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Metalated porous porphyrin polymers as efficient heterogeneous catalysts for cycloaddition of epoxides with CO₂ under ambient conditions

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ABSTRACT

We have successfully synthesized a porphyrin based porous organic polymer (POP-TPP) from free-radical polymerization of tetrastyrylporphyrin monomer under solvothermal conditions. Besides high surface area $(1200 \text{ m}^2/\text{g})$ and high thermal stability, the obtained polymer features open metal chelating sites, and thus the catalytic activities of metalloporphyrins can be reasonably adjusted by introducing various metal ions. After metalation with Co³⁺, Zn²⁺, and Mg²⁺, the Co/POP-TPP, Zn/POP-TPP, and Mg/POP-TPP as heterogeneous catalysts are very active for cycloaddition of epoxides with CO2 to cyclic carbonates at ambient conditions with n-Bu₄NBr as a nucleophilic additive. Particularly, under the relatively low CO₂ concentration (15% in volume), the activity of heterogeneous Co/POP-TPP catalyst is even higher than that of the corresponding homogeneous Co/TPP catalyst. More importantly, there is no activity loss even if the Co/POP-TPP is recycled for 18 times. The excellent catalytic activity and superior recyclability of the obtained catalysts indicate that the porphyrin based porous organic polymer is a promising candidate for construction of efficient heterogeneous catalysts in the future.

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1. Introduction

Chemical fixation of CO₂ to form economically valuable cyclic carbonates has been paid much attention recently due to the combination of the solution of CO₂ greenhouse gas and the wide applications of the cyclic carbonates [1–4]. For this reaction, a number of homogeneous catalysts such as ionic liquids [5,6], alkali metal halides [7], metal salen complexes [8–13], and metalloporphyrins [14-18], and heterogeneous catalysts such as metal oxides [19–21], zeolites [22,23], ion-exchanged resins [24], mesoporous materials [25-27], nanoporous polymers [28,29], and metalorganic frameworks (MOFs) [30,31] have been employed. Notably, most of these catalysts normally require harsh conditions such as relatively high temperature, high CO₂ pressure, and high catalyst loadings. Undoubtedly, a catalyst system that is enabled to convert CO₂ at atmospheric pressure or even lower partial CO₂ pressures and room temperature with only heat from the surrounding environment to avoid the generation of new CO₂ is exceedingly desirable [32,33].

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Compared with the other catalysts, the metal-salen complexes and metal-porphyrins can realize the transformation under relatively mild conditions [34–40]. Particularly, when these active species are immobilized in the porous materials [33,41-43] such as zeolites [42], they exhibit not only high activities but also a long catalyst life. In spite of this, these immobilized heterogeneous catalysts generally show lower activities than the homogeneous counterparts as a result of fewer accessible active sites in comparison with the soluble ones [33,42,43]. Therefore, it is strongly desirable to obtain the heterogeneous catalysts with both long catalyst life and very high activities.

Recently, there are encouraging heterogeneous catalysts such as Cu-MOF [44] and metal-salen based conjugated microporous polymers (metal-salen-CMP) [45], exhibiting excellent catalytic performance for production of cyclic carbonates, and even outperforming the corresponding homogeneous catalysts under real mild conditions such as at room temperature and atmospheric pressure [44–46]. However, in these catalysts it is still observed a little metal leaching.

More recently, it has been reported that porous organic polymers (POPs) with excellent framework stabilities and hierarchical porosities are endowed with very high accessibility and







