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Article

Combination of binary active sites into heterogeneous porous polymer catalysts for efficient transformation of CO₂ under mild conditions

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ABSTRACT

The transformation of CO₂ into cyclic carbonates via atom-economical cycloadditions with epoxides has recently attracted tremendous attention. On one hand, though many heterogeneous catalysts have been developed for this reaction, they typically suffer from disadvantages such as the need for severe reaction conditions, catalyst loss, and large amounts of soluble co-catalysts. On the other hand, the development of heterogeneous catalysts featuring multiple and cooperative active sites, remains challenging and desirable. In this study, we prepared a series of porous organic catalysts (POP-PBnCl-TPPMg-x) via the copolymerization metal-porphyrin compounds and phosphonium salt monomers in various ratios. The resulting materials contain both Lewis-acidic and Lewis-basic active sites. The molecular-level combination of these sites in the same polymer allows these active sites to work synergistically, giving rise to excellent performance in the cycloaddition reaction of CO₂ with epoxides, under mild conditions (40 °C and 1 atm CO₂) in the absence of soluble co-catalysts. POP-PBnCl-TPPMg-12 can also efficiently fixate CO₂ under low-CO₂-concentration (15% v/v N₂) conditions representative of typical CO₂ compositions in industrial exhaust gases. More importantly, this catalyst shows excellent recyclability and can easily be separated and reused at least five times while maintaining its activity. In view of their heterogeneous nature and excellent catalytic performance, the obtained catalysts are promising candidates for the transformation of industrially generated CO₂ into high value-added chemicals.

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1. Introduction

Owing to the high dependence of modern society on fossil fuels and the resulting excessive carbon dioxide (CO₂) emissions, the concentration of CO₂ in the atmosphere has increased from 280 ppm to around 400 ppm; this increase has led to global warming and other climate issues [1,2]. On one hand, the development of methods to effectively reduce the CO₂ concentration in the atmosphere has become one of the most urgent research fields in recent years. On the other hand, CO₂ represents a non-toxic, inexpensive, and abundant C₁ resource [3,4] that can be transformed into various high-value-added industrial products such as formic acid, carbon monoxide, and cyclic carbonates [5–9]. Among these, cyclic carbonates, which can be facilely synthesized from CO₂ and epoxides, via green and atom-economic (100%) cycloaddition reactions, have been widely utilized as aprotic polar solvents and petroleum additives [10–13].

A number of homogeneous [14–20] and heterogeneous [21–31] catalysts have been developed for the cycloaddition of CO₂ with epoxides. Among them, binary catalytic systems, composed of metal complexes as the catalyst and ammonium salts as the co-catalyst, were found to greatly promote the transformation of CO₂ under ambient conditions by the synergy of the Lewis-acidic active sites and Lewis-basic nucleophilic centers [32]. Based on this synergistic mechanism, a series of binary homogeneous catalysts, including metal salens [13] and metalloporphyrins [20], and heterogeneous catalysts such as metal-organic frameworks (MOFs) [29] and conjugated microporous polymers [31] have been developed for the efficient transformation of CO₂ into cyclic carbonates under mild conditions, assisted by a soluble co-catalyst. Although the stability and reusability of heterogeneous catalysts are superior to those of homogeneous catalysts, the use of soluble co-catalysts in heterogeneous systems complicates catalyst separation and product purification, which are major considerations in practical applications. Therefore, the design and preparation of efficient heterogeneous catalysts for the cycloaddition of CO₂ with epoxides under mild conditions and in the absence of soluble co-catalysts, would be highly desirable.

Numerous studies have focused on the preparation of bifunctional heterogeneous catalysts for the efficient transformation of CO₂ into cyclic carbonates [33–35]. For example, Cao and co-workers [36] successfully prepared a bifunctional imidazolium-decorated Zr-MOF (Imeim-UiO-66), for the cycloaddition of CO₂ with epoxides, through a post-synthetic modification method. Shi et al. [37] synthesized a series of di-ionic materials (POF-Zn²⁺-Cl⁻, POF-Zn²⁺-Br⁻, and POF-Zn²⁺-I⁻) via a feasible ion exchange strategy; these materials could act as multifunctional heterogeneous catalysts for the coupling reaction of CO₂ with epoxides. Yang et al. [38] also prepared a bifunctional heterogeneous catalyst for the synthesis of cyclic carbonates from CO₂ and epoxides using cationic Zn-porphyrin-polymer-coated carbon nanotube materials. However, despite the inspiring progress in this field, the relatively harsh reaction conditions required and the low activity of these catalysts, due to the spatial separation and relatively low

molar ratio of the Lewis acidic sites and nucleophilic ionic units in the framework, still limits their practical application. The construction of heterogeneous catalytic systems, containing multifunctional active sites in the proper proportions and with the appropriate molecular-level spacing for the efficient cycloaddition of CO₂ with epoxides under mild, low CO₂-pressure conditions, remains a challenge [39,40].

