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Quaternary Ammonium Salt Grafted Nanoporous Covalent Organic Polymer for Atmospheric CO_2 Fixation and Cyclic Carbonate Formation

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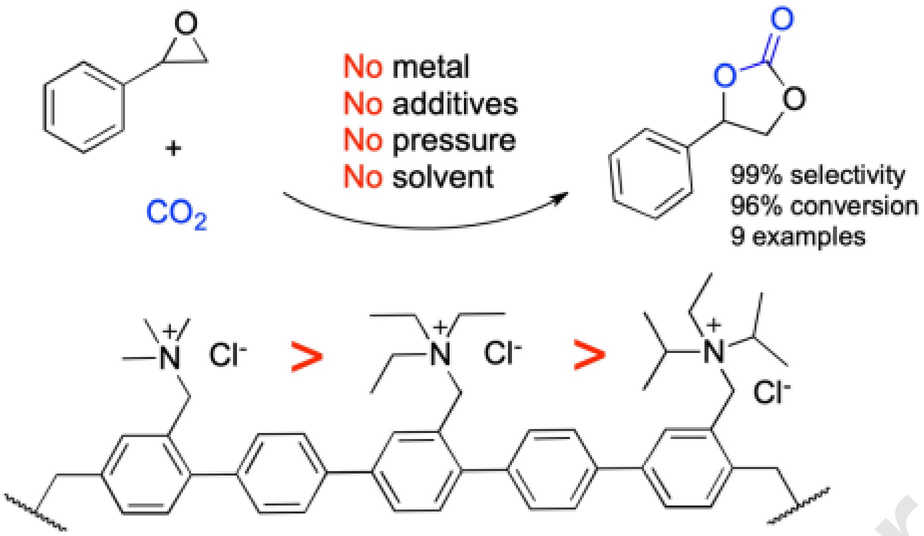
GRAPHICAL ABSTRACT



Highlights

- Nanoporous polymers retained porous structure after post-modification with quaternary ammonium functionalities
- Cycloaddition of CO_2 to epoxides was achieved with metal free and cost-effective porous catalyst
- The nanoporous catalyst worked under atmospheric pressure and without use of any additives or co-catalysts and showed wide substrate scope
- Steric hindrance of grafted ammonium salts changed microporosity, CO2 binding energy (Qst) and led to varying kinetics in cycloaddition reactions

Abstract:

Non-redox carbon dioxide utilization through cycloaddition of CO_2 to epoxides offer great promise but suffer from lack of heterogeneous catalysts that don’t need additives or pressure. Here we report a systematic post-synthetic modification procedure on a highly porous hydrocarbon framework for efficient grafting of quaternary ammonium salts. The active sites were tuned and characterized while maintaining the porous structure. The metal free and cost-effective catalysts showed quantitative selectivity and very high conversion yields in atmospheric pressure catalysis for cyclic carbonate formation from CO_2 and epoxides. The reaction proceeded without additives or co-catalysts, and tolerant for a wide substrate scope. We found that the steric hindrance of the alkyl units on ammonium salts affect microporosity, CO_2 binding and the kinetics of cycloaddition reactions. The catalysts were also recyclable, an attractive prerequisite for industrial implementation.

1. Introduction

Global warming of 1.5ºC since the pre-industrial levels is believed largely due to the excessive carbon dioxide (CO_2) emissions, through its dominant role as a greenhouse gas.[1] With the rise in CO_2 levels, issues emerged as global climatic change, worsening economies and concerns for general health of the world population.[2] In order to curb the potential harms further, Carbon Capture and Utilization (CCU) strategies were developed with the hope that CCU could provide reduction in carbon emissions and at the same time producing economically viable products by utilizing CO_2.[3-5] For this strategy to be feasible, one should consider the carbon footprint, thus conversion must take absolute minimal amount of energy.[6, 7]

