Tristar system. The CO_2-adsorption isotherms were measured at 298 and 273 K using a water and ice water bath, respectively. The samples were outgassed for 10 h at 100 °C before the measurements. Liquid NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) at $\delta=0$ ppm, and J values are given in Hz. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer.

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