Porous organic polymers (POPs) [41–51] with large surface areas, high physicochemical stability, hierarchical porosity, and easily tunable compositions are emerging as promising functional materials for various applications, including gas adsorption and catalysis. Recently, Xiao et al. [52–54] developed a facile strategy to construct POPs via the radical polymerization of the corresponding vinyl-functionalized monomers. For example, through the polymerization of vinyl-functionalized phosphine-based monomers, a series of insoluble POPs, with high ligand concentrations and outstanding swelling properties, were synthesized. These materials could serve as excellent heterogeneous catalysts for hydroformylation.

Inspired by the synthesis of POPs, herein, we successfully prepared a binary heterogeneous porous catalyst with metal-porphyrin and phosphonium sites via the facile copolymerization of vinyl-functionalized quaternary phosphonium and metalloporphyrin monomers. Interestingly, the resulting insoluble catalyst efficiently converted CO₂ into cyclic carbonates under very mild conditions (40 °C, 1 atm) in the absence of soluble co-catalysts. These features are beneficial for the elimination of CO₂ through chemical fixation.

2. Experimental

2.1. Materials

The solvents, tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF), were distilled over LiAlH₄ and CaH₂, respectively. Pyrrole and 4-bromostyrene were purchased from Aladdin (Shanghai) and Meryer Chemical Technology (Shanghai) and were distilled before use. Other commercially available reagents and solvents, including *N*-methyl-2-pyrrolidone (NMP), azobisisobutyronitrile (AIBN), benzyl chloride, benzyl bromide, butyl bromide, epichlorohydrin, propylene oxide, 1,2-epoxyhexane, and styrene oxide, were purchased in their high purity form and used without further purification.

2.2. Catalyst preparation

The vinyl-functionalized porphyrin monomer (v-TPP) and the corresponding metallomonomer (v-TPPM) were synthesized according to a previous report [55]; the synthetic procedures are presented in the experimental section of the supporting information. The vinyl-functionalized quaternary phosphonium salts (v-PBnCl and v-PPrBr) and the homogeneous phosphonium salt (PBnCl) were also synthesized according to a procedure from the literature with a few modifications, as shown in the supporting information [56].

2.3. Synthesis of binary porous organic polymers (POP-PBnCl-TPPMg-*x*)

Binary porous polymers were synthesized via the solvothermal copolymerization of a vinyl-functionalized quaternary phosphonium salt with a *v*-TPPMg monomer; the molar ratio of phosphonium to porphyrin was designated as *x*. In a typical run, *v*-TPPMg (92.6 mg, mmol) and benzyl tris(4-vinylphenyl) phosphonium chloride (*v*-PBnCl, 0.7 g, mmol) were dissolved in DMF (10 mL), followed by the addition of AIBN (50 mg, mmol). After treatment in an autoclave at 100 °C for 24 h, the reaction mixture was washed with DMF and purified using Soxhlet extraction (CH₂Cl₂, 72 h) to give the dark-blue product, which was denoted as PIP-BnCl-TPPMg-12 (0.75 g, 94.9% yield). The catalysts POP-PBnCl-TPPMg-4, POP-PBnCl-TPPMg-10, POP-PBnCl-TPPMg-20, POP-PPrBr-TPPMg-12, POP-PBnCl-TPPZn-12, and POP-PBnCl-TPP-12, were prepared similarly, as described in the supporting information.

2.4. Characterization

Nitrogen sorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020M system; the samples were pre-treated under vacuum at 100 °C for 12 h. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. CO₂ sorption isotherms were measured using a Micromeritics ASAP2010 at 0 and 25 °C under 1 atm of CO₂. Before the measurement, the samples were pre-treated in vacuum at 100 °C for 12 h. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo ESCALAB 250 with Al K α irradiation with the X-ray source at $\theta = 90^\circ$, and the binding energies were calibrated using the C 1s peak at 284.9 eV. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet iS10 (Thermo Fisher) IR spectrometer in the range 400–4000 cm^{−1}. For the pyridine-adsorption FTIR test, 50 mg of catalyst was fixed in the sample cell and pretreated at 150 °C for 2 h in vacuum; the temperature of the cell was then reduced to 100 °C and gaseous pyridine was introduced. After 1 h adsorption period, the sample was subjected to a vacuum at 50 °C for 1 h, after which the IR spectra were collected. Thermal gravimetric analysis (TGA) experiments were performed using a SDT Q600 V8.2 Build100 thermogravimetric analyzer under a flow of N₂.

Inductively coupled plasma optical emission spectrometry (ICP-OES) data were collected using a Perkin-Elmer Plasma 40 emission spectrometer. Scanning electron microscopy (SEM) images of the samples were recorded using a Hitachi SU 1510 apparatus. Transmission electron microscopy (TEM) experiments were performed using a JEM-2100F field emission electron microscope (JEOL, Japan) with an acceleration voltage of 110 kV. ¹H Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta = 0$ ppm. ¹³C (100.5 MHz) magic-angle spinning (MAS) NMR spectra were recorded using a Varian Infinity Plus 400 spectrometer equipped with a magic-angle spinning probe in a 4 mm ZrO₂ rotor.