outstanding binding ability of catalytically active species [47,48]. For instance, Rh metalated porous organic ligand polymers of triphenylphosphine (POL-PPh₃) as heterogeneous catalysts exhibit not only comparable activities and selectivities to those of the homogeneous counterparts in olefin hydroformylations but also extraordinary recyclabilities [49]. It is also shown that the metalated (Fe and Mn) porous organic polymers (POPs) containing free-base porphyrin subunits by the condensation of a bis(phthalic acid)porphyrin with tetra(4-aminophenyl)methane [50] are very active catalysts in both olefin epoxidation and alkane hydroxylation. Inspired by these successful examples, we have rationally designed and synthesized a hierarchically porous organic polymer (POP-TPP) constructed from polymerization of the vinylfunctionalized tetraphenylporphyrin monomer (tetrastyrylporphyrin). After metalation, these porous heterogeneous catalysts with very high degree of the accessible active sites exhibit comparable activities in cycloaddition of epoxides with CO₂ to those of the homogeneous catalysts. More importantly, there is no activity loss even if the Co/POP-TPP is recycled for 18 times. Particularly, when the concentration of CO₂ is reduced to about 15% CO₂ in volume (the concentration of emission from the industrial processes to the air), the Co/POP-TPP heterogeneous catalyst shows even much better activity than the corresponding homogeneous Co/TPP catalyst. The enrichment of the CO_2 by the porous materials is responsible for this phenomenon. Our work therefore provides an avenue for energy-effective CO₂ transformation in particular for the direct conversion of industrial combustion CO₂.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were distilled over LiAlH₄ and CaH₂, respectively. N-methyl-2pyrrolidone (NMP) was obtained from Aladdin (Shanghai), which was used without further purification. Pyrrole and 4-bromostyrene were from Aladdin and Meryer Chemical Technology (Shanghai), respectively, which were distilled before the use. Other commercially available reagents [azobisisobutyronitrile (AlBN), epichlorohydrin, propylene oxide, 1,2-epoxyhexane, styrene oxide, allyl glycidyl ether, and butyl glycidyl ether] were purchased with high purity and used without further purification.

2.2. Catalyst preparation

2.2.1. Synthesis of 4-vinylbenzaldehyde

An excess of DMF was added into the solution of (4-vinylphenyl)magnesium bromide (100 mmol) at 0 °C under N₂, stirred at room temperature overnight, and then quenched by the addition of 50 mL of saturated NH₄Cl solution. After extraction with ethyl acetate, washing with brine, drying over MgSO₄, filtering, concentrating under vacuum, and purifying by flash column chromatography on silica gel (volume ratio of petroleum ether to EtOAc at 10), the 4-vinylbenzaldehyde (**1**, Fig. S1) as yellowish oil (12.1 g, 91.7% yield) was finally obtained. ¹H NMR (CDCl₃, 400 MHz): δ 9.98 (s, 1H, ArCHO), 7.83 (d, 2H, *J* = 8.0 Hz, ArH), 7.54 (d, 2H, *J* = 8.0 Hz, ArH), 6.76 (m, 1H, CH=), 5.90 (m, 1H, =CH₂), and 5.42 (m, 1H, =CH₂) ppm. ¹³C NMR (CDCl₃, 100.5 MHz): δ 192.15 (ArCHO), 143.83 (ArC), 136.26 (C=), 136.03 (ArC), 130.49 (ArC), 127.13 (ArC), and 117.8 (=C) ppm.

2.2.2. Synthesis of tetrastyrylporphyrin (TSP) monomer

The TSP was synthesized in a typical "one-pot" reaction according to the literature [51]. Pyrrole (0.7 mL, 10 mmol) and 4-vinylbenzaldehyde (1.32 g, 10 mmol) were added to a flask containing propionic acid (100 mL) preheated to 140 °C in air. After reaction for 1 h, the solution was cooled to room temperature. After filtering and washing with methanol and ethyl acetate as well as drying, the title compound was obtained as purple crystals (0.41 g, 22.6% yield). ¹H NMR (CDCl₃, 400 MHz): δ 8.89 (s, 8H, β -porphH), 8.17 (d, 8H, *J* = 8.0 Hz, PhH), 7.79 (d, 8H, *J* = 8.0 Hz, PhH), 7.06 (m, 4H, CH=), 6.10 (d, 4H, *J* = 20.0 Hz, =CH₂), 5.51 (d, 4H, *J* = 8.0 Hz, =CH₂), and -2.75 (s, 2H, NH) ppm. ¹³C NMR (CDCl₃, 100.5 MHz): δ 141.69 (mesoporphC), 136.94 (ArC), 136.71 (C=), 134.84 (β -porphC), 124.62 (ArC), 119.91 (ArC), and 114.68 (=C) ppm.

