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Supporting Information

PolyHIPE-Derived Amine–Porphyrin Monoliths for Mild Cycloaddition of Low-Concentration CO_2

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Materials

Divinylbenzene (DVB, Aladdin, 80% grade) and Styrene (ST, Aladdin, 98%) were washed with sodium hydroxide solution before use. Potassium persulfate ($K_2S_2O_8$, Aladdin, analytical grade), Span-80 (Aladdin, analytical grade) were obtained from Aladdin Corporation of Shanghai and used as received. 5, 10, 15, 20-tetraphenylporphyrin (TPP), tetrahydrofuran, cobalt acetate, hydrazine hydrate (HZ) and epoxides were obtained from Aladdin Corporation. Dichloromethane, anhydrous aluminium chloride, methanol and tetrabutyl ammonium bromide (TBAB) were purchased from Innochem Chemical Reagents Corporation of Beijing.

Synthesis of PolyHIPEs

PolyHIPEs with interconnected macroporous structures were synthesized using styrene and divinylbenzene as comonomers. In a typical procedure, styrene and divinylbenzene were mixed at a volume ratio of 9:1, with a total monomer volume of 10 mL. Then, 3 mL of Span-80 was added as the surfactant. Separately, an aqueous solution was prepared by dissolving $K_2S_2O_8$ (0.3 g) and $CaCl_2$ (1.0 g) in 90 mL of water. This aqueous phase was slowly added dropwise into the vigorously stirred oil phase. After the addition was complete, the high-speed stirring was continued for another 30 minutes to stabilize the high internal phase emulsion (HIPE). The resulting viscous, cream-like emulsion was then transferred into test tubes and polymerized at 60 °C for 40 h. Upon completion of polymerization, the resulting monoliths were washed twice with ethanol and water, respectively, followed by Soxhlet extraction for 40 h. The final product was dried at 50 °C for 45 h to yield PolyHIPEs featuring interconnected macroporous networks.

Synthesis of monolith-TPP

The monolith-TPP was synthesized via a hyper-crosslinking strategy using PolyHIPE as the structural template and tetraphenylporphyrin (TPP) as a comonomer. The detailed preparation procedure is as follows: First, 2.5 g of TPP was accurately weighed and dissolved in 50 mL of dichloromethