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Hollow and Microporous Catalysts Bearing Cr(III)-F Porphyrins for Room Temperature CO₂ Fixation to Cyclic Carbonates

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Hollow and microporous metal free/Cr-porphyrin networks were prepared via the Sonogashira coupling of metal-free or Cr- tetra(4-ethynylphenyl) porphyrins and 1,4-diiodobenzene on the surface of silica templates followed by silica etching. Zinc was introduced to hollow and microporous metal free porphyrin network (H-MPN) through postsynthetic modification to form H-MZnPN. Hollow and microporous Cr(III)-F porphyrin networks (H-MCrPN) showed the best catalytic activities in the room temperature CO_2 fixation with epoxides to cyclic carbonates. In addition, the H-MCrPN could be reused at least for five runs, maintaining original catalytic activity. The good performance of H-MCrPN is attributed to its microporosity, the shortened diffusion pathways for substrates due to the hollow structure, and the efficient Lewis acidic activity of Cr(III)-F moieties.

Introduction

Chemical CO₂ fixation has attracted great attention of scientists.¹ One of the facile CO₂ fixation methods is the reaction of CO₂ with epoxides to form cyclic carbonates which are important polymer precursors, solvent of electrolytes for secondary batteries, etc.² Ammonium or phosphonium halides facilitate this reaction through the ring opening nucleophilic attack of halides to epoxides.³⁻⁷ The resulting alkoxide intermediates trap CO₂ to form cyclic carbonates. This CO₂ fixation process without Lewis acid catalysts usually requires high reaction temperatures (>100°C) despite being an exothermic reaction. Lewis acids including Zn or Crcompounds can accelerate this reaction⁸⁻¹⁴ and can therefore lower the reaction temperature below 100°C.⁹⁻¹⁴ Such CO₂ fixation catalysts that work at room temperature are most desirable in the viewpoint of energy efficiency. In order to allow recycling of Lewis acids, heterogeneous catalysts for CO2 fixations have been developed.15 However, their catalytic performance at room temperature was less explored.¹⁶⁻²⁰

Recently, microporous organic networks (MONs) containing catalytic sites have been prepared via the networking of predesigned building blocks, revealing stability and ability of facile chemical tuning.²¹⁻²² Moreover, MONs bearing Lewis acids have shown reasonable activities in the CO₂ conversion to cyclic carbonates at reaction temperatures below 100°C.9-11,14-21 However, more exploration is required to improve the catalytic activities of materials at room temperature. The microporosity of MONs enables substrates to diffuse into the materials. Hence, the Lewis acid sites in inner MONs can be utilized in chemical conversions. However, the conventional micron or submicron sized MONs suffer from the long diffusion pathways of substrates and the possible clogging of the pathways by products. Our research group has shown that the MONs can be engineered to form hollow structures with thin shells (shell thickness < 50 nm) by template methods.²⁷ The so-obtained reduced diffusion pathways for substrates can improve catalytic activity.28-30

In this work, we report the room temperature catalytic activities of hollow and microporous Cr and Zn porphyrin networks (H-MCrPN and H-MZnPN) in the CO_2 fixation to cyclic carbonates.

Experimental

General Information

Transmission electron microscopy (TEM) was conducted using a JEOL 2100F. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were conducted using a JSM6700F. N₂ adsorption-desorption isotherm curves were obtained at 77K using a BELSORP II-mini analyzer. Pore size distribution of materials was analyzed based on a density functional theory (DFT) method. Powder X-ray diffraction

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⁺ Electronic Supplementary Information (ESI) available: Characterization data of building blocks and model studies, PXRD patterns and XPS spectra of H-MCrPN, H-MPN, and H-MZnPN, size evaluation of substrates and products, chemoselectivities for cyclic carbonates depending on cocatalysts, IR spectra of H-MCrPN before and after reaction, NMR spectra of cyclic carbonates, and CO₂ adsorption behaviors of H-MCrPN. See DOI: 10.1039/x0xx00000x