2.5. Catalytic cycloaddition of CO₂ with epoxides

Typically, the cycloaddition reaction was conducted in a Schlenk tube using 10 mmol of the epoxide, and CO₂ was purged with a balloon at 40 °C over the various catalysts for 48 h. The reactants and products were determined using ¹H NMR spectroscopy (Bruker Avance-400 spectrometer, 400 MHz). To evaluate the catalysts at low CO₂ concentration, 15% CO₂ mixed with 85% N₂ by volume was used. For the recycling tests, the catalyst was separated by centrifugation, washed with CH₂Cl₂, and dried at 60 °C in vacuum for 6 h. The recycled catalysts were then used in the next run without further treatment.

3. Results and discussion

3.1. Synthesis and characterization

Figure 1(A) shows the solid-state ¹³C NMR spectrum of POP-PBnCl-TPPMg-4, which contained several peaks in the 30–150 ppm range. A comparison of this spectrum with the solution-state ¹³C NMR spectra of *v*-PBnCl and *v*-TPPMg (Figs. S1 and S2) suggested that the new peaks that appeared at 42–50 ppm in POP-PBnCl-TPPMg-4 could be attributed to polymerized vinyl groups, while the solution-state signals at approximately 110 ppm ascribed to the vinyl carbons in *v*-PBnCl and *v*-TPPMg almost disappeared after radical polymerization. These results indicated that most of the vinyl groups were polymerized in the solvothermal process. The

Fig. 1. ¹³C (A) and ³¹P (B) solid state NMR spectra of POP-PBnCl-TPPMg-4.

Scheme 1. Schematic illustration of the synthesis of the POP-PBnCl-TPPMg-*x* catalysts.

peak at approximately 150 ppm was assigned to the porphyrin skeletons, which are also consistent with those of magnesium porphyrin monomers. The peaks at approximately 116 ppm and 130 ppm were assigned to phenyl groups in the porphyrin and phosphonium salt monomers, which were also identical with those of *v*-PBnCl and *v*-TPPMg. Additionally, a sharp peak was observed at approximately 22 ppm in the solid-state ^{31}P NMR spectrum of PIP-BnCl-TPPMg-4 (Fig. 1(B)); this peak was also in good agreement with the phosphonium salt monomer (Fig. S3), confirming the full maintenance of the phosphonium salt units in the polymer after the copolymerization reaction.

Based on the observations that the copolymerization of the binary monomers occurred and that the vinyl groups almost disappeared in the samples, the suggested structure of POP-PBnCl-TPPMg-*x* is shown in Scheme 1. All the obtained samples were insoluble in conventional organic solvents such as DMF, DMSO, CH_2Cl_2 , CHCl_3 , THF, and toluene.

To determine the chemical composition of POP-PBnCl-TPPMg-4, we carried out XPS. The survey spectrum of POP-PBnCl-TPPMg-4 (Fig. S4) clearly shows signals corresponding to C, N, P, Cl, and Mg, indicating the co-existence of

these elements in the sample. The high-resolution spectra of the sample showed an Mg 1s peak at a binding energy of 1302.7 eV (Fig. S5(A)) and Cl 2p peaks at 196.8 and 198.1 eV (Fig. S5(B)), which were highly consistent with those of the metal-porphyrin and phosphonium salt monomers (Fig. S6), providing further evidence that the metal-porphyrin and phosphonium units were maintained in POP-PBnCl-TPPMg-4. Similar XPS results were observed for POP-PBnCl-TPPMg-12 (Figs. S7 and S8). The co-existence of metal-porphyrin sites and phosphonium sites in the heterogeneous catalyst POP-PBnCl-TPPMg-12 was confirmed by the pyridine-IR test (Fig. S9). The metal content in the heterogeneous catalysts was determined using ICP-OES, which determined the Mg content in POP-PBnCl-TPPMg-4 and POP-PBnCl-TPPMg-12 to be 0.78 and 0.32 wt%, respectively; these values were in agreement with the theoretical values of the monomers. The metal contents of the various samples are presented in Table S1.

Figure 2(A) shows the N_2 sorption isotherms of POP-PBnCl-TPPMg-4, which exhibited typical type I and type IV curves. The sharp increase in the isotherm at relative pressures (P/P_0) below 0.1 was due to the filling of the micropores, while the apparent hysteresis loop at relative pressures (P/P_0) higher than 0.40 resulted from the contribution of mesoporosity. Correspondingly, the pore size of POP-PBnCl-TPPMg-4 was mainly distributed between 0.7 and 9.3 nm based on calculations using the nonlocal density functional theory method (Fig. 2(B)). The BET surface area and pore volume of POP-PBnCl-TPPMg-4 were calculated to be $411 \text{ m}^2/\text{g}$ and $0.34 \text{ cm}^3/\text{g}$, respectively. We also obtained N_2 sorption isotherms of the other samples (Fig. S10); the textural parameters of the various samples are presented in Table S1.

Figs. 2(C) and 2(D) show the SEM and TEM images of POP-PBnCl-TPPMg-4, which clearly prove its hierarchical porosity. Similar results were also observed for

Fig. 2. N_2 sorption isotherms (A), pore size distribution (B), SEM image (C), and TEM image (D) of POP-PBnCl-TPPMg-4.

