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Porous cationic polymers: The impact of counteranions and charges on CO$_2$ capture and conversion

Onur Buyukcakir,$^a$ Sang-Hyun Je,$^a$ Dong Shin Choi, Siddulu Naiudu Talapaneni,$^a$ Yongbeom Seo,$^b$ Yousung Jung,$^a$ Kyriaki Polychronopoulou,$^c$ and Ali Coskun$^{a,d}$

Porous cationic polymers (PCPs) with surface areas up to 755 m$^2$ g$^{-1}$ bearing positively charged viologen units in their backbones and different counteranions have been prepared. We have demonstrated that by simply varying counteranions both gas sorption and catalytic properties of PCPs can be tuned for metal-free capture and conversion of CO$_2$ into value-added products such as cyclic carbonates with excellent yields.

Porous polymers have emerged as promising solid-sorbents in recent years due to their simple synthesis, structural tunability, high surface area combined with high physical and chemical stability for applications including gas/liquid separation, gas storage, catalysis, sensors and charge carriers.$^5$ The burning of fossil fuels is the major source of anthropogenic CO$_2$ emissions and there is an urgent need for porous sorbents,$^2$ which can selectively capture CO$_2$ from a flue gas mixture and preferentially convert it into value-added products to not only mitigate CO$_2$ emissions, but also to create incentive for research efforts in this area. To date, a great number of porous polymers have been prepared and utilized in the context of CO$_2$ capture and separation.$^3$ These investigations revealed that the nature of chemical functionality along with the textural properties of polymers$^4$ are important parameters to tailor CO$_2$ affinity of these frameworks. In particular, polar functional groups such as amines,$^5$ triazoles,$^6$ carboxylic acids,$^7$ triazine cores,$^8$ imines,$^9$ tetrazoles,$^{10}$ benzimidazole,$^{11}$ azo linkages$^{12}$ were shown to enhance CO$_2$-philicity of polymers via dipole-quadruple interactions between CO$_2$ and the polar functional groups. In recent years, charged porous polymers have been also investigated for gas storage applications. There are, however, rather limited number of charged porous polymers reported in the literature mainly due to the difficulties associated with their synthesis and low physicochemical of stability of these materials.$^{13}$ In spite of these obstacles, however, there is still a great motivation to design new charged porous networks as organic zeolites due to their promising gas-adsorption properties$^{14}$ and exchangeable counterions, which introduces new catalytic abilities such as CO$_2$ conversion to them.$^{15}$ In addition, unlike other porous materials, properties of cationic frameworks could be altered by simply changing the nature of counterions for the desired application. Herein, we report (Fig. 1) the synthesis of three structurally similar charged porous polymers incorporating different counteranions (Cl$^-$, BF$_4^-$ and PF$_6^-$) via Sonogashira-Hagihara palladium catalyzed cross coupling reaction. The porous cationic polymers (PCPs) showed high affinity towards CO$_2$ ($Q_{st} = 28.5 - 31.6$ kJ mol$^{-1}$, 78.1 – 101.7 mg g$^{-1}$ at 273 K, 1 bar) and good CO$_2$/N$_2$ selectivity (42-48). Cationic nature of the framework allowed us to tune gas sorption and catalytic properties of PCPs by simply varying counteranions rather than changing the structure for desired application. While PCPs incorporating BF$_4^-$ (PCP-BF$_4$) and PF$_6^-$ (PCP-PF$_6$) counteranions showed high-affinity towards CO$_2$, $^{a}$ Graduate School of Energy, Environment, Water and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guesong Dong, Daejeon, 305-716, Republic of Korea.
$^b$ Institute of Basic Science (IBS), KAIST, Daejeon, Republic of Korea.
$^c$ Mechanical Engineering, Khalifa University, Abu Dhabi, UAE.
$^d$ Department of Chemistry, KAIST, Daejeon, Republic of Korea.
$^e$ Electronic Supplementary Information (ESI) available: General methods, experimental details, synthesis and additional spectroscopic characterization. See DOI: 10.1039/x0xx000000x.
PCP-Cl as a porous organocatalyst showed excellent catalytic activity for CO₂ capture and conversion into cyclic carbonates using epoxides with high product yields up to 99% and excellent product and substrate selectivity.