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(PXRD) studies were conducted using a Rigaku MAX-2200 (Cu-K α radiation). Solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy was performed using a 500 MHz Bruker ADVANCE II NMR spectrometer with a mode of crosspolarization/total side band suppression (CP-TOSS) at the NCIRF of Seoul National University. A 4 mm magic angle spinning probe was used with a spinning rate of 5 kHz. Solution state ¹H and ¹³C NMR spectra were obtained using a 400 MHz and 500 MHz Varian spectrometers. Infrared absorption (IR) spectroscopy was performed using a Bruker VERTEX 70 FT-IR spectrometer. Diffuse reflectance spectroscopy was conducted using a Shimadzu UN-3600. The UV/vis absorption spectroscopy was performed using a JASCO V-630. X-ray photoelectron spectra (XPS) were obtained using a Thermo VG and Al-Ka radiation. Elemental analysis was conducted using a CE EA110 analyzer.

Synthetic Procedures for H-MCrPN

Silica spheres with diameters of ~420 nm were prepared by the synthetic procedures of the literature.³¹ In our study, the following procedures were applied. Ethanol (200 mL), water (23.5 mL), and NH₄OH solution (28~30%, 7 mL) were added to a 250 mL round bottomed flask. The reaction mixture was stirred at 1150 rpm for 5 min. After tetraethyl orthosilicate (17.5 mL) was added, the reaction mixture was stirred at room temperature for 18 h. The silica spheres were separated by centrifugation, washed with hexane, and dried under vacuum.

Tetra(4-ethynylphenyl) porphyrin was prepared by the synthetic procedures in the literature.³² Tetra(4-ethynylphenyl) Cr(III)-Cl porphyrin was prepared by the following procedures. Tetra(4-ethynylphenyl) porphyrin (0.20 g, 0.28 mmol) was dissolved in distilled DMF (5 mL) by heating at 170°C for 10 min in a flame-dried 50 mL two neck Schlenk flask equipped with a reflux condensor under argon.³³⁻³⁵ CrCl₂ (0.124 g, 1.01 mmol) was dissolved in distilled DMF (3 mL) in a 10 mL vial by sonnication. CrCl₂ solution (0.75 mL) was added dropwise to porphyrin solution at 170°C and then, the reaction mixture was stirred at 170°C for 10 min under argon.33-35 This addition was repeated three more times. The reaction mixture was heated at 170°C for 30 min under argon.33-35 After the reaction mixture being cooled to room temperature, water (200 mL) was added. The reaction mixture was put aside at room temperature overnight to induce the formation of precipitates which were separated by filtration. The solid was washed with water and hexane and dried in an oven at 90 °C. After the solid being dissolved in chloroform, the target product was separated by column chromatography (aluminium oxide, eluent: chloroform and a 40:1 mixture of chloroform and methanol). The red bands contained the tetra(4-ethynylphenyl) Cu(II)-porphyrin (formed by Cu residues) and metal-free porphyrin. The dark green band contained the tetra(4-ethynylphenyl) Cr(III)-Cl porphyrin. To further purify the product, chloroform solution of tetra(4ethynylphenyl) Cr(III)-Cl porphyrin was treated by HCl solution (12 M) overnight.³⁴ The removal of impurities was confirmed by the disappearance of Q band at 630 nm in UV-vis absorption spectroscopy.³⁴ The product was extracted by chloroform and then, the solvent was evaporated. Pure tetra(4ethynylphenyl) Cr(III)-Cl porphyrin was isolated by recrystallization from a mixture of chloroform and hexane, washed with hexane, and dried under vacuum. The tetra(4ethynylphenyl) Cr(III)-Cl porphyrin was characterized by IR

S1 in the ESI) For the preparation of SiO₂@MCrPN, silica spheres (0.250 g), (PPh₃)₂PdCl₂ (8.4 mg, 0.012 mmol), and CuI (2.3 mg, 0.012 mmol) were added to a mixture of distilled triethylamine (15 mL), distilled toluene (10 mL), and distilled DMF (5 mL) under argon. The reaction mixture was sonicated at room temperature for 2 h. After tetra(4-ethynylphenyl) Cr(II)-Cl porphyrin (96 mg, 0.12 mmol) and 1,4-diiodobenzene (79 mg, 0.24 mmol) being added, the reaction mixture was heated at 90°C for 48 h under argon. After cooled to room temperature, the solid (SiO₂@MCrPN) was separated by centrifugation, washed with methanol, methylene chloride, and acetone, and dried under vacuum. HF solution (48~51% HF aqueous solution, 5 mL) was diluted by adding water (25 mL) and methanol (20 mL). SiO₂@MCrPN was treated with a diluted HF solution in a 50 mL Falcon tube. The reaction mixture was stirred at room temperature for 2 h. The solid (H-MCrPN) was separated by centrifugation, washed with a 3:2 mixture of water and methanol, and acetone, and dried under vacuum.

spectroscopy, confirming intact terminal alkyne groups. (Fig.