2.2.3. Synthesis of porous organic tetraphenylporphyrin polymer (POP-TPP)

The POP-TPP was synthesized from a solvothermal polymerization of the TSP monomer. As a typical run, 1 g of TSP was dissolved in 10 mL of NMP, followed by the addition of 50 mg of AIBN. After maintaining in an autoclave at 200 °C for 72 h, the POP-TPP product with reddish brown color was finally obtained after washing with DMF and purifying by Soxhlet extraction (CH_2Cl_2 , 72 h; 0.96 g, 96% yield).

2.2.4. Synthesis of Co/POP-TPP

After degassing DMF (ca. 150 mL) with N₂ for 5 min in a three neck round-bottom flask, the POP-TPP (1 g) was added, and the mixture was heated to 120 °C. Then, $CoCl_2 \cdot GH_2O$ (1.01 g) was added, continuously stirring under N₂ at 120 °C for overnight. After cooling down to room temperature, HCl (3 M, 60 mL) was added slowly into the mixture in the air. After filtering, washing with water, drying in air, purifying by Soxhlet extraction, and drying under vacuum condition, the Co/POP-TPP catalyst with brown color was finally obtained (0.98 g, 90.3% yield).

2.2.5. Synthesis of Zn/POP-TPP and Mg/POP-TPP

The synthesis of Zn/POP-TPP [52] and Mg/POP-TPP [53] was very similar to that of the Co/POP-TPP, except for the use of different inorganic cations and solvents. The Zn/POP-TPP and Mg/POP-TPP were finally obtained as dark green and brown solids in 89.9% and 95.1% yield, respectively. The details are presented in Supplementary Materials.

2.3. Characterization

Nitrogen sorption isotherms collected at -196 °C were measured with Micromeritics ASAP 2020M systems, and the samples were pre-treated under vacuum at 100 °C for 12 h. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. CO₂ sorption isotherms were collected from Micromeritics ASAP2010 at 25 °C under the pressure of 1 atm CO₂. Before the measurement, the samples were treated under vacuum at 100 °C for 12 h. X-ray Photoelectron Spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with Al K α irradiation at θ = 90° for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. UV-Vis spectra were recorded using a Shimadzu UV2450 spectrometer. Thermal gravimetric analysis (TGA) experiments were performed on a SDT Q600 V8.2 Build100 thermogravimetric analyzer under N₂ flow. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) experiments were measured with a Perkin-Elmer plasma 40 emission spectrometer. The scanning electron microscopy (SEM) images of the samples were recorded on a Hitachi SU 1510 apparatus. Transmission electron microscopy (TEM) experiments were performed on a JEM-2100F field emission electron microscope (JEOL, Japan) with an acceleration voltage of 110 kV. ¹H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts were expressed in *ppm* downfield from TMS at $\delta = 0$ ppm. ¹³C (100.5 MHz) magic-angle spinning (MAS) NMR spectra were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO₂ rotor.

2.4. Catalytic cycloaddition of epoxides with CO₂

Typically, the reactions were conducted in a Schlenk tube with 12.5 mmol of epoxides with CO₂ purged at a balloon at room temperature over the catalysts in the presence of tetrabutylammonium bromide (*n*-Bu₄NBr, 0.29 g, 0.9 mmol) for 24 h. The reactants and products were determined by gas chromatography (Shimadzu GC-2014C, a flame ionization detector) with a flexible quartz capillary column coated with OV-17, where ethylbenzene was used as an internal standard. The typical conditions were as follows: injection temperature at 220 °C; detection temperature at 240 °C; column temperature at 60 °C for 2 min in the beginning, a ramp of 10 °C/min to 220 °C and holding at 220 °C for 25 min. For the conversion of styrene oxide, it was also analyzed by ¹H NMR spectroscopy (Bruker Avance-400 spectrometer, 400 MHz) in the reaction mixture. For catalytic evaluation under low CO₂ concentration, 15% CO₂ mixed with 85% N₂ in volume was used and other conditions were the same. For recycling tests, the catalyst was separated by centrifugation, washed with EtOAc and CH₂Cl₂ for three times, and dried under vacuum. Then, the catalyst was used for the next run with addition of fresh *n*-Bu₄NBr and epichlorohydrin.