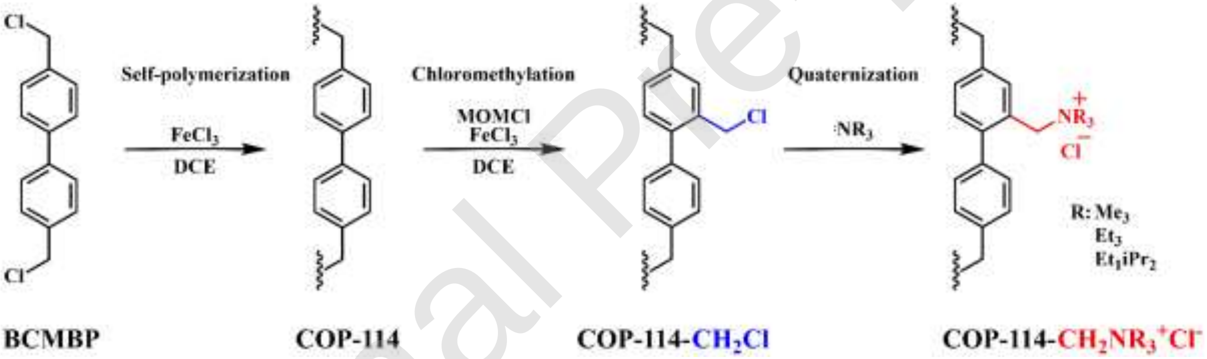
The formation of cyclic carbonates from epoxides and CO_2 has gained attention due to its exceptional advantages, such as no reduction of carbon necessary, green process using CO_2 directly as a feedstock, and exothermic reaction (ΔH_r = -144 kJ/mol).[8-10] Also, cyclic carbonates are used in various applications as polar aprotic solvents, precursor for biomedical applications, raw materials for engineering plastics and lastly, electrolytes in batteries. To date, there has been considerable research efforts for catalyzed cycloaddition of CO_2 to epoxides. Homogeneous catalysts of organometallic complexes are found highly active.[11] For example, an aluminum complex with amino triphenolate ligand shows initial TOFs up to 36,000 h^{-1} at 90 ºC and 10 bar pressure of CO_2.[12] Magnesium(II) porphyrin trimer complex based on m-phenylene-bridged shows 46,000 h^{-1} at 160 ºC and 17 bar pressure of CO_2.[13] Chromium(III) salophen bromide complex shows excellent catalytic activity at room temperature.[14] Often, high pressure requirements and costly ingredients are proving unattractive for homogenous catalysis. The main challenge, however, is the tedious separation of catalyst from cyclic carbonate and the left-over metals, even in trace amounts. Alternatively, heterogeneous catalysts are suggested since they are easily separated. For example, ionic liquids[15-17], transition metal complexes[18-20], metalated porous polymers[21-24], metal-organic frameworks (MOFs)[25-28], and porous organic polymers (POPs)[29-33] were studied. The problem with heterogeneous catalysts is that they are not as active as homogeneous counterparts. To solve the issue, additives such as aprotic solvents, transition metals, and co-catalysts such as tetraalkyl ammonium salts, potassium iodide (KI), triethanolamine are employed.[34-39] In most cases, even process modifications were needed, such that high pressure and high catalyst loading with increased temperatures became common. Clearly an active heterogeneous catalyst that does not need any extreme conditions, additives or co-catalysts is needed. There are some encouraging recent developments, but the search for an optimum catalyst is still ongoing.[10, 30, 40]

In this work, we designed a series of novel porous polymeric quaternary ammonium salts as catalytic sites through grafting methodology. After post-synthetic modification, the catalysts retained materials properties such as, high surface area, porosity, and metal-free structure that are feasible to conduct atmospheric CO_2 uptake and remarkable catalytic activity under additive-free and 1 bar of CO_2 pressure. Moreover, catalytic ammonium loading ratio and steric hindrance effect has been investigated using four variations of catalysts with three different alkyl chain lengths of quaternary ammonium salts. The higher loading of ammonium salts and the less sterically hindered catalytic sites showed higher CO_2 uptake and affinity, leading to enhanced kinetics in cycloaddition reactions. To the best of our knowledge, this is the first study of nano-porous networks with grafted quaternary ammonium salts and their application for CO_2 capture and subsequent utilization in ambient conditions without additive or co-catalyst.

2. Experimental section

2.1 Materials

4,4'-bis-(chloromethyl)-1,1'-biphenyl (BCMBP, 95%) was purchased from Sigma-Aldrich, USA. Chloromethyl methyl ether (MOMCl) was provided by Kanto, Japan. Trimethylamine (TMA, 33% in ethanol) was supplied by Alfa Aesar, USA. Triethylamine (TEA, 99%), N,N-diisopropylethyl amine (DIPEA, 99%), anhydrous iron(III) chloride ($FeCl_3$, 98%), tetrahydrofuran (THF), methanol, ethanol, and 1,2-dichloroethane (DCE, 99%) were supplied by SAMCHUN, South Korea.



Scheme 1. The synthetic route for COP-114-$CH_2NR_3^+Cl^-$ through post-synthetic modification

2.2 Synthesis of COP-114

To make the porous network, we used Friedel-Crafts reaction (Scheme 1). Starting polymer, namely COP-114, was synthesized through a direct one-step self-polymerization and formed a microporous framework.[41] In a typical synthesis of COP-114, we treated BCMBP (5.34 g, 0.02 mol) with $FeCl_3$ (3.50 g, 0.02 mol) in dry DCE (25 mL) at 80 °C under a nitrogen atmosphere for 24 hours, following a slightly modified one-step self-polymerization procedure.[42] After cooling to room temperature, water was then added to the mixture. The precipitate was filtered and rinsed with water and methanol until the filtrate became clear. The solid was redispersed in 4M hydrochloric acid through sonication until well suspended in solution. The mixture was once again filtered through vacuum suction then, washed with water, methanol and Soxhlet extracted with THF for 24 hours.

2.3 Synthesis of COP-114-CH_2Cl

To introduce anchoring points, we used chloromethylation where MOMCl (4 mL) was added on COP-114 (2 g) along with $FeCl_3$ (4.5 g) in dry DCE (50 mL) at room temperature for 72 hours. Water was then added and the precipitate was filtered using vacuum suction. The obtained solid was rinsed with water, methanol and THF. The obtained dark brown powder was dried under vacuum at 100 ^oC overnight. To the best of our knowledge, this is the first Friedel Crafted based porous polymers that were modified by chloromethylation.