Synthetic Procedures for H-MZnPN

For the preparation of $SiO_2(a)MPN$, silica spheres (0.25 g), (PPh₃)₂PdCl₂ (8.4 mg, 0.012 mmol), and CuI (2.3 mg, 0.012 mmol) were added to a mixture of distilled triethylamine (10 mL), distilled toluene (20 mL), and distilled THF (10 mL) under argon. The reaction mixture was sonicated at room temperature for 2 h. After tetra(4-ethynylphenyl) porphyrin (85 mg, 0.12 mmol) and 1,4-diiodobenzene (79 mg, 0.24 mmol) being added, the reaction mixture was heated at 90°C for 48 h under argon. After being cooled to room temperature, the solid (SiO₂@MPN) was separated by centrifugation, washed with methanol, methylene chloride, and acetone, and dried under vacuum. HF solution (48~51% in aqueous solution, 5 mL) was diluted with water (25 mL) and methanol (20 mL). The SiO₂@MPN was treated with the diluted HF solution in a 50 mL Falcon tube at room temperature for 2 h. Violet powder (H-MPN) was separated by centrifugation, washed with a 3:2 mixture of water and methanol, and acetone, and dried under vacuum. H-MPN (0.21 g) and zinc acetate (0.26 g, 1.4 mmol) were added to a distilled methanol (60 mL) in a flame-dried 100 mL one neck Schlenk flask under argon. The reaction mixture was heated at 90°C for 24 h under argon. After the reaction mixture being cooled to room temperature, the powder (H-MZnPN) was separated by centrifugation, washed with methanol, THF, and acetone, and dried under vacuum.

Procedures for Catalytic Reaction

Tetraalkylammonium halide, PPNCl, H-MCrPN (0.86 mmol Cr porphyrin/g), and H-MZnPN (0.99 mmol Zn porphyrin/g) were dried at 60°C under vacuum for 12 h. MON catalyst (H-MCrPN: 71 mg, 0.061 mmol Cr porphyrin, H-MZnPN: 62 mg, 0.061 Zn porphyrin), ammonium halide (tetrahexylammonium

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bromide, 0.39 g, 0.90 mmol), and epoxide (styrene oxide, 1.42 mL, 12.5 mmol) were added to a flame-dried two neck Schlenk tube under argon. The reaction mixture was bubbled with CO₂ for 5 min and stirred (200 rpm) at room temperature (~27°C) with a CO₂ balloon. The conversion of expoxides was analyzed by ¹H NMR spectroscopy. For the recycle tests, the catalysts were separated by filtration (syringe filter: SX0001300), washed with methanol, methylene chloride, and acetone, dried under vacuum at 60°C, and reused for the next run.