Fig. 3. CO₂ sorption isotherms at different temperatures (A) and the isosteric heat (Q_{st}) of CO₂ adsorption (B) for POP-PBnCl-TPPMg-4.

POP-PBnCl-TPPMg-12 (Fig. S11). The energy-dispersive X-ray (EDX) spectroscopy results confirmed that POP-PBnCl-TPPMg-4 and POP-PBnCl-TPPMg-12 contained C, N, Mg, P, and Cl (Fig. S12). Fig. S13 shows the thermal gravimetric analyses of the various samples. The samples exhibited thermal stability at temperatures of 200 °C and higher, which demonstrated that they fully met the requirements for application as heterogeneous catalysts in the cycloaddition of CO₂ with epoxides under mild conditions.

Figure 3(A) shows the CO₂ sorption isotherms of the POP-PBnCl-TPPMg-4 measured at 0 and 25 °C under 1 atm of CO₂. Notably, the CO₂ adsorption capacity of POP-PBnCl-TPPMg-4 was 28 cm³/g at 0 °C but decreased to 19 cm³/g at 25 °C. These values are comparable to those of previously reported porous materials (Table S2). The isosteric heat of CO₂ adsorption (Q_{st}) of POP-PBnCl-TPPMg-4 was estimated to be 28.8 kJ/mol (Fig. 3(B)), which is lower than those of previously reported porous organic polymers (Table S2). Similarly, the isosteric heat (Q_{st}) of POP-PBnCl-TPPMg-12 was calculated to be 31.8 kJ/mol from the corresponding CO₂ sorption isotherm (Fig. S14 and Table S2); this value was slightly higher than that of POP-PBnCl-TPPMg-4. Obviously, these relative high adsorption capacities and low Q_{st} values were favorable for the accumulation and reactivity of CO₂ in the porous materials.

3.2. Catalytic evaluation

Table 1 presents the performance of the various samples as heterogeneous catalysts in the cycloaddition of CO₂ with epichlorohydrin in the absence of a soluble co-catalyst. Notably, POP-PBnCl-TPPMg-4 exhibited a conversion of 52.4% with a selectivity of 99.0% (Table 1, entry 1) under mild conditions (40 °C and 1 atm of CO₂), while POP-PBnCl-TPPMg-12 had higher activity (89.3%) and similar selectivity (94.3%, Table 1, entry 2). These results suggest that the enhancement of phosphonium salt units in the catalyst enhanced its catalytic performance. However, a dual homogeneous catalyst system (PBnCl+TPPMg-12, where PBnCl is the Lewis base and TPPMg is the Lewis acid center) with the same phosphonium (PBnCl)/metal ratio as POP-PBnCl-TPPMg-12 had better activity (98.0%) and selectivity (99.0%) in 36 h at 40 °C (Table 1, entry 3).

To understand the differences between the homogeneous and heterogeneous catalysts, catalytic tests were performed using the catalysts POP-PBnCl, POP-TPPMg, and POP-PBnCl+POP-TPPMg-12. The results showed that POP-PBnCl (20.3% conversion, Table 1, Entry 4), POP-TPPMg (<1.0% conversion, Table 1, entry 5), and the mixed catalyst system POP-PBnCl+POP-TPPMg-12 (20.8% conversion, Table 1, entry 6) had much lower activity than POP-PBnCl-TPPMg-12 (89.3% conversion) under the same conditions. These results indicated that the catalytic systems obtained from the physical mixture of the monomers and from the copolymerization of the monomers were quite different from each other; the major difference might result from the distance between the PBnCl units and the TPPMg units. In the physical mixture (POP-PBnCl+POP-TPPMg-12), the PBnCl and TPPMg units are separated, making it very difficult for these units to function synergistically. When the PBnCl and TPPMg units are copolymerized at the molecular level in the POP-PBnCl-TPPMg-12,

Table 1

Catalytic performances of the various catalysts in the cycloaddition of CO₂ with epichlorohydrin to form a cyclic carbonate.^a

Entry	Catalyst	Temperature (°C)	Conversion (%)	Selectivity ^b (%)
1	POP-PBnCl-TPPMg-4	40	52.4	99.0
2	POP-PBnCl-TPPMg-12	40	89.3	94.3
3 ^c	PBnCl+TPPMg-12	40	98.0	99.0
4	POP-PBnCl	40	20.3	99.0
5	POP-TPPMg	40	< 1.0	99.0
6	POP-PBnCl+POP-TPPMg-12	40	20.8	99.0
7 ^d	POP-PBnCl-TPP-12	40	24.2	99.0
8	POP-PBnCl-TPPMg-12	50	> 99.0	96.2
9	POP-PBnCl-TPPMg-12	30	54.3	99.0
10	POP-PBnCl-TPPMg-10	40	81.3	99.0
11	POP-PBnCl-TPPMg-20	40	99.0	99.0
12	POP-PBnCl-TPPZn-12	40	82.0	99.0
13	POP-PPrBr-TPPMg-12	40	91.7	99.0

^a Conditions: Epichlorohydrin (925 mg, 10 mmol) was used as the substrate with 0.05 mol% of the catalyst (based on the metal species) under 1 atm of CO₂ (a balloon) for 48 h.