2.4 Synthesis of COP-114-$CH_2NR_3^+Cl^-$

Finally, we loaded tertiary amines to form quaternary ammonium salts. In order to make a series of COP-114-$CH_2NR_3^+Cl^-$, COP-114-CH_2Cl (1 g) was dispersed in a solution of either TMA (50 mL, 0.210 mol), TEA (30 mL, 0.211 mol), or DIPEA (37 mL, 0.212 mol). For catalytic site loading comparison, one of the TMA solutions were stirred at room temperature for 48 h and another TMA mixture was heated up to 70 ^oC under a condenser and constantly stirred for 48 h. For steric hindrance comparison, the TEA mixture was stirred at 70 ^oC for 48 h. The DIPEA mixture was stirred at 125 ^oC for 48 hours. All reaction mixtures were cooled down to room temperature and filtered using vacuum suction. While filtering each mixture, the obtained solid was washed extensively with ethanol and THF. The obtained bright brown powders were dried under vacuum at 50 ^oC overnight.

2.5 Characterizations

Chemical compositions of the structures were determined by X-ray photoelectron spectroscopy (XPS) analysis (K-alpha, Thermo VG scientific) and elemental analysis by Thermo Finnigan FlashEA 1112 (C, H, N) and Flash 2000 series Thermo Scientific Thermo Scientific (C, H, N, S). In order to prevent halogen contamination, all samples were pretreated with vanadium(V) oxide. Quantitative amount of each elements was observed using dynamic flash combustion oxidation method with gas chromatography column thermal conductivity detector. Fourier transform infrared spectroscopy (FT-IR) was measured with a Nicolet iS50, Thermo Fisher Scientific Instrument. Simple hydrophobicity test was carried out by dispersing the precursor, COP-114 and final product, COP-114-$CH_2NR_3^+Cl^-$ in a mixture of n- hexane and water. Surface area and porosity analysis was performed with N_2 adsorption at 77K (3-flex, Micromeritics) using Brunauer-Emmett-Teller (BET) method and non-local density functional theory (NLDFT). All samples were degassed at 70 ^oC overnight before analysis for more accurate measurement. Surface area in micropores, pore size distribution and pore volumes were calculated using NLDFT. Surface textural properties and morphologies were analyzed by using a field emission scanning electron microscope (FESEM, Magellan 400) with osmium coating to reduce the surface charging on the samples. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60A. The samples were treated by increasing temperature to 800 ^oC with a 10 ^oC/min ramping rate under a N_2 flow (50 mL/min).

3. Results and discussion

3.1 Catalyst characterization

A series of COP-114-$CH_2NR_3^+Cl^-$ structures were prepared by self-polymerization, chloromethylation via Friedel Crafts, and quaternization as shown in Scheme 1. The COP-114 structure was chosen particularly because of the lack of nitrogens in its framework, leading to easy characterization after grafting with ammonium salts. For initial chemical characterization, we carried out XPS analysis, hydrophilicity test, FT-IR, and elemental analysis. In XPS, each step of the post-synthetic modification was verified by survey scan (Fig. 1a). The first spectra (black line) corresponds to COP-114 of which the network contains only C and H atoms proved by the strong C1s peak and little Cl 2p peak which is from the remaining chloromethyl groups after reaction. In the second step, COP-114-CH_2Cl (blue line) revealed the increasing peaks of Cl 2s and Cl 2p owing to Cl atoms of chloromethyl group that are attached to the network. Survey spectra of COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ (red line) contains a peak from N 1s, which the first two spectra did not show at all. Additionally, the presence of O 1s is owing to samples exposed to the moisture, which can be trapped in the pores. State of each element in COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ was verified by C 1s, N 1s, Cl 2p. The N 1s spectrum was fitted into two peaks that indicate C-N^+ bond (quaternary ammonium, 402.38 eV) and C-N bond (tertiary amine, 399.27 eV), respectively (Fig. 1b). According to the peak intensities of N 1s, most of the nitrogen atoms were in the form of quaternary ammonium salts. Small intensity of tertiary amine peak might indicate Stevens rearrangement or Sommelet-Hauser rearrangement might be occurring in the presence of tertiary amines.[43] C 1s spectrum was deconvoluted into five peaks which corresponds to C=C (sp^2 C, 284.34eV), C-C/C-H (sp^3 C, 284.73 eV), C-N^+ (quaternary, 286.03 eV), C-Cl (chloromethyl, 286.63 eV), π-π^* (π-conjugation, 290.68 eV) (Fig. 1c). To note, the most intense sp^2 C π-π^* peak is attributed to the π-π^* transition of electrons with clear evidence for the structure to be made up of cross-linked networks with aromatic rings. Cl 2p spectrum was fitted to Cl^- chloride ion, $2p_{3/2}$ and $2p_{1/2}$ at 196.63 and

198.19 eV; C-Cl chloromethyl $2p_{3/2}$ and $2p_{1/2}$ at 199.96 and 201.62 eV (Fig. 1d). Existence of chloride ion after modification showed strong evidence that quaternary step was indeed successful. The remaining C-Cl bonding peaks indicates that chloromethyl group were not completely changed to quaternary ammonium due to the size of tertiary amine.

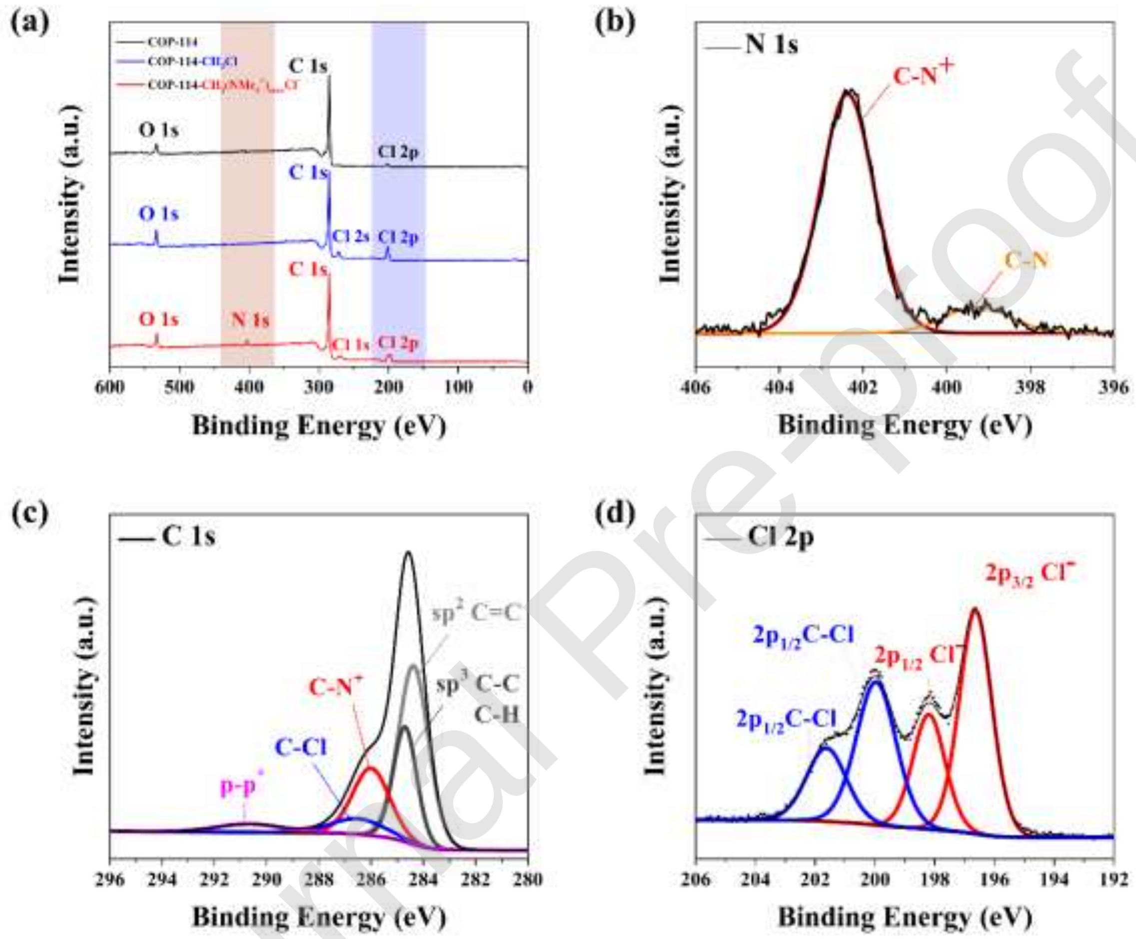


Fig. 1 The XPS spectra; (a) survey scan of COP-114 (black), COP-114-CH_2Cl (blue), and COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ (red). (b) C 1s, (c) N 1s, and (d) Cl 2p spectra of COP-114-$(CH_2NMe_3^+)_{max}Cl^-$.

In order to quickly verify the post-modification process, a simple hydrophilicity test was performed by dispersing the original porous polymer (COP-114) and the modified structure

($COP-114-CH_2NR_3^+Cl^-$) in a n-hexane and water mixture (Fig. S1). Since COP-114 was hydrophobic, it remained only in hexane phase and because $COP-114-CH_2NR_3^+Cl^-$ was hydrophilic from its quaternary ammonium salts, it readily dispersed in water. FT-IR spectra also verified existing chemical functional groups (Fig. S2). After chloromethylation, C-Cl ($660 cm^{-1}$) peak appeared in $COP-114-CH_2Cl$ and surface area was decreased (Fig. S3). Then, in $COP-114-CH_2NMe_3^+Cl^-$, a C-N peak has emerged at $1253\ cm^{-1}$ and C-Cl peak disappeared.

In order to calculate the relative number of catalytic sites, functional group molecular ratio was determined using the molar percentage of nitrogens to the carbon from the framework (Table S1). First, temperature had positive correlation with nitrogen loading and quaternary functional group molecular ratio on $COP-114-CH_2NEt_3^+Cl^-$ and $COP-114-CH_2NiPr_2Et^+Cl^-$. However, the synthesis of $COP-114-CH_2NMe_3^+Cl^-$ was adversely affected by the increased temperature since the reaction at 70 ^oC showed that nitrogen loading and functional group ratios were reduced. We suspect that TMA reagent was partially lost at 70 ^oC, even under reflux, owing to the low boiling point of TMA (2.9 ^oC). We also found that homogeneity of the solution by vigorous stirring affected the $COP-114-CH_2NMe_3^+Cl^-$ most. Lastly, steric hindrance of tertiary amines was found to affect quaternization reaction. $COP-114-CH_2NMe_3^+Cl^-$ always showed higher nitrogen loading than $COP-114-CH_2NEt_3^+Cl^-$ and COP-114- $CH_2NiPr_2Et^+Cl^-$, under same synthetic conditions. As expected, the bigger tertiary amines could not penetrate deeper and proceed with nucleophilic attack on chloromethyl group as well. Hence, aliphatic chain length, methyl (Me) < ethyl (Et) < isopropyl (iPr), explained the loading trend. Thermal stability was tested by TGA and showed degradation predominantly after 400 ^oC, and the initial weight loss of about 2~3% was due to the captured moisture from air (Fig. S4).