The cyclic carbonates in this study are all known compounds.36-42 1H and 13C NMR spectra of the cyclic carbonate products matched well with those in the literature. ³⁶⁻ ⁴² ¹H and ¹³C NMR data of the products are as follows.⁴³ Product of Entry 1 in Table 1: 4-phenyl-1,3-dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 4.33$ (dd, J = 8.6, 7.9 Hz, 1H), 4.81 (t, J = 8.4 Hz, 1H), 5.69 (t, J = 8.0 Hz, 1H), 7.19-7.52 (m, 5H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 71.2, 78.0, 125.9, 129.3, 129.8, 135.8, 154.8 ppm. Product of Entry 2 in Table 1: 4-butyl-1,3-dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta =$ 0.85-0.98 (m, 3H), 1.23-1.88 (m, 6H), 4.08 (dd, J = 8.4, 7.3 Hz, 1H), 4.56 (t, J = 8.1 Hz, 1H), 4.66-4.80 (m, 1H) ppm. ¹³C NMR $(CDCl_3, 125 \text{ MHz}): \delta = 13.8, 22.3, 26.5, 33.6, 69.4, 155.1 \text{ ppm}.$ Product of Entry 3 in Table 1: 4-hexyl-1,3-dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 0.89$ (t, J = 6.2 Hz, 3H), 1.22-1.88 (m, 10H), 4.07 (t, J = 7.8 Hz, 1H), 4.53 (t, J = 8.1 Hz, 1H), 4.71 (dt, J = 14.5, 7.3 Hz, 1H) ppm. 13 C NMR (CDCl₃, 125 MHz): $\delta = 14.0, 22.5, 24.3, 28.8, 31.5, 33.9, 69.4, 155.1$ ppm. Product of Entry 4 in Table 1: 4-(methoxymethyl)-1,3dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): δ = 3.43 (s, 3H), 3.58 (dd, J = 11.1, 3.7 Hz, 1H), 3.67 (dd, J = 11.1, 3.4 Hz, 1H), 4.39 (dd, J = 8.4, 6.1 Hz, 1H), 4.53 (t, J = 8.4 Hz, 1H), 4.86 (ddt, J = 8.6, 6.1, 3.6 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 59.8, 66.2, 71.5, 75.0, 154.9 ppm. Product of Entry 5 in Table 1: 4-(hydroxymethyl)-1,3-dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 2.74$ (t, J = 6.2 Hz, 1H), 3.72 (ddd, J = 12.9, 6.8, 3.5 Hz, 1H), 3.99 (ddd, J = 12.9, 5.5, 3.0 Hz, 1H), 4.39-4.62 (m, 2H), 4.82 (ddt, J = 8.4, 6.5, 3.3 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): $\delta = 61.7, 65.8, 76.6, 155.3$ ppm. Product of Entry 6 in Table 1: 4-[(allyloxy)methyl]-1,3-dioxolan-2-one, ¹H-NMR $(CDCl_3, 500 \text{ MHz}): \delta = 3.63 \text{ (dd, } J = 11.1, 3.7 \text{ Hz}, 1\text{H}), 3.71$ (dd, J = 11.1, 3.7 Hz, 1H), 3.95-4.15 (m, 2H), 4.41 (dd, J = 8.4, 6.0 Hz, 1H), 4.53 (t, J = 8.4 Hz, 1H), 4.80-4.92 (m, 1H), 5.13-5.38 (m, 2H), 5.78-6.02 (m, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): $\delta = 66.3, 68.9, 72.7, 75.0, 118.0, 133.7, 154.9$ ppm. Product of Entry 7 in Table 1: 4-(phenoxymethyl)-1,3dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 4.14$ (dd, J = 10.6, 3.6 Hz, 1H), 4.18-4.26 (m, 1H), 4.52 (dd, J = 8.5, 5.9 Hz, 1H), 4.61 (t, J = 8.5 Hz, 1H), 4.97-5.09 (m, 1H), 6.87-7.05 (m, 3H), 7.22-7.36 (m, 2H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 66.2, 66.9, 74.3, 114.7, 122.0, 129.7, 154.8, 157.8 ppm. Product of Entry 8 in Table 1: 4-(tert-butoxymethyl)-1,3-dioxolan-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.20$ (d, J = 4.6 Hz, 9H), 3.53 (dd, J = 10.3, 3.6 Hz, 1H), 3.62 (dd, J = 10.3, 4.5 Hz, 1H), 4.39 (dd, J = 8.2, 5.8 Hz, 1H), 4.48 (t, J = 8.3 Hz, 1H), 4.78 (ddd, J =8.3, 5.6, 4.5 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): $\delta =$ 27.3, 61.3, 66.6, 73.9, 75.1, 155.2 ppm. Product of Entry 9 in Table 1: cyclopenta-1,3-dioxol-2-one, ¹H-NMR (CDCl₃, 500

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MHz): $\delta = 1.62-1.72$ (m, 2H), 1.74–1.88 (m, 2H), 2.04–2.26 (m, 2H), 5.11(dd, J = 3.6, 1.6Hz, 2H) ppm. ¹³C NMR (CDCl₃, 125 MHz): $\delta = 21.6$, 33.2, 81.8, 155.5 ppm. Product of Entry 10 in Table 1: cyclohexa-1,3-dioxol-2-one, ¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.38-1.50$ (m, 2H), 1.59–1.72 (m, 2H), 1.83–1.99 (m, 4H), 4.69 (p, J = 6.1 Hz, 2H) ppm. ¹³C NMR (CDCl₃, 125 MHz): $\delta = 19.2$, 26.8, 75.7, 155.3 ppm.