3. Results and discussions

3.1. Catalyst characterization

Scheme 1 shows the synthesis of the porous porphyrin polymer, POP-TPP, which was rationally prepared from solvothermal polymerization of TSP monomer at 200 °C. The TSP monomer was facilely obtained from the commercially available 4-bromovinylbenzene. The use of the low-cost 4-bromovinylbenzene offers a good opportunity to widely apply the POP-TPP. Particularly, the solvothermal polymerization provides a highly efficient strategy for construction of porphyrin monomers into porous polymer as reflected by the quantitative yield of the POP-TPP. In contrast, the syntheses of POPs from conventional coupling reactions have relatively low yields [54]. After introduction of various inorganic cations, a series of metalated POP-TPPs (Co/POP-TPP, Zn/POP-TPP, and Mg/POP-TPP) were finally obtained.

Fig. 1 shows ¹³C MAS NMR spectrum of the POP-TPP, giving a series of peaks ranged from 25 ppm to 150 ppm. Compare to TSP monomer (Fig. S2), the POP-TPP appears additional peaks at 27.5 ppm and 41.0 ppm, which are assigned to those of polymerized vinyl groups. At the same time, it almost cannot observe the peak at 110.9 ppm related to the vinvl groups, indicating that the POP-TPP has very high degree for the polymerization of the vinyl groups. The peaks at 119–140 ppm in the POP-TPP are related to the tetraphenylporphyrin group, which are well consistent with those of the TSP monomer (Fig. S2). In contrast, the ¹H MAS NMR spectrum of POP-TPP (Fig. S3) is relatively poor, but we still can distinguish the free pyrrole hydrogen in the porphyrin ring at -2.13 ppm. This result is in good agreement with that of the monomer in the liquid NMR (-2.75 ppm, Fig. S2), indicating that the porphyrin structure in the sample is well retained after the polymerization.

Fig. 2A shows nitrogen sorption isotherms of the POP-TPP and Co/POP-TPP. Both give typical curves of type I with type IV. The steep increase below 0.1 of relative pressure (P/P_0) is due to the filling of the micropores, while the hysteresis loop higher than 0.40 (P/P_0) is resulted from the contribution of mesoporosity and macroporosity. Correspondingly, their pore sizes are mainly distributed at 0.4–2 nm and 12–150 nm (Fig. S4). The BET surface areas of the POP-TPP and Co/POP-TPP are 1200 and 924 m²/g, with a pore volume of 1.3 and 1.0 cm³/g, respectively. Similarly, the Mg/POP-TPP and Zn/POP-TPP also exhibit high surface areas and large



Scheme 1. Synthesis of POP-TPP and M/POP-TPP.



Fig. 1. ¹³C MAS NMR spectrum of the POP-TPP. "*" The rotation bands.

pore volume (Fig. S5). Fig. 2B and C shows SEM and TEM images of the POP-TPP respectively, giving direct evidence for the presence of porosity in the POP-TPP. This porosity structure is very favorable for the mass transfer in the reactions [55].

Fig. 2D shows thermogravimetric analysis (TGA) of the POP-TPP and Co/POP-TPP in N₂ flow, giving the polymer decomposition temperature as high as 350 °C. This result suggests that the POP-TPP has excellent thermal stability, which is very important for catalytic applications in the organic transformations. Notably, the Co/POP-TPP has less weight loss than the POP-TPP, which is not consistent with the loading of Co (3.2 wt%) in the Co/POP-TPP. This phenomenon might be related to the difference in the thermal stability of the POP-TPP structure in N_2 flow before and after introduction of Co species. Possibly, the interaction between the Co with porphyrin rings could improve the thermal stability of Co/POP-TPP, resulting in relatively low amount for the sample decomposition in the final product.