Table 1. Porosity parameters, CO_2 uptakes and heat of adsorption values of COP-114-$CH_2NR_3^+Cl^-$

Catalyst	S_{BET} [a] $[m^2 g^{-1}]$	S_{micro} [b] $[m^2 g^{-1}]$	V_{micro} [c] $[cm^3 g^{-1}]$	V_{total} [d] $[cm^3 g^{-1}]$	N [e] (%)	Functional group molecular ratio [f]	CO_2 adsorption [g] $[mmolg^{-1}]$ 273K	298K	323K	Q_{st} CO_2 [h] $[kJmol^{-1}]$
COP-114-$(CH_2NMe_3^+)_{max}Cl^-$	621	165	0.155	0.766	2.76	$C_1\,(NMe_3)_{4.01\%}$	2.680	1.629	0.972	30.5 $_{(28.0)}$
COP-114-$CH_2NMe_3^+Cl^-$	1066	401	0.296	1.016	2.65	$C_1\,(NMe_3)_{3.48\%}$	2.362	1.383	0.811	29.8 $_{(27.1)}$
COP-114-$CH_2NEt_3^+Cl^-$	976	321	0.282	0.728	2.29	$C_1\,(NEt_3)_{3.35\%}$	2.224	1.285	0.732	29.5 $_{(27.6)}$
COP-114-$CH_2NiPr_2Et^+Cl^-$	686	183	0.169	0.905	2.25	$C_1\,(N\,iPr_2Et)_{3.65\%}$	1.441	0.844	0.506	23.1 $_{(21.6)}$

[a] Surface areas of COP-114-$CH_2NR_3^+Cl^-$ were calculated from N_2 isotherms measured at 77K using BET theory, in the range of relative pressure determined by the Rouquerol plots. [b,c,d] Determined from non-local density functional theory (NLDFT). [e] Measured by dynamic flash combustion method. [f] Calculated from Equation S1. [g] CO_2 uptake values of COP-114-$CH_2NR_3^+Cl^-$ s at 1 bar. [h] The isoteric heat of adsorption values (Q_{st}) for CO_2 at zero coverage and the values inside the parentheses refers to heat of adsorption at high loading.

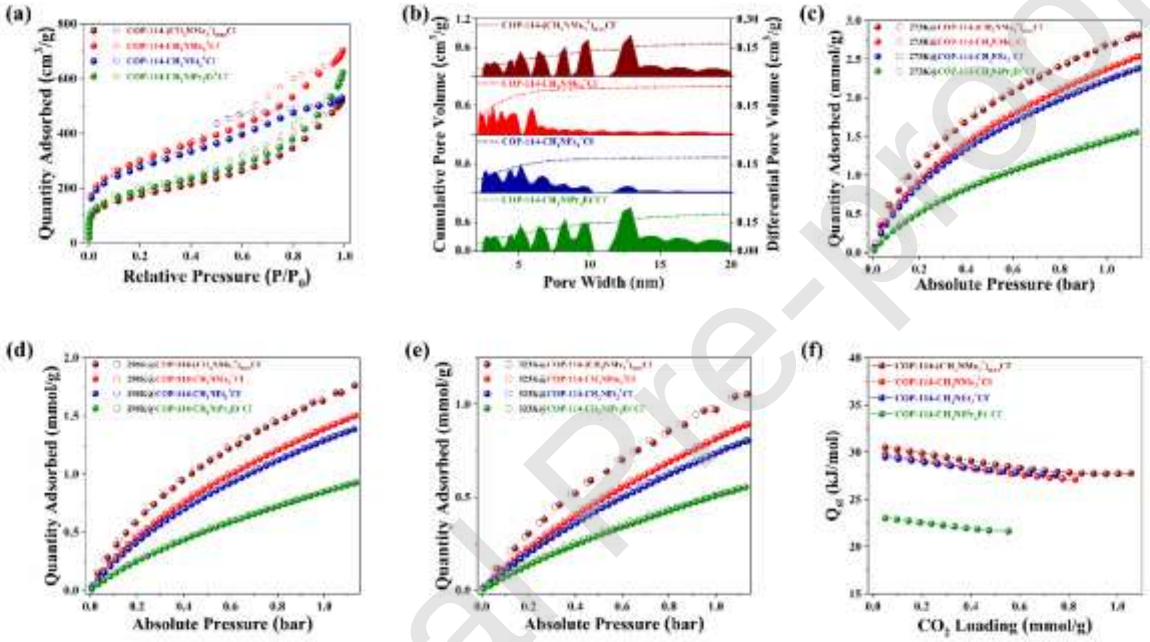


Fig. 2 Porosity and gas uptake studies of COP-114-$CH_2NR_3^+Cl^-$ derivatives. (a) Nitrogen adsorption and desorption isotherms at 77K. (b) Corresponding NLDFT pore size distributions. CO_2 adsorption and isotherms collected up to 1bar (c) 273K, (d) 298K, (e) 323K, and (f) the isosteric heat of adsorption (Q_{st}) plots for CO_2.