^b Determined by solution-state NMR.

^c Molar ratio of PBnCl and TPPMg of 12 and reaction time of 36 h.

^d The amount of POP-PBnCl-TPP-12 used was the same as for the other catalysts.

good synergy of the PBnCl and TPPMg units can be achieved in the cycloaddition. When the dual homogeneous catalyst system (PBnCl+TPPMg-12) was employed, the PBnCl and TPPMg units could come into close proximity with one another, providing perfect synergy between the units and maximizing the catalytic activity. This suggests that the design of highly efficient heterogeneous catalysts for the cycloaddition of CO₂ should combine metal-porphyrin and phosphonium salt units at the molecular level and that these units should be positioned as close to one another as possible. One way to achieve such a design is to copolymerize the two active site monomers in a porous polymer.

To increase the synergy between the PBnCl and TPPMg units, more PBnCl units were introduced to give POP-PBnCl-TPPMg-20. Catalytic tests showed that POP-PBnCl-TPPMg-20 achieved 99.0% conversion with 99.0% product selectivity in the cycloaddition of CO₂ with epichlorohydrin; these results were comparable to those of the homogeneous catalyst PBnCl+TPPMg-12. In contrast, when the number of PBnCl units was reduced, the activity of the resulting catalyst POP-PBnCl-TPPMg-10 was lower than that of POP-PBnCl-TPPMg-12. These results indicated that a suitable ratio of PBnCl and TPPMg units in the catalysts is also important for the catalytic cycloaddition of CO₂.

It is worth mentioning that the metal species in the catalyst is necessary for its activity. If the metal species is less in the catalyst, low conversion was observed (POP-PBnCl-TPP-12, 24.2% conversion, Table 1, entry 7), which demonstrated the importance of the metal-porphyrin as the Lewis acidic center in the heterogeneous catalyst.

Furthermore, the catalytic activity of POP-PBnCl-TPPMg-12 was sensitive to the reaction temperature. When the temperature was increased to 50 °C (Table 1, entry 8), a conversion of higher than 99.0% with a selectivity of 96.2% was achieved. When the temperature was reduced to 30 °C, the catalyst showed a conversion of 54.3% with a selectivity of 99.0% (Table 1, entry 9).

Moreover, we can easily tune the monomers of the metal centers and the phosphonium salts to prepare various heterogeneous catalysts using this copolymerization process. For example, using a vinyl-functionalized Zn-porphyrin monomer as the Lewis acidic center, we obtained the Zn-based heterogeneous catalyst POP-PBnCl-TPPZn-12, which also exhibited promising catalytic performance (82.0% conversion and 99.0% selectivity, Table 1, entry 11). Using propyl-tris(4-vinylphenyl) phosphonium bromide (v-PPrBr), we successfully prepared the catalyst POP-PPrBr-TPPMg-12, which was very active for the cycloaddition of CO₂ (91.0% conversion and 99.0% selectivity, Table 1, entry 12).

The concentration of CO₂ in practical applications is always low; industrial exhaust gases typically contain 7%–15% CO₂ by volume. Therefore, the catalytic performance of the heterogeneous catalysts at low CO₂ concentration in the absence of a soluble co-catalyst was an important parameter. As shown in Table S3, after a reaction time of 96 h, the heterogeneous catalyst POP-PBnCl-TPPMg-12 reached 77.5% conversion with 52.3% selectivity (Table S3, entry 2), while the homogeneous catalyst system PBnCl+TPPMg-12 achieved a conversion of

39.5% with a selectivity of 99.0% (Table S3, entry 6). Solution-state NMR revealed that the dominant by-products were oligomers formed by the oligomerization of epichlorohydrin, which could be catalyzed by the metalloporphyrin [57]. After 96 h of reaction (Table S3, entries 1 and 2), the selectivity toward the by-products was approximately 47.7%. Since relatively little by-product was formed under the pure CO₂ conditions (5.7% selectivity), we surmised that these side reactions might be influenced by the reaction conditions. To overcome this issue, we added a suitable solvent to suppress these side reactions. As expected, after the addition of 1 mL of CH₃CN, the conversion of the heterogeneous catalyst POP-PBnCl-TPPMg-12 improved to 95.1% with a selectivity of 73.8%, as shown in Fig. 4. The heterogeneous nature and good performance of POP-PBnCl-TPPMg-12 may be important, for the cycloaddition of epoxides with industrial exhausts containing diluted CO₂, in the future.

To ascertain the versatility of the heterogeneous catalysts, we examined the performance of POP-PBnCl-TPPMg-12 in the cycloaddition of CO₂ with various epoxides under the optimized conditions. As presented in Table 2, high catalytic activity was observed for butylene oxide, with a conversion of 80.6% and a selectivity of 99.0% at 40 °C for 48 h (Table 2, entry 1). However, a dramatic decrease in conversion was observed when the molecular size of the substrate was increased; the conversion decreased to 47.8% for 1,2-epoxyhexane at 40 °C over a 48 h duration; the selectivity was 99.0%. When more sterically-hindered substrates were employed, such as allyl glycidyl ether (Table 2, entry 3), styrene oxide (Table 2, entry 4), butyl glycidyl ether (Table 2, entry 5), and glycidyl phenyl ether (Table 2, entry 6), higher reaction temperatures and longer reaction times were helpful for enhancing the catalytic activity and selectivity of the cycloaddition of CO₂.