Fig. 3 shows XPS spectra of the POP-TPP, Co/POP-TPP, and Co/ TPP. The N1s spectra of the POP-TPP exhibit two peaks at 399.8 and 397.7 eV, which is related to the contribution of two different nitrogen pairs, that is, aminic nitrogen (-NH-) and iminic nitrogen (–N=) in the porphyrin ring. Interestingly, after the introduction of cobalt species and oxidation in the air, the Co/POP-TPP exhibits N1s peak at 398.6 eV. After deconvolution, the sample gives major N1s peaks at 399.8 and 398.6 eV. The peak at 398.6 eV is related to the coordination of cobalt species with porphyrin rings, while the peak at 399.8 eV is assigned to the shortage of the metalation in the porphyrin rings [56]. The integrations of the different parts of the XPS N1s signals show that the Co loading is about 3.7 wt%, which is close to the value (3.2 wt%) obtained from the ICP analysis. In contrast, if the porphyrin ring is fully metalated, the theoretical value should be 7.6 wt% (there is one Co site in each porphyrin ring). This result also supports that the metalation in the Co/POP-TPP is partial.

In addition, the sample Co2p spectra in the Co/POP-TPP show the values of $Co2p_{1/2}$ and $Co2p_{3/2}$ at 796.1 and 780.5 eV respectively, which is well consistent with those in the Co/TPP, giving the values at 796.3 and 780.7 eV, respectively [57]. These values are quite different from those (803.5, 797.9 eV and 787.2, 781.6 eV) in the starting salt of CoCl₂·6H₂O. The disappearance of the intense satellite lines (803.5 and 787.2 eV, due to the presence of high spin Co²⁺ species) suggests that the cobalt species in the Co/POP-TPP is in the +3 oxidation state [12,57].

UV–Vis spectroscopy is also used to exploit the Soret band of the porphyrin polymer before and after the metalation. As shown in Fig. S6, the POP-TPP has absorption peaks at 426, 515, 553,



Fig. 2. (A) N₂ sorption isotherms, (B) SEM image, (C) TEM image, and (D) TG curves of (a) the POP-TPP and (b) Co/POP-TPP. Line b in (A) has been offset by 300 cm³/g along with the vertical axis for clarity.



Fig. 3. (A) N1s and (B) Co2p XPS spectra of (a) POP-TPP, (b) CoCl₂·6H₂O, (c) Co/TPP, and (d) Co/POP-TPP.

596, and 654 nm, which is consistent with those reported in tetraphenylporphyrin (TPP) monomer (415, 515, 550, 590, and 650 nm) [51]. After introduction of transition metal cations, the samples give new absorption peaks (Co/POP-TPP: 428, 526, 550, 597, and 657 nm; Zn/POP-TPP: 433, 524, 559, 602, and 658 nm; Mg/POP-TPP: 430, 521, 562, 600, and 655 nm). In these spectra, it is very difficult to observe the Soret bands, but it is very clear to find the Q bands. The partial metalation could be supported by the shift of the Q bands before and after the metalation. The ICP measurements of Zn/POP-TPP and Mg/POP-TPP show that the Zn and Mg loading is 4.5 wt% and 2.8 wt%, respectively.

It is worth noting that the Co/POP-TPP has superior chemical stability. After treatment in the water solution for several days, we cannot observe any cobalt species leaching. Even if the treatment was conducted in strong acidic media (3 M HCl), only about 10% cobalt species are removed and the porous structure in the polymer is still basically maintained (755 m²/g and pore volume at 0.67 cm³/g, Fig. S7).