Procedures for the Model Studies (The Conversion of Cr(III)-Cl Porphyrin to Cr(III)-F Porphyrin)

This conversion was reported in the literature.⁴⁴ HF solution (50% in aqueous solution, 5 mL) was diluted with water (25 mL) and methanol (20 mL). Tetra(4-ethynylphenyl) Cr(III)-Cl porphyrin (96 mg, 0.12 mmol) was treated with a diluted HF solution at room temperature for 4 h. The tetra(4-ethynylphenyl) Cr(III)-F porphyrin was isolated by centrifugation, washed with a mixture (3:2) of water and methanol, acetone, and dried under vacuum. Tetra(4-ethynylphenyl) Cr(III)-F porphyrin was characterized by UV-visible absorption spectroscopy⁴⁴ and EDS. (Fig. S2 in the ESI) After conversion of Cr-Cl to Cr-F in porphyrins, the Soret band of Cr-porphyrins shifted from 451 nm to 441 nm, matching with the observation in the literature.⁴⁴ The EDS confirmed the conversion of Cr-Cl to Cr-F.

Result and Discussion

Fig. 1 shows synthetic routes to H-MCrPN and H-MZnPN.



Fig. 1 Synthetic schemes for H-MCrPN and H-MZnPN.

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For the synthesis of H-MCrPN, Cr porphyrin with four 4ethynylphenyl groups was prepared as a building block. During the synthesis of H-MZnPN, we found that Zn was etched out of Zn-porphyrins by the reaction with HF. We therefore decided to incorporate Zn to porphyrin networks by a post-synthetic modification. Thus, metal-free porphyrin having four 4ethynylphenyl groups was prepared as a building block. Microporous networks were formed on the surface of silica spheres (~420 nm) via the Sonogashira coupling of the tetra(4ethynylphenyl) Cr(III)-Cl porphyrin or metal free tetra(4ethynylphenyl) porphyrin with 2 eq. 1,4-diiodobenzene. The inner silica was etched by the treatment with HF solution. During the etching, the Cr-Cl was converted to Cr-F.⁴⁴⁻⁴⁵ The reaction of hollow and microporous metal free porphyrin networks (H-MPNs) with zinc acetate resulted in H-MZnPNs.

SEM and TEM analysis confirmed the hollow structures of H-MCrPN, H-MPN, and H-MZnPN with diameters of ~500 nm and shell thicknesses of ~40 nm. (Fig. 2)



Fig. 2 SEM images of (a, d) H-MCrPN, (b, e) H-MPN, and (c, f) H-MZnPN. TEM images of (g) H-MCrPN, (h) H-MPN, and (i) H-MZnPN.

The analysis of N₂ isotherm curves of H-MCrPN, H-MPN, and H-MZnPN revealed surface areas of 794, 677, and 802 m²/g, and micropore volumes of 0.24, 0.20, and 0.24 cm³/g, respectively. (Fig. 3a) The hysteresis loops were observed in the N₂ isotherm curves of the materials, possibly due to the swelling of a nonrigid porous structure or the irreversible uptake of N₂ in pores.⁴⁶ The higher surface areas of H-MCrPN and H-MZnPN than that of H-MPN might result from the suppressed π - π stacking of polymer chains by metals or the removal of possibly entrapped impurities during metal coordination. The PXRD showed amorphous character for H-MCrPN, H-MPN, and H-MZnPN, matching with the properties of MONs in the literature.⁴⁷⁻⁴⁸ (Fig. S3 in the ESI) The IR spectroscopy of H-MCrPN and H-MZnPN showed the vibration peaks of metal-porphyrin at 999 cm^{-1,49} while H-MPN lacked a corresponding peak. (Fig. 3b) The solid state ¹³C CP/TOSS NMR of H-MPN showed alkyne peaks at 80~90 ppm and aromatic peaks at 110~140 ppm. (Fig. 3c) After Zn coordination to H-MPN, main peaks appeared at 120, 130, 142, and 149 ppm, corresponding to those of Zn-porphyrin rings.⁵⁰⁻⁵¹



Fig. 3 (a) N₂ isotherm curves at 77K, pore size distribution diagrams based on the DFT method and (b) IR spectra of H-MCrPN, H-MPN, and H-MZnPN. (c) Solid state ¹³C CP/TOSS NMR spectra of H-MPN and H-MZnPN.

The coordination of metal to porphyrin rings can be characterized by UV-vis absorption spectroscopy.52 The H-MPN showed unique Q-band peaks at 526, 560, 598, and 658 nm. (Fig. 4a) After Zn coordination to H-MPN, the location of the Q band peaks significantly changed to 559 and 604 nm. Similarly, two major Q bands were observed at 574 and 612 nm in the absorption spectrum of H-MCrPN. The XPS spectra of H-MCrPN and H-MZnPN showed the $2p_{1/2}$ and $2p_{3/2}$ orbital peaks of Cr at 586.6 and 576.8 eV⁵³ and the $2p_{1/2}$ and $2p_{3/2}$ orbital peaks of Zn at 1021.6 and 1044.7 $eV^{51,54}$, respectively. (Fig. 4b) Also, One main N 1s oribtal peaks of H-MCrPN and H-MZnPN appeared at 398.4 and 398.1 eV, corresponding to Cr-N- and Zn-N-, respectively.⁵⁵⁻⁵⁶ (Fig. S4 in the ESI) In comparison, H-MPN showed no Zn 2p oribtal peaks and instead, showed two main N 1s orbital peaks at 397.8 and 399.6 eV, corresponding to =N- and -NH- species of metal free porphyrins, respectively. 55-56 These observations further confirm Zn coordination to H-MPN via postsynthetic modification. The EDS elemental mapping analysis of H-MCrPN and H-MZnPN showed the homogeneous distribution of Cr(III)-F porphyrin and Zn-porphyrin moieties in the materials, respectively. (Fig. 4c) As shown in According to the elemental analysis of N contents (4.84 and 5.55wt% for H-MCrPN and H-MZnPN, respectively), the amounts of metal porphyrin moieties in H-MCrPN and H-H ZnPN were calculated to be 0.86 and 0.99 mmol/g, respectively.



Fig. 4 (a) UV-vis absorption, (b) XPS spectra of H-MCrPN, H-MPN, and H-MZnPN, and (c) EDS elemental mapping of H-MCrPN and H-MZnPN.

Considering the high surface areas of H-MCrPN⁵⁷ and H-MZnPN and excellent dispersion ability in organic solvents including styrene oxide, we studied their catalytic performance in the CO_2 fixation with styrene oxide to the corresponding cyclic carbonate at room temperature under ambient CO_2 pressure (balloon). Fig. 5 summarizes the results.

As shown in Figs. 5a-c, H-MCrPN showed superior catalytic activities compared to H-MZnPN, indicating that the Cr-F moiety is a better Lewis acid than Zn in the porphyrins. The effect of alkyl groups in tetraalkylammonium halides was significant in the CO₂ fixation with styrene oxide to cyclic carbonate. As the chain length of alkyl groups increased from methyl to butyl and hexyl, the conversion yield after 48 h gradually increased from 7% to 86 and 93%, respectively. (Fig. 5d) This trend is attributed to the relative solubility of tetraalkylammonium halides in styrene oxide. Further increase of the alkyl chain length did not improve the catalytic activity; (n-octyl)₄NBr showed a lower conversion yield (72% after 48 h) than (n-hexyl)₄NBr (93% after 48 h), which is attributable to a size effect of the cocatalyst. As the size of tetraalkylammonium halides increased, the diffusion rate into the pores might decrease.



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Fig. 5 CO₂ fixation with styrene oxide to cyclic carbonate depending on catalysts (a-c) and co-catalysts (d-f). Reaction conditions: styrene oxide (12.5 mmol), no additional solvent, H-MCrPN or H-MZnPN (0.49 mol% metal porphyrins, 0.061 mmol), tetraalkylammonium halide or PPNCI (0.90 mmol), room temperature, and CO₂ (balloon). THABr: (*n*-hexyl)₄NBr, TBABr: (*n*-butyl)₄NBr, TOABr: (*n*-octyl)₄NBr, TMABr: Me₄NBr, PPNCI: [(Ph₃P)₂N]Cl, TBACI: (*n*-butyl)₄NCl, and TBAI: (*n*-butyl)₄NI.

When we screened different anions of tetrabutylammonium halides, bromide and iodide showed similar conversion yields (82% and 80% after 48 h, respectively) in the CO₂ fixation at room temperature. (Fig. 5e) The chloride showed a lower conversion yield (71% after 48 h) than bromide. Thus, the optimal combination of H-MCrPN with (*n*-hexyl)₄NBr (THABr) showed the best performance (93% conversion yield after 48 h,

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TON=190) in the CO₂ fixation with styrene oxide to cyclic carbonate at room temperature. As far as we are aware, this is one of the best performances of heterogeneous MON catalysts for the room temperature CO₂ fixation with styrene oxide to cyclic carbonate.^{16-20,58} Without H-MCrPN or H-MZnPN, tetraalkylammonium halides and [(Ph₃P)₂N]Cl showed poor conversions of styrene oxide, indicating that the conversion was catalyzed by Cr(III)-F moieties in the H-MCrPN. (Fig. 5f) In control experiments, nonhollow MCrPN materials showed much pooper catalytic activities than H-MCrPN, indicating the hollow structural effects. (Fig. S5 in the ESI)

Next, we screened various epoxides, in which THABr are soluble, as substrates for the room temperature CO_2 fixation to cyclic carbonates. Table 1 summarizes the results of catalytic performance of H-MCrPN.

Table 1. Catalytic performance of H-MCrPN in the CO_2 fixation with epoxides to cyclic carbonates.^a



^a Reaction conditions: epoxide (12.5 mmol), no additional solvent, H-MCrPN (71 mg, 0.86 mmol Cr porphyrin/g, 0.49 mol% Cr porphyrins, 0.061 mmol), THABr (0.90 mmol), room temperature, and CO₂ (balloon). The reactions of entries 1-5, 7, and 8 showed no byproducts (In these reactions, selectivities for cyclic carbonates were 100%.). ^b The reaction time, conversion based on ¹H NMR, and isolated yield in parenthesis. ^c The selectivity for cyclic carbonate was 92% and the byproduct was a homopolymer of epoxide. ^d The partial formation of cyclic carbonate resulted in the solidification of reaction medium. Thus, poor conversion could not be improved. ^e The selectivity for cyclic carbonate was 79% and the byproduct was a homopolymer of epoxide. ^f The selectivity for cyclic carbonate was 75% and the byproduct was a homopolymer of epoxide.

Epoxides (12.5 mmol) with phenyl and butyl substituents worked well in the room temperature CO_2 fixation catalyzed by H-MCrPN (0.49 mol% of Cr(III)-F porphyrins) and THABr (0.90 mmol), showing 93% and 70% conversion after 48 h, respectively. (Entries 1-2 in Table 1) When the alkyl chain length of epoxides was increased from butyl to hexyl, the conversion decreased to 55% after 48 h. (Entry 3 in Table 1)

The sizes of epoxide substrates were calculated in a range of 4.8~10.6 Å, indicating the possible size-dependent constrain effect in micropores (main pore sizes of 6.8 and 13 Å) of H-MCrPN. (Figs. 3a and S6 in the ESI) Epoxides with ether or alcohol groups such as 2-methoxymethyl)oxirane and glycidol worked well in the reaction and showed 100% and 88% conversion after 48 h, respectively. (Entries 4-5 in Table 1) This indicates that the Lewis acidic activation of epoxides by H-MCrPN works well with additional ether and alcohol groups. However, as the sizes of side substituents increased, conversion became gradually slower. (Entries 6-8 in Table 1) The 2-(allyloxymethyl)oxirane and 2-(tert-butoxymethyl)oxirane showed 83% and 71% conversion after 48 h, respectively. In the case of 2-(phenoxymethyl)oxirane, the partial formation of cyclic carbonate resulted in the solidification of reaction medium and in a poor conversion yield. (Entry 7 in Table 1) Epoxides with two tertiary carbons were also tested for the room temperature CO₂ fixation. Relatively bulky cycopentene oxide and cyclohexene oxide showed slow conversions (72 and 39% after 120 h, respectively). (Entries 9-10 in Table 1) The chemoselectivities to cyclic carbonates were perfect in the cases of most epoxide substrates excepting glycidol (Entry 5 in Table 1, selectivity: 79%) 2-(allyloxymethyl)oxirane (Entry 6 in Table 1, selectivity: 92%), and cyclohexene oxide (Entry 10 in Table 1, selectivity: 75%). Byproducts were homopolymers of epoxides. When we screened the co-catalysts for the conversions of glycidol and cyclohexene oxide, THABr showed the best chemoselectivities. (Fig. S7 in the ESI)



Fig. 6 (a) Recycle tests of H-MCrPN. Reaction conditions: styrene oxide (12.5 mmol), no additional solvent, H-MCrPN (71 mg, 0.86 mmol Cr porphyrin/g, 0.49 mol% Cr porphryins, 0.061 mmol Cr porphyrins), THABr (0.90 mmol), room temperature, 48 h, and CO_2 (balloon). Green, orange and violet bars of a graph indicate conversions of styrene oxide, isolated yields of cyclic carbonate, and chemoselectivities for cyclic carbonates. (b) UV-vis absorption spectra, (c) SEM images, and (d) XPS spectra of the original H-MCrPN and the recovered one after five successive reactions.

The recyclability of H-MCrPN was studied. As shown in Fig. 6a, the H-MCrPN maintained good activities throughout five recycle tests. In the fifth cycle, the recycled H-MCrPN showed 94% conversion of styrene oxide, while 93% conversion was observed in the first reaction. The UV-vis and IR absorption spectroscopy of the H-MCrPN recovered after the fifth cycle showed nearly identical spectrum with those of the original material. (Figs. 6b and S8 in the ESI) The pyrrole vibration peak at 999 cm⁻¹ was completely retained in the IR spectrum of the H-MCrPN recovered after the fifth cycle. (Fig. S8 in the ESI) The SEM image of the H-MCrPN recovered after the fifth cycle showed the complete retention of hollow structure. (Fig. 6c) The XPS studies also supported the retention of Cr-F species after five cycles. (Fig. 6d)

Conclusions

This work shows that efficient heterogeneous catalytic systems can be developed based on structure-engineered MONs for the room temperature CO_2 fixation to cyclic carbonates. The high surface area and microporosity of MONs enabled the inner Lewis acid sites to be utilized for the activation of epoxides. The reduced diffusion pathways of substrates in the H-MCrPN due to the hollow structure and the efficient Lewis acid function of Cr(III)-F resulted in the efficient CO_2 fixation with styrene oxide with TON 190 at room temperature under ambient (balloon) pressure. We believe that more diverse Lewis acid moieties can be incorporated to the hollow and microporous networks.

Conflicts of interests

There are no conflicts of interest to declare.

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- 58 In the literature,¹⁸ nonhollow microporous polymer catalysts bearing Cr(III)-Cl salens (0.44 mol% Cr salens, 7.2 mol% ammonium salt) showed a 51.6% conversion yield of styrene oxide at room temperature after 48 h (TON: 117). In comparison, H-MCrPN (0.49 mol% Cr porphyrins, 7.2 mol% ammonium salt) showed a 93% conversion yield of styrene oxide at room temperature after 48 h (TON: 190). (Table S1 in the ESI)

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Hollow and microporous Cr(III)-F porphyrin networks (H-MCrPNs) showed excellent catalytic activities in the room temperature CO_2 fixation with epoxides to cyclic carbonates substrates due to the hollow structure, and the efficient Lewis acidic activity of Cr(III)-F moieties.