The reusability and stability of heterogeneous catalysts are very important in practical applications. As shown in Fig. 5, the catalyst POP-PBnCl-TPPMg-12 could be reused five times without any loss of activity, indicating the high durability of this heterogeneous catalyst. The BET surface area of the reused

Fig. 4. Catalytic performance of the heterogeneous catalyst POP-PBnCl-TPPMg-12 (blue line) and the homogeneous catalyst PBnCl+TPPMg-12 (red line) in the cycloaddition of CO₂ with epoxides under a low CO₂ concentration (15% CO₂ and 85% N₂, v/v). Note: For the heterogeneous catalyst, 1 mL of CH₃CN was used as the solvent, while the homogeneous catalysis was performed in solvent-free conditions. The solid and dotted lines represent the conversion and selectivity, respectively.

Table 2Cycloaddition of CO₂ with various substrates over the catalyst POP-PBnCl-TPPMg-12.^a

Entry	Epoxide	Product	T (°C)	Time (h)	Conversion ^b (%)	Selectivity ^b (%)
1			40	48	80.6	99.0
2			40	48	47.8	99.0
3			80	48	90.1	99.0
4			80	48	74.6	99.0
5			80	72	57.8	99.0
6			80	72	28.3	99.0

^a Reaction conditions: substrate (10 mol), POP-PBnCl-TPPMg-12 catalyst (31.7 mg, 0.05 mol% based on the metal species), 1 atm CO₂.^b Determined by solution-state NMR.

PIP-PBnCl-TPPMg-12 calculated from its N₂ sorption isotherm was 433 m²/g, and its pore volume was 0.32 cm³/g (Fig. S15 and Table S1); these values indicated that the porous structure of the catalyst was fully retained after being recycled five times. The FTIR spectrum of PIP-PBnCl-TPPMg-12-R5 was almost the same as that of fresh PIP-PBnCl-TPPMg-12 (Fig. S16). The XPS spectrum of PIP-PBnCl-TPPMg-12-R5 showed an Mg 1s peak with a binding energy of 1303.6 eV and Cl 2p peaks at 196.4 and 198.0 eV; this data was also in good agreement with that of fresh PIP-PBnCl-TPPMg-12 (Fig. S17). The Mg content of PIP-PBnCl-TPPMg-12-R5 measured using ICP was about 0.30 wt%, which was almost the same as that of the fresh catalyst. These results further demonstrated the robustness and stability of the heterogeneous catalyst PIP-PBnCl-TPPMg-12.

4. Conclusions

In conclusion, we have constructed a heterogeneous porous catalyst with binary active sites via the facile copolymerization of vinyl-functionalized metal porphyrin and phosphonium salt monomers. Due to the combination of Lewis acidic sites and Lewis basic sites at the molecular level in the porous organic polymers, the resulting catalysts showed excellent catalytic activity and selectivity in the cycloaddition of CO₂ with epoxides under mild conditions in the absence of soluble

co-catalysts. In particular, the heterogeneous catalyst POP-PBnCl-TPPMg-12 exhibited much better performance than the corresponding homogeneous catalyst system PBnCl+TPPMg-12 at low CO₂ concentration (15 vol% N₂). POP-PBnCl-TPPMg-12 did not exhibit any loss of activity or selectivity after being recycled five times. The combination of the heterogeneity and high activity of POP-PBnCl-TPPMg-12 is potentially important for the cycloaddition of CO₂ with epoxides in the future.

References

- [1] C. Mandil, Tracking industrial energy efficiency and CO₂ emissions, IEA Publications, Paris, France, **2007**.
- [2] M. Pera-Titus, *Chem. Rev.*, **2014**, 114, 1413–1492.
- [3] H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.*, **2001**, 101, 953–996.
- [4] T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.*, **2007**, 107, 2365–2387.
- [5] Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang, B. Han, *Angew. Chem. Int. Ed.*, **2008**, 47, 1127–1129.
- [6] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, *J. Am. Chem. Soc.*, **2005**, 127, 13118–13119.
- [7] Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, *Angew. Chem. Int. Ed.*, **2012**, 51, 3364–3367.
- [8] S. N. Riduan, Y. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.*, **2009**, 48, 3322–3325.
- [9] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.*, **2015**, 6, 5933.
- [10] B. Schöffner, F. Schöffner, S. P. Verevkin, A. Börner, *Chem. Rev.*, **2010**, 110, 4554–4581.
- [11] X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.*, **2012**, 41, 1462–1484.
- [12] J. Sun, S.-I. Fujita, M. Arai, *J. Organomet. Chem.*, **2005**, 690, 3490–3497.
- [13] Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.*, **2017**, 19, 3707–3728.
- [14] R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.*, **2001**, 123,

Fig. 5. Recycling test of POP-PBnCl-TPPMg-12 in the cycloaddition of CO₂ with epoxides.