Fig. 4 shows CO₂ sorption isotherms of POP-TPP, Co/POP-TPP, and Co/TPP. Clearly, the porous organic polymer POP-TPP has a good adsorption capacity with a value of 29.7 cm³/g at 25 °C under 1 atm CO₂. After the metalation of cobalt, the Co/POP-TPP exhibits a little high adsorption capacity (32.6 cm³/g at 25 °C under 1 atm CO₂). These results are comparable with those reported previously [44,46,58]. In contrast, the Co/TPP has much lower adsorption capacity. In addition, the Zn and Mg ions metalated porous organic polymers (Zn/POP-TPP and Mg/POP-TPP) also show excellent CO₂ adsorption capacity (34.6 and 37.5 cm³/g, Fig. S8) at 25 °C under 1 atm CO₂. The enrichment of the CO₂ in the nanopores is expected to be beneficial for the promotion of the CO₂ conversion [44,46].



Fig. 4. CO2 sorption isotherms of (a) the Co/TPP, (b) POP-TPP and (c) Co/POP-TPP measured at 25 °C.

3.2. Catalytic evaluation

Cycloaddition of epoxides with CO_2 was chosen as a model for the conversion of CO_2 . This reaction was investigated under pure CO_2 and a mixture of CO_2 and N_2 (15% CO_2 + 85% N_2 in volume).

3.2.1. Evaluation under pure CO₂

Table 1 presents catalytic data in the cycloaddition of epichlorohydrin with CO₂ to cyclic carbonate under ambient conditions (29 °C and 1 atm) over various catalysts. Notably, the POP-TPP gives the conversion at 52.1% (entry 1 in Table 1), but the Co/ POP-TPP exhibits the conversion at 95.6% (entry 2 in Table 1), which is completely comparable with that of the homogeneous Co/TPP catalyst (97.4%, entry 3 in Table 1). These results indicate that the Co/POP-TPP is very active and cobalt species play an important role for this reaction [12,59,60]. As control tests, the reactions are performed with Co/POP-TPP and Co/TPP in the absence of n-Bu₄NBr or without Co/POP-TPP and Co/TPP in the presence of n-Bu₄NBr, as presented in Table 1 (entry 4–6). These results also show the importance of the n-Bu₄NBr in the cycloaddition reaction of epichlorohydrin with CO₂.

When molar ratio of epoxide to catalyst (S/C, based on cobalt species) is increased from 455 to 1820, the high conversion (96.1%) can still be obtained with a long reaction time (96 h, entry 7 in Table 1). When the *n*-Bu₄NBr amount is reduced from 290 mg to 50 mg, the conversion has some decreases from 95.6% (entry 2 in Table 1) to 88.9% (entry 8 in Table 1), confirming the importance of n-Bu₄NBr in the promotion of cycloaddition of CO₂ and epoxides. Fig. S10 shows the kinetic curves in the cycloaddition over the Co/POP-TPP and Co/TPP catalysts. Under the same conditions, the heterogeneous catalyst of Co/POP-TPP exhibits a little lower activity than the homogeneous catalyst of Co/TPP. Similarly, the activities of Zn/POP-TPP and Mg/POP-TPP (93.2% and 80.5%, entry 9 and 11 in Table 1) are also explored and show a little lower than those of the Zn/TPP and Mg/TPP (93.5% and 99.3%, entry 10 and 12 in Table 1). In addition, the TOFs of these metalated heterogeneous catalysts have been calculated, and it is found that the TOF of Co/POP-TPP (436 h^{-1}) catalyst is higher than the TOF of the Zn/ POP-TPP (326 h^{-1}) and Mg/POP-TPP (171 h^{-1}) catalysts.

Fig. 5 shows the dependence of the activities on recycling number in the cycloaddition of epichlorohydrin with CO_2 over the binary system of Co/POP-TPP and *n*-Bu₄NBr. In each recycling, the fresh epichlorohydrin and *n*-Bu₄NBr were added. It is mentionable that, after recycling for 18 times, the heterogeneous catalyst Co/ POP-TPP basically remains its activity, giving the conversion at about 93.6% (Table 1, entry 13). Particularly, the cobalt species is undetectable in the filtrate, which is reasonably attributed to the superior chemical stability of the Co/POP-TPP. The BET surface area of the Co/POP-TPP catalyst after recycling for 18 times is 507 m²/g

Table 1

Cycloaddition of epichlorohydrin with CO₂ to form cyclic carbonate (Fig. S9) over various catalysts.