The synthesis of PCPs were achieved by the Pd-catalyzed Sonogashira-Hagihara coupling reaction between tetrakis(4-ethynylphenyl)methane and 1,1’ bis(4-iodophenyl)-[4,4’-bipyridine]-1,1’-diium salts, namely, dichloride (Cl₂), ditrifluoroborate (BF₃) and difluorophosphate (PF₆) in a 1:1 solvent mixture of DMF:NEt₃ at 100°C. The reaction mixture was kept at 100°C for 48 h to yield desired PCPs. (see synthesis section for details, ESI).

PCPs were extensively characterized using solid-state cross-polarization magic-angle spinning (CP-MAS) ¹³C, ¹¹B and ³¹P NMR, scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), FTIR spectroscopy, thermogravimetric analysis (TGA), and elemental analysis (EA) (for details, ESI). First, the structural integrity of polymers was verified by using CP-MAS ¹³C NMR (see Fig. S1, ESI). The broad chemical shifts appeared in the region between 120 and 150 ppm is associated with the aromatic carbon atoms of the framework. The peaks located at 90 ppm and 60 ppm, which was attributed to the ethynyl carbons and the quaternary carbon core of tetrphenylmethane, respectively, also verified the successful synthesis of PCPs. The scanning electron microscopy (SEM) analysis was performed in order to investigate the bulk scale morphology of PCPs (see Fig. S2, ESI). PCPs formed uniform spherical particles with a particle size ranging from 20 to 50 nm. The broad featureless PXRD patterns of PCPs indicate that they have amorphous character (see Fig. S3, ESI).

As the lack of thermal stability even during the polymerization reaction is an important issue for cationic polymers, we have also investigated the thermal stability of PCPs (see Fig. S4, ESI). PCPs exhibited exceptional thermal stability and remained stable up to 390°C under air and up to 420°C under N₂ atmosphere presumably due to well-spaced charged groups within three-dimensional network. The slight weight loss below 200°C was mostly associated with the trapped moisture and solvent molecules in the pores. The structural integrity of PCPs was further verified using FTIR analysis. The bands located at 1650, 1400 cm⁻¹ (C=O and C=N, stretching) and 2111 cm⁻¹ (C≡C, stretching) along with the absence of C≡C-H stretching band at 3281 cm⁻¹ confirmed the successful coupling reaction between the monomers (see Fig. S5, ESI). The counteranion content of PCPs was verified by using energy dispersive X-ray absorption spectroscopy (EDS) to monitor chlorine, boron and phosphorous atoms for PCP-Cl, PCP-BF₃ and PCP-PF₆, respectively (see Fig. S6, ESI).

Furthermore, the chemical shift located at -0.5 ppm in the 31P MAS-NMR spectrum of PCP-BF₃ and the multiplet peak at -145 ppm in ¹³C MAS-NMR spectrum of PCP-PF₆ in which multiplicity originated from ¹¹B,¹⁹F coupling, further indicated the successful incorporation of positive charges into the framework along with their respective counteranions (see Fig. S7, ESI).

Argon adsorption/desorption isotherms collected (Fig. 2, Table 1) at 87 K were used to evaluate the porosity of PCPs. As depicted in Fig. 2a, PCPs exhibit reversible type I isotherms (in combination with type II for PCP-Cl). The observed rapid gas sorption at relatively low-pressure range (below P/P₀ = 0.1) indicates the permanent microporous nature of polymers. The increase in the adsorption trend at higher relative pressure range along with the H₂ hysteresis for desorption could be attributed to the presence of mesopores. The Brunauer-Emmett-Teller (BET) surface areas of PCPs were calculated (Table 1) from the argon adsorption/desorption isotherms by determining the linear BET range from the Rouquerol plots³⁶. The isosteric heat of adsorption values for CO₂ in the gas mixtures of CO₂/N₂ at 273 K and 298 K (b) CO₂/N₂ selectivity of PCPs calculated from IAST technique for mole ratio of 15:85 gas mixtures of CO₂/N₂ at 273 K and 298 K. (d) Isosteric heats of adsorption (Q_st) of CO₂ for PCPs.

Successful CO₂ capture is an important issue for cationic polymers using epoxides with high product yields up to 99% and excellent product and substrate selectivity.

**Table 1** CO₂ and N₂ uptakes at 1 bar, CO₂/N₂ selectivities, heat of adsorption values of CO₂ for PCPs.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>BET, m²·g⁻¹</th>
<th>CO₂ adsorption, mg·g⁻¹ at 1 bar</th>
<th>N₂ adsorption, mg·g⁻¹ at 1 bar</th>
<th>CO₂/N₂ (15:85)</th>
<th>Q_st (kJ·mol⁻¹) at 273 K</th>
<th>Q_st (kJ·mol⁻¹) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP-Cl</td>
<td>755</td>
<td>101.7</td>
<td>61.4</td>
<td>3.9</td>
<td>2.2</td>
<td>34</td>
</tr>
<tr>
<td>PCP-BF₃</td>
<td>586</td>
<td>97.0</td>
<td>58.4</td>
<td>4.1</td>
<td>2.2</td>
<td>44</td>
</tr>
<tr>
<td>PCP-PF₆</td>
<td>433</td>
<td>78.1</td>
<td>47.0</td>
<td>2.9</td>
<td>1.5</td>
<td>48</td>
</tr>
</tbody>
</table>

³⁶Calculated according to Rouquerol plots from argon isotherms. From IAST at CO₂/N₂ ratio of 0.15:0.85 at 1 bar. The isosteric heat of adsorption values for CO₂ at zero coverage (the values inside parentheses denotes the heat of adsorption (Q_st) at high loading).
(see Fig. S8 and Fig. S9, ESI). The BET surface areas of PCP-Cl, -BF₄, and -PF₆ were found to be 755, 586 and 433 m² g⁻¹, respectively. We observed a decrease in surface areas of PCPs with increasing ionic radius of counteranions from Cl⁻ (2.70 Å) to BF₄⁻ (3.44 Å) and PF₆⁻ (3.70 Å). The pore size distributions of PCPs were estimated from the argon adsorption/desorption isotherms (Fig. 2b) by using nonlocal density functional theory (NLDFT). All polymers exhibited similar pore size distribution patterns with varying intensities. The major peaks were located below 2 nm agrees well with the microporosity of PCPs.

The CO₂ and N₂ adsorption isotherms of PCPs were measured (Fig. 3, Figs. S10 and S11, ESI) up to 1 bar at 273 K and 298 K, the corresponding data were presented in Table 1. Due to higher surface area of PCP-Cl compared to the other PCPs, it exhibited the highest CO₂ adsorption capacity of 101.7 mg g⁻¹ and 61.4 mg g⁻¹ at 273 K and 298 K, respectively. This comparatively high CO₂ uptake capacity of PCP-Cl (SBET = 755 m² g⁻¹, 6.2 wt% CO₂ at 298 K) compared to the neutral frameworks prepared from three dimensional tetraphenylethane building blocks using Sonagashira coupling reaction (CMP-4, SBET = 1917 m² g⁻¹, 6.6 wt% CO₂ at 298 K) can be attributed to increased electrostatic interactions between CO₂ molecules and charged units along with the counteranions within the framework. PCP-BF₄ also showed significant CO₂ uptake (97.0 mg g⁻¹ at 273 K), although its surface area is much lower compared to PCP-Cl. This increase in CO₂ adsorption indicates the enhanced CO₂ binding affinity due to Lewis acid-base interaction between BF₄⁻ ions and CO₂ molecules. The same interaction was also observed for the PCP-PF₆ which showed CO₂ uptake capacity of 78.1 mg g⁻¹ at 273 K. Furthermore, the corresponding isosteric heat of adsorption (Qₑ) values of PCPs for CO₂ at zero coverage was found to be in the range of 28.5 – 31.6 kJ mol⁻¹, which is much higher than the values reported for structurally similar non-charged porous polymers (26 and 22 kJ mol⁻¹ for MOP-1 and -3, respectively). The high CO₂ affinity of PCP-BF₄ and PCP-PF₆ can also be further verified by probing their Qₑ values, which were found to be about 4 kJ mol⁻¹ higher than that of PCP-Cl. This anion-dependent isosteric heats of adsorption values were investigated further using density functional calculations. We first obtained the anion binding geometry to the cationic monomeric unit and all the counteranions were calculated (see Fig. S12, ESI) to be the most stable when placed on top of the carbon linked to the charged nitrogen atom of pyridine unit. The calculated Mulliken charges followed the expected trend, that is, larger and softer anions are capable of retaining more charges than smaller and harder ones. The absolute binding energies were slightly underestimated (see Table S1, ESI) compared to the experimental Qₑ values, presumably due to the interpenetrated structure of PCPs, which could allow interaction of CO₂ with multiple binding sites. It is, however, important to note that the trend across the different anions is in good agreement with the experimental Qₑ values. The binding geometry between CO₂ and the pyridinium ion were found to be very similar for all three anionic cases, suggesting that specific interactions between CO₂ and the anion may play a decisive role in determining different Qₑ values. Indeed, in agreement with the trend of Qₑ for different anions with the same cationic backbone, we particularly note that the distance between the carbon atom of CO₂ and halide atoms of anions (Cl⁻, or F of BF₄⁻ and PF₆⁻) follows well the binding strength trend. In other words, a specific CO₂-halide interaction via a proper choice of counteranions appears to play an important role to tune the binding strength of CO₂ even for the same cationic units.

The selectivity ability of PCPs for CO₂/N₂ separation from post combustion flue gas was calculated (Fig. 3) using Ideal adsorbed solution theory (IAST) from CO₂ and N₂ adsorption isotherms measured at 273 K and 298 K, which summarized in Table-1. The CO₂/N₂ selectivities of PCPs at 273 K, 1 bar was found to be in the range of 42-48 and the selectivities decreased to 30-36 with increasing the temperature to 298 K.

The usage of CO₂ as a C1 building block for making value added products is an alternative approach to tackle with the increasing CO₂ emissions. The conversion of CO₂ into cyclic carbonates is one of the promising routes, which is an important chemical feedstock not only in the production of polycarbonates but also as organic solvents. Although ionic liquids based on pyridinium salts and polymer/nanoparticle-supported pyridinium catalysts have been well-documented for CO₂ conversion, to the best of our knowledge, this is the first demonstration of a porous heterogeneous organocatalyst, in which bipyridinium moieties are working as active centres in a porous network. In order to demonstrate the performance of PCP-Cl as a porous organocatalyst for CO₂ capture and conversion, We first investigated (Table 2) its catalytic activity

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxides</th>
<th>Cyclic Carbonate</th>
<th>Time (h)</th>
<th>Yield (%)²⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂C</td>
<td></td>
<td>12 h</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td></td>
<td>12 h</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>H₂C</td>
<td></td>
<td>12 h</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>12 h</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>12 h</td>
<td>41</td>
</tr>
</tbody>
</table>

²⁰ The products were characterized by ¹H NMR and the yields refer to isolated products.
in the conversion of CO₂ using (±)-Propylene oxide to form the corresponding cyclic carbonate at 100°C under 3 MPa of CO₂. The conversion yields were calculated according to ¹H NMR analysis (See Fig. S13-S17, ESI). We observed an impressive 99% yield for the formation of propylene carbonate, indicating the importance of CO₂-phlic porous network for CO₂ capture and conversion. In full consistency with the literature,²³ PCP-Cl showed the best performance due to high nucleophilicity and leaving ability of Cl⁻ (see for the proposed mechanism Fig. S18, ESI), whereas PCP-BF₃ and PCP-PF₆ showed lower catalytic activity. In order to test the recyclability of PCP-Cl, we recycled the catalyst four times, in which we observed no change in activity and product yields. This indicates that the catalyst is highly stable and can be reused for multiple cycles. Once establishing PCP-Cl as an excellent porous organocatalyst for the CO₂ conversion, we have also investigated various challenging epoxide substrates. Interestingly, we observed a decrease in product yields (from 99% to 16%) with increasing kinetic diameter of the substrates presumably due to the presence of well-developed micropores in PCP-Cl, thus leading to substrate selectivity. It is important to note that such substrate selectivity is rather difficult to achieve using homogeneous organocatalysts.

In conclusion, we have introduced highly stable cationic organic zeolites incorporating bipyridinium subunits. We have demonstrated that by simply varying counteranions within the porous network structure both gas sorption properties and catalytic activity of porous polymers could be altered. PCPs also shown to be excellent porous organocatalysts for the conversion of CO₂ into cyclic carbonates. These results indicate the promising aspect of cationic polymers for metal-free, capture and conversion of CO₂ into value-added products, thus utilizing CO₂ as a renewable and environmentally friendly C1 building block.

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Notes and references
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