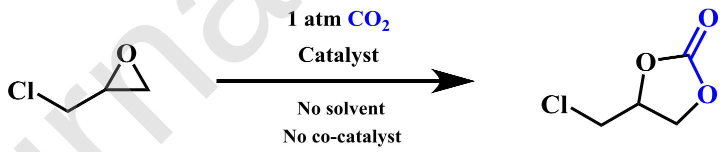
To measure porosity, we used N_2 as a probe gas at 77K. All series of COP-114-$CH_2NR_3^+Cl^-$ maintained their porous network properties after post-synthetic modification. They exhibited hysteretic type IV adsorption isotherms, which feature micro-mesoporous structures (Fig. 2a). The specific surface areas of COP-114-$CH_2NR_3^+Cl^-$ were investigated using N_2 adsorption isotherms through Brunauer-Emmett-Teller (BET) theory, where the valid ranges of pressures were calculated from the respective Rouquerol plots. The calculated BET surface areas show that COP-114-$(CH_2NMe_3^+)_{max}Cl^-$, COP-114-$CH_2NMe_3^+Cl^-$, COP-114-$CH_2NEt_3^+Cl^-$, COP-114-$CH_2NiPr_2Et^+Cl^-$ were found to be 621, 1066, 976, 686 m^2g^{-1}, respectively (Table 1). To investigate further, pore size distributions and micro-porosity were estimated using non-local density functional theory (NLDFT). All structures showed hieararchical nature, where micro, meso-porous networks coexist with average pore sizes below 20 nm (Fig. 2b). SEM images also reflect porous network morphologies corresponding to the calculated pore distributions (Fig. S5). The more functionalized COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ exhibited smaller surface area and porosity compared to COP-114-$CH_2NMe_3^+Cl^-$, because of the additional pore filling during quaternization. On the other hand, steric hindrance was in play when alkyl groups increased in size, yielding lower surface areas following the aliphatic length trend of Me < Et < iPr.

3.2 CO_2 adsorption

CO_2 sorption capacity is predominantly determined by the combination of effects of the anion, cation, and polymer architecture in ionic liquids (ILs), polymerized ionic liquids (PILs), and ionic porous organic polymers.[44-50] CO_2 adsorption measurements were conducted at temperatures of 273K, 298K, and 323K to investigate affinity towards CO_2 based on the quaternary ammonium chloride site and the inherent microporosity (Fig. 2c-e). Also, isosteric heat adsorption values were calculated by using the Clausius-Clapeyron equation to understand the chemical effect of quaternary ammonium salts on CO_2 binding strength (Table S2-S3). Each sample had similar Q_{st} values according to CO_2 loading at 0.1 and 1 mmol/g (Fig. 2f). COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ showed high CO_2 uptake of 2.680, 1.629, 0.972 mmol/g at 273K, 298K, 323K, respectively and the Q_{st} value was 30.5 kJ/mol (Table 1). It is likely to be resulted from the charged nature of the polymer enhancing the CO_2 binding in comparison to the non-charged network.[29, 51] With aforementioned functional ratio and steric hindrance, the higher functionalized and the less steric hindered resulted in the highest uptake as expected. Of note, surface area of COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ is lower than COP-114-$CH_2NMe_3^+Cl^-$ resulting in less physisorptive sites compared to COP-114-$CH_2NMe_3^+Cl^-$. However, CO_2 capacity and Q_{st} value of COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ is higher than COP-114-$CH_2NMe_3^+Cl^-$ indicating the contribution of the quaternary ammonium cation and chloride on CO_2 binding. On the other hand, the less sterically hindered quaternary ammonium (iPr < Et < Me) showed the higher CO_2 adsorption and Q_{st}. This behavior could be explained as longer chains blocking the interactions between CO_2 and the functional groups and also more likely of micropore blocking.[52]

3.3 CO_2 conversion

Table 2. Optimization of reaction conditions for the cycloaddition of CO_2 to epichlorohydrin[a]



Entry	Catalyst	Amount (mg)	Temperature (°C)	Time (h)	Conversion[b] (%)	Selectivity[b] (%)
1	**COP-114-$(CH_2NMe_3^+)_{max}Cl^-$**	5	100	24	55	99
2		10	100	24	84	99
3		15	100	24	89	99
4		20	100	24	99.7	99
5		25	100	24	>99	99
6		20	28	24	2.86	99
7		20	40	24	14.0	99
8		20	60	24	56.3	99

9		20	80	24	90.7	99
10	COP-114	20	100	24	0	-

[a]Reaction conditions: catalyst, epichlorohdrin (5 mmol), and CO_2 1bar. [b]Determined by using ^{1}H-NMR and ^{13}C-NMR.