Entry	Catalysts	Additives	Temp. (°C)	Time (h)	Conv. (%) ^a	Select. (%) ^a
1 ^b	POP-TPP	n-Bu ₄ NBr	29	24	52.1	>99.0
2 ^c	Co/POP-TPP	<i>n</i> -Bu ₄ NBr	29	24	95.6	99.0
3 ^c	Co/TPP	<i>n</i> -Bu ₄ NBr	29	24	97.5	99.0
4	Co/POP-TPP	None	29	24	9.7	99.0
5	Co/TPP	None	29	24	18.5	99.0
6	None	<i>n</i> -Bu ₄ NBr	29	24	34.0	99.0
7 ^d	Co/POP-TPP	<i>n</i> -Bu ₄ NBr	29	96	96.1	99.0
8 ^e	Co/POP-TPP	<i>n</i> -Bu ₄ NBr	29	24	88.9	99.0
9 ^f	Zn/POP-TPP	<i>n</i> -Bu ₄ NBr	29	24	93.2	>99.0
10 ^f	Zn/TPP	n-Bu ₄ NBr	29	24	93.5	>99.0
11 ^g	Mg/POP-TPP	<i>n</i> -Bu ₄ NBr	29	24	80.5	>99.0
12 ^g	Mg/TPP	<i>n</i> -Bu ₄ NBr	29	24	99.3	>99.0
13 ^h	Co/POP-TPP	n-Bu ₄ NBr	29	24	93.6	99.0

^a Determined by GC analysis.

^b 48 mg of POP-TPP was used.

^c 50 mg of Co/POP-TPP (1.6 mg Co) or 19 mg of Co/TPP (1.6 mg Co) was used.

^d Co/POP-TPP catalyst (12.5 mg, 0.4 mg Co).

^e 50 mg of *n*-Bu₄NBr.

^f 50 mg of Zn/POP-TPP (2.3 mg Zn) or 23.5 mg of Zn/TPP (2.3 mg Zn) was used.

^g 50 mg of Mg/POP-TPP (1.4 mg Mg) or 37.0 mg of Mg/TPP (1.4 mg Mg) was used.

h Recycles for 18 times.



Fig. 5. Conversion (a) and selectivity (b) of the recycling tests in the cycloaddition of epichlorohydrin with CO_2 over the Co/POP-TPP catalyst.

with pore volume of $0.60 \text{ cm}^3/\text{g}$ (Fig. S11). The reduction of the surface area and pore volume might be due to accumulation of the by-products in the pores of the heterogeneous catalyst. These results indicate that the heterogeneous catalyst Co/POP-TPP has excellent recyclability for the cycloaddition, which should be potentially important for industrial applications of this heterogeneous catalyst.

Table 2 presents catalytic data in the cycloaddition of propylene oxide (entry 1 in Table 2, Fig. S12), 1,2-epoxyhexane (entry 2 in Table 2, Fig. S13), allyl glycidyl ether (entry 3 in Table 2, Fig. S14), styrene oxide (entry 4 in Table 2, Fig. S15), and butyl glycidyl ether (entry 5 in Table 2, Fig. S16) with CO₂ over the Co/POP-TPP catalyst. This catalyst is still active for the conversion of these epoxides, but the activities are strongly dependent on their structures. Clearly, size-dependent catalysis is observed when using the substrates with larger dimensions which give rise to lower activities.

 Table 2

 Cycloaddition of CO2 with various substrates over the Co/POP-TPP catalyst.^a

Entry	Epoxide	Product	T (°C)	Time (h)	Conv. (%) ^b	Select. (%) ^b
1	⊳ o	$\langle f^{\circ}$	29	24	95.8	99.0
2	∽∽∽⊂ ⁰		29	24	88.0	99.0
3	O		29	48	85.5	99.0
4	C C C	() - ()	29 (50)	118 (48)	77.9 ^c (74.2) ^c	99.0
5			29 (50)	72 (48)	68.6 (88.8)	99.0

^a Reaction conditions: substrate (12.5 mol), Co/POP-TPP catalyst (50 mg, 1.6 mg Co), n-Bu₄NBr (0.29 g), and 1 atm CO₂.