Graphical Abstract

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Combination of binary active sites into heterogeneous porous polymer catalysts for efficient transformation of CO₂ under mild conditions

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Heterogeneous catalysts integrating binary active sites are constructed via a facile radical copolymerization method. The catalysts can simultaneously capture and convert CO₂ into value-added products under very mild and environmentally friendly conditions.

- 11498–11499.
- [15] X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo, H. Wang, *J. Catal.*, **2004**, 227, 537–541.
- [16] J. Sun, S.-i. Fujita, F. Zhao, M. Arai, *Green Chem.*, **2004**, 6, 613–616.
- [17] Z.-Z. Yang, L.-N. He, C.-X. Miao, S. Chan, *Adv. Synth. Catal.*, **2010**, 352, 2233–2240.
- [18] J. Sun, L. Han, W. Cheng, J. Wang, X. Zhang, S. Zhang, *ChemSusChem*, **2011**, 4, 502–507.
- [19] T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda, J.-Y. Hasegawa, *J. Am. Chem. Soc.*, **2014**, 136, 15270–15279.
- [20] Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, *Green Chem.*, **2015**, 17, 2853–2858.
- [21] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.*, **1997**, 1129–1130.
- [22] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.*, **1999**, 121, 4526–4527.
- [23] H. Yasuda, L.-N. He, T. Sakakura, *J. Catal.*, **2002**, 209, 547–550.
- [24] D. Liu, G. Li, J. Liu, Y. Wei, H. Guo, *ACS Appl. Mater. Interfaces*, **2018**, 10, 22119–22129.
- [25] Q. Su, Y. Qi, X. Yao, W. Cheng, L. Dong, S. Chen, S. Zhang, *Green Chem.*, **2018**, 20, 3232–3241.
- [26] M. Zhang, B. Chu, G. Li, J. Xiao, H. Zhang, Y. Peng, B. Li, P. Xie, M. Fan, L. Dong, *Microporous Mesoporous Mater.*, **2019**, 274, 363–372.
- [27] G. Zhang, H. Yang, H. Fei, *ACS Catal.*, **2018**, 8, 2519–2525.
- [28] B. Aguila, Q. Sun, X. Wang, E. O'Rourke, A. M. Al-Enizi, A. Nafady, S. Ma, *Angew. Chem. Int. Ed.*, **2018**, 57, 10107–10111.
- [29] Z. Zhou, C. He, J. Xiu, L. Yang, C. Duan, *J. Am. Chem. Soc.*, **2015**, 137, 15066–15069.
- [30] C. Chen, J. Zhang, G. Li, P. Shen, H. Jin, N. Zhang, *Dalton Trans.*, **2014**, 43, 13965–13971.
- [31] Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat. Commun.*, **2013**, 4, 1960.
- [32] M. North, R. Pasquale, *Angew. Chem. Int. Ed.*, **2009**, 48, 2946–2948.
- [33] Y. Leng, D. Lu, C. Zhang, P. Jiang, W. Zhang, J. Wang, *Chem. Eur. J.*, **2016**, 22, 8368–8375.
- [34] R. Guan, X. Zhang, F. Chang, N. Xue, H. Yang, *Chin. J. Catal.*, **2019**, 40, 1874–1883.
- [35] J. Chen, M. Zhong, L. Tao, L. Liu, S. Jayakumar, C. Li, H. Li, Q. Yang, *Green Chem.*, **2018**, 20, 903–911.
- [36] J. Liang, R.-P. Chen, X.-Y. Wang, T.-T. Liu, X.-S. Wang, Y.-B. Huang, R. Cao, *Chem. Sci.*, **2017**, 8, 1570–1575.
- [37] D. Ma, J. Li, K. Liu, B. Li, C. Li, Z. Shi, *Green Chem.*, **2018**, 20, 5285–5291.
- [38] S. Jayakumar, H. Li, J. Chen, Q. Yang, *ACS Appl. Mater. Interfaces*, **2018**, 10, 2546–2555.
- [39] R.-C. Luo, Y.-J. Chen, Q. He, X.-W. Lin, Q.-H. Xu, X.-H. He, W.-Y. Zhang, X.-T. Zhou, H.-B. Ji, *ChemSusChem*, **2017**, 10, 1526–1533.
- [40] Q. Sun, B. Aguila, J. Perman, N. Nguyen, S. Ma, *J. Am. Chem. Soc.*, **2016**, 138, 15790–15796.
- [41] Y. Zeng, R. Zou, Y. Zhao, *Adv. Mater.*, **2016**, 28, 2855–2873.
- [42] B. Li, Y. Zhang, D. Ma, Z. Shi, S. Ma, *Nat. Commun.*, **2014**, 5, 5537.
- [43] A. Alsaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, *Nature*, **2016**, 529, 190–194.
- [44] Y. Yue, R. T. Mayes, J. Kim, P. F. Fulvio, X.-G. Sun, C. Tsouris, J. Chen, S. Brown, S. Dai, *Angew. Chem. Int. Ed.*, **2013**, 52, 13458–13462.
- [45] Y. Du, H. Yang, J. M. Whiteley, S. Wan, Y. Jin, S.-H. Lee, W. Zhang, *Angew. Chem. Int. Ed.*, **2016**, 55, 1737–1741.
- [46] P. Zhang, H. Li, G. M. Veith, S. Dai, *Adv. Mater.*, **2015**, 27, 234–239.
- [47] Y. Zhang, B. Li, S. Ma, *Chem. Commun.*, **2014**, 50, 8507–8510.
- [48] L.-B. Sun, X.-Q. Liu, H.-C. Zhou, *Chem. Soc. Rev.*, **2015**, 44, 5092–5147.
- [49] S. Fischer, J. Schmidt, P. Strauch, A. Thomas, *Angew. Chem. Int. Ed.*, **2013**, 52, 12174–12178.
- [50] Y. Zhang, S. N. Riduan, *Chem. Soc. Rev.*, **2012**, 41, 2083–2094.
- [51] R. K. Totten, M. H. Weston, J. K. Park, O. K. Farha, J. T. Hupp, S. T. Nguyen, *ACS Catal.*, **2013**, 3, 1454–1459.
- [52] Q. Sun, Z. Dai, X. Meng, F.-S. Xiao, *Chem. Soc. Rev.*, **2015**, 44, 6018–6034.
- [53] Q. Sun, Z. Dai, X. Meng, L. Wang, F.-S. Xiao, *ACS Catal.*, **2015**, 5, 4556–4567.
- [54] Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F.-S. Xiao, *J. Am. Chem. Soc.*, **2015**, 137, 5204–5209.