After verifying the CO_2 binding ability at the high end of the physisorptive regime, COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ was tested for cycloaddition of CO_2 to epoxides. To optimize the conditions, we chose the most commonly studied substrate, epichlorohydrin and reacted with atmospheric CO_2 under various conditions (Table 2). Catalyst loading was set for 20 mg (4% w/w with respect to the substrate) after checking that the catalyst loading of 15 mg converts 89% and 25 mg, 99% (entries 3, 5). Increasing the temperature from room temperature to 100 °C had a pronounced positive effect on the yield of the cyclic carbonate (entries 4, 6-9). Kinetics of cycloaddition reaction was monitored at the optimized conditions (Fig. 3a, Table S2). As expected, increasing nitrogen ratio is corresponding to higher conversion and catalysts with longer alkyl chains showed less conversion. The results of kinetic curve are similar to that of Q_{st}. Thereby, a proposed mechanism for cycloaddition reaction using COP-114-$CH_2NR_3^+Cl^-$ as a catalyst could be the activation of epoxide through interaction between its oxygen atom and the quaternary ammonium center, and a subsequent nucleophilic attack by Cl^- anion to form an oxy anion intermediate (Fig. 3b).[53, 54] This active intermediate then reacts with CO_2 interacted quaternary ammonium salt to form the corresponding cyclic carbonates.[55] It is important to note that polycarbonate has not formed in any of the tested conditions, mainly due to it being a kinetic product. [56]

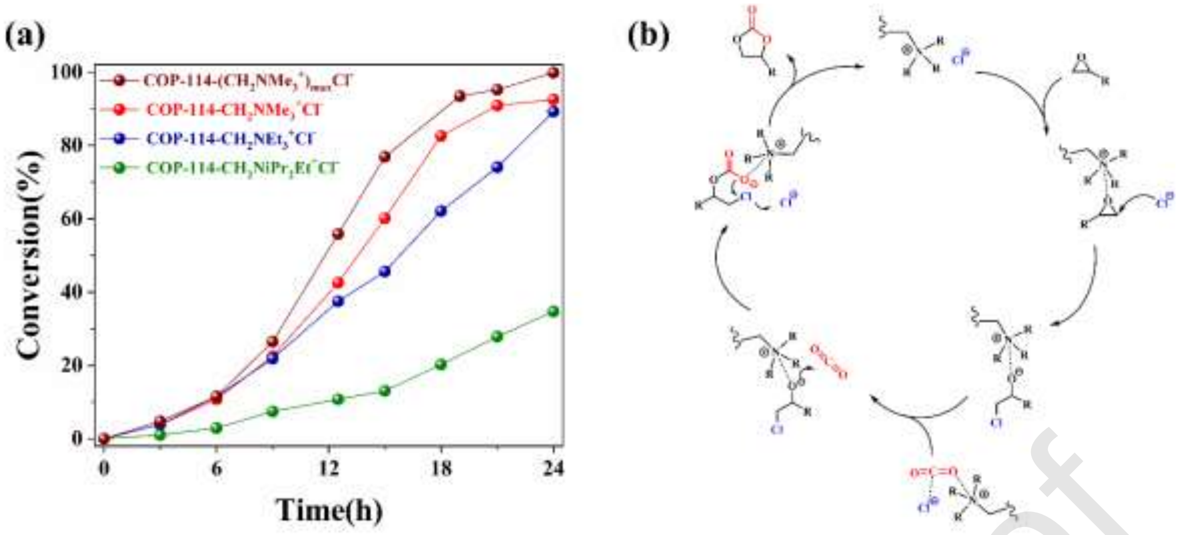
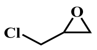
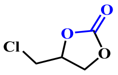
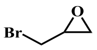
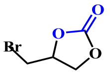
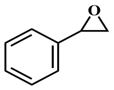
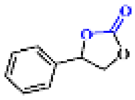
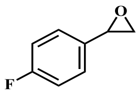
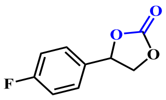
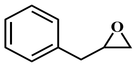
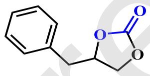
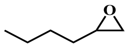
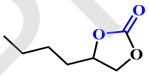
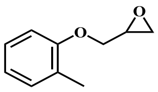
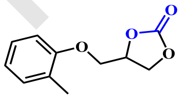
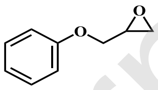
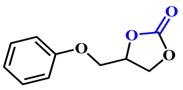
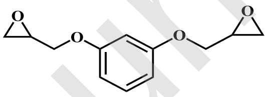
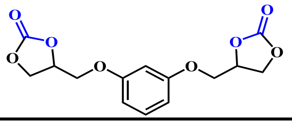


Fig. 3 (a) Kinetics curve for the cycloaddition reaction of CO_2 to epichlorohydrin. (b) Proposed mechanism for the observed catalytic reaction.

After optimization of catalyst conditions, we selected a range of epoxides for both chemical variation and their industrial importance (Table 3). All substrates we tested have near quantitative selectivity to the corresponding cyclic carbonate and no polycarbonate was detected. Conversion yields varied based on the reactivity and sterics of the epoxide.[57] As shown in entries 1-4, conversion ratio was decreasing orderly from epichlorohydrine to epichlorobromine, and then styrene oxide, to 2-(4-fluorophenyl)oxirane. Epichlorohydrin is more reactive than bromo derivative due to the strong inductive effect and yields higher conversions in the same conditions. The delocalization on styrene is rather interrupted by the strong electron withdrawing effect by fluorine substitution, hence lower stability of the intermediate. Hexyl epoxide has both lower boiling point and lower resonance than the other heavier hydrocarbons (entries 5~9) and therefore lower conversion was observed. Among the ether side groups (entries 7~9), the bis epoxide had harder conversion mainly because of sterics, but also due to the double drain on the electronic stabilization of the phenyl ring. Interestingly, ortho substituted version of 1,2-epoxy-3-phenoxypropane has higher conversion yield (entries 7-8). We suspect that it is mainly because of the higher boiling point, although a more thorough understanding is necessary.

Table 3. Cycloaddition reactions of CO_2 with epoxides catalyzed by COP-114-$(CH_2NMe_3^+)_{max}Cl^-$.*

Entry	Epoxides	Product	Conversion (%)	Selectivity (%)
1			99.7	99
2			98.8	99
3			95.8	99
4			58.2	99
5			95.5	99
6			86.7	99
7			95.0	99
8			90.8	99
9			28.3	99

*Reaction conditions: Catalyst (20mg), epoxides (5mmol), and CO_2 1bar.

Lastly, we tested for recyclability under the optimized reaction conditions. COP-114-$(CH_2NMe_3^+)_{max}Cl^-$ showed recyclable activity for cycloaddition of CO_2 to epichlorohydrin with high conversion (99%) and selectivity (99%) in each cycle (Fig. 4).

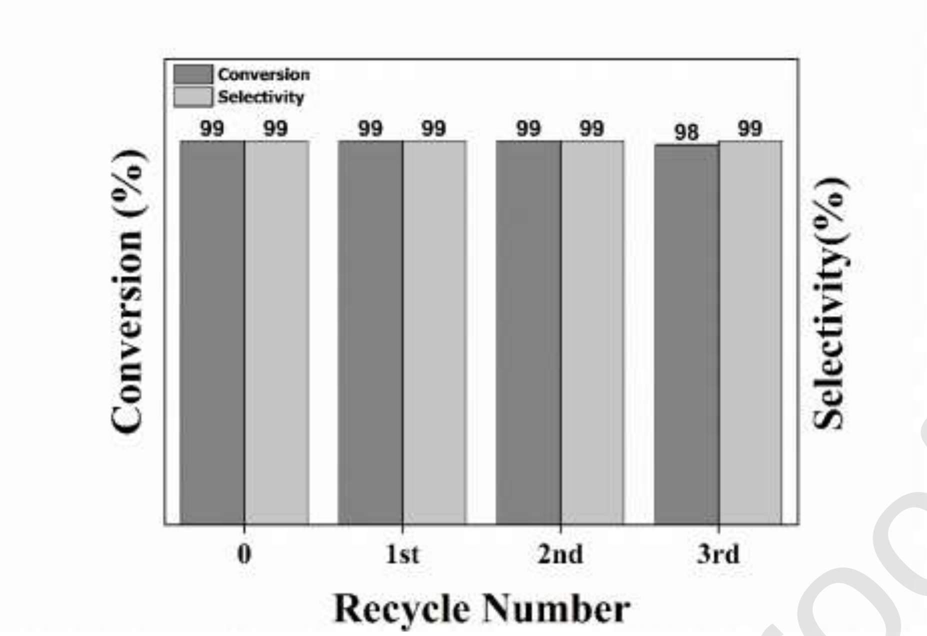


Fig. 4 Conversion and selectivity yields of the recycling tests in the cycloaddition of CO_2 to epichlorohydrin using COP-114-$(CH_2NMe_3^+)_{max}Cl^-$.

4. Conclusions

In summary, we have shown that the grafted porous polymers of quaternary ammonium salts from COP-114 could retain porous features and provide increased availability of active sites per mass of the heterogeneous catalysts. The catalysts were able to capture atmospheric CO_2 and subsequently convert epoxides to cyclic carbonates under ambient CO_2 pressure without a co-catalyst, solvent, or additive. They provide outstanding selectivity and very high conversion yields for a wide variety of epoxides under harsh conditions. Since commercially available catalysts require costly co-catalyst support or additives, the structures built in this work offer significant promise in their industrial implementation. In addition, we were able to study catalyst loading, steric factors and other parameters like stirring rate, thanks to the simple and nitrogen free construct of the COP-114. The porous polymers reported were the first examples of quaternary ammonium salt grafting and also the first of such structures in cycloaddition reaction of CO_2 to epoxides. The results indicate a feasible route for the CCU methods that are not energy intensive and could be commercially viable. Further work would be directed in understanding framework improvements, such as imparting Lewis acid/base sites. Since our work clearly identified the power of the quaternary ammonium salts in porous materials, the structural enhancements would be the logical next step.

CRediT statement

Doyun Kim: Methodology, Validation, Investigation, Formal Analysis, Writing

Saravanan Subramanian: Investigation

Damien Thirion: Formal analysis

Youngdong Song: Formal analysis

Aqil Jamal: Funding acquisition

Mona S. Otaibi: Formal Analysis

Cafer T. Yavuz: Conceptualization, Validation, Writing, Supervision, Project administration, Funding acquisition

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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