^b Determined by GC analysis.

^c Determined by liquid NMR.



Fig. 6. The dependences of (a and b) conversion and (c and d) selectivity in the cycloaddition of epichlorohydrin (12.5 mmol) with CO_2 on reaction time over (a and c) the Co/TPP (1.6 mg Co) and (b and d) Co/POP-TPP catalysts (1.6 mg Co) under low CO₂ concentration (1 atm pressure, 15% CO₂ mixed with 85% N₂) at 29 °C with co-catalyst of *n*-Bu₄NBr (50 mg).

3.2.2. Evaluation under Low CO₂ concentration

Because the emission of CO_2 in industrial processes normally has low concentration (below 15%), the investigation on the cycloaddition under relatively low CO_2 concentration should be more significant than that under pure CO_2 .

Fig. 6 shows dependence of the activities on the reaction time in the cycloaddition of epichlorohydrin with CO₂ over the Co/POP-TPP and Co/TPP catalysts under low CO₂ concentration (15% CO₂ + 85% N₂ in volume, 1 atm) at 29 °C. Very interestingly, the activities over the Co/POP-TPP are obviously higher than those over the Co/TPP. For example, when the reaction time reaches to 48 h, the Co/POP-TPP gives the conversion at 45.4% and the selectivity at 88.7%, while the Co/TPP exhibits the conversion at 37.4% and the selectivity at 81.0%. Considering the same catalytically active sites between the Co/POP-TPP and Co/TPP and higher activities over the Co/TPP than those over the Co/POP-TPP in the cycloaddition under pure CO₂, we suggest that higher activities over the Co/POP-TPP than those over the Co/TPP under low CO₂ concentration (15% in volume) are reasonably attributed to the contribution of the porosity in the Co/POP-TPP. Possibly, the presence of sample porosity is favorable for enrichment of CO₂ to the nearby the active sites in the Co/POP-TPP, effectively improving the reaction rate. Similar phenomena have been reported previously [55,61-63]. In addition, this suggestion is also strongly supported by the CO₂ adsorption on the Co/POP-TPP and Co/TPP, as evidenced in Fig. 4. For example, under relative pressure of CO₂ at 0.15, the porous Co/POP-TPP has adsorption capacity of CO_2 at 8 cm³/g (16 mg/g), while the nonporous Co/TPP almost does not adsorb CO₂. Obviously, higher activities over the heterogeneous catalyst of Co/POP-TPP than those over the homogeneous catalyst of Co/TPP under low CO₂ concentration are potentially important for applications of CO₂ emission in industrial processes.

4. Conclusion

In summary, a porphyrin based porous organic polymer (POP-TPP) is successfully synthesized from polymerization of vinyl-functionalized porphyrin monomer. After metal coordination, the catalysts (Co/POP-TPP, Zn/POP-TPP, and Mg/POP-TPP) with *n*-Bu₄NBr as a nucleophilic additive are really active in heterogeneous cycloaddition of epoxides with CO₂ to cyclic carbonates under ambient conditions. Particularly, the heterogeneous Co/POP-TPP catalyst can recycle for 18 times and the activity was remained. When this reaction is performed under relatively

low CO₂ concentration (15% CO₂ + 85% N₂ in volume, similar to the emission of CO₂ in industrial processes), the heterogeneous catalyst of Co/POP-TPP shows even better activity than the homogeneous catalyst of Co/TPP. The high activity and recyclability of the Co/POP-TPP in the cycloaddition reaction of epoxides and CO₂ to form cyclic carbonate under very mild reaction condition might offer an opportunity to design an efficient heterogeneous catalyst for chemical fixation of CO₂ in the future.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.03.005.

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