- [55] Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng, F.-S. Xiao, *J. Catal.*, **2016**, 338, 202–209. 2017, 10, 1160–1165.
 [57] Y. Tezuka, M. Ishimori, T. Tsumta, *Makromol. Chem.*, **1983**, 184, 895–906.
- [56] Q. Sun, Y. Jin, B. Aguila, X. Meng, S. Ma, F.-S. Xiao, *ChemSusChem*,

双中心多孔聚合物作为多相催化剂实现CO₂在温和条件下高效转化

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摘要: 由于对化石燃料的高度依赖和二氧化碳(CO₂)的过度排放, 大气中CO₂浓度从280 ppm上升到400 ppm左右, 导致全球变暖和其他气候问题。在这种情况下, 如何有效降低空气中的CO₂浓度成为近年来最迫切的研究领域之一。另一方面, 作为一种无毒、廉价且丰富的C1资源, CO₂也可以转化为各种高附加值的工业产品, 如甲酸、一氧化碳、甲烷、甲醇以及碳酸酯等。其中CO₂与环氧化物转化生成环碳酸酯的环加成反应具有良好原子经济性, 在近年来引起了人们的广泛关注。尽管已有多相和多相均相催化剂应用于该反应, 但已有的催化剂特别是多相催化剂往往具有反应条件苛刻、催化剂易损失以及需要可溶性的共催化剂等缺点, 从而限制了它们的进一步实际应用。因此, 发展多相催化剂实现在温和和无共催化剂条件下的CO₂环加成转化仍是一个挑战。

本文通过自由基共聚的方法, 以乙烯基功能化的金属卟啉和季磷盐作为单体制备了一种新型多孔有机聚合物(POP-PBnCl-TPPMg-x)。考虑到金属卟啉和季磷盐常作为CO₂环加成反应中的Lewis酸和Lewis碱活性中心, 我们通过自由基共聚实现了这两种活性中心在分子水平上的结合与协同。所得的催化剂的组成和结构通过固体核磁、X射线光电子能谱、氮气吸附、扫描电子显微镜、透射式电子显微镜等手段进行了表征。值得指出的是, 所得多相催化剂具有良好的CO₂吸附与富集效应, 十分有利于CO₂的催化转化。我们以温和(40 °C和1 atm CO₂)并没有任何无可溶性共催化剂存在条件下, 进行CO₂与环氧化物的环加成作为探针反应, 测试了不同催化剂的催化活性。以催化剂POP-PBnCl-TPPMg-12为例, 其催化活性远超过单组分的POP-PBnCl和POP-TPPMg多相催化剂, 也超过了二者机械混合的POP-PBnCl+POP-TPPMg-12催化剂, 接近均相催化剂PBnCl+TPPMg-12的水平。这表明通过共聚合方法所得到的催化剂可以实现Lewis酸和Lewis碱两种活性中心的分子水平的结合。本文进一步研究了多相催化剂POP-PBnCl-TPPMg-12和均相催化剂PBnCl+TPPMg-12在低浓度CO₂(15% N₂ v/v, 工业废气中CO₂的浓度)条件下的催化活性, 发现在该条件下多相催化剂表现出比均相催化剂更为优异的催化转化性能, 且展现出良好的稳定性和循环使用性能, 在循环使用5次后仍无明显的活性损失。该催化剂所具有的多相特点和优良的催化性能, 因而有望成为实现工业CO₂脱除并转化成高附加值产品的潜在高效催化剂。

关键词: 共聚; 多孔有机聚合物; 双活性中心; CO₂固定; 多相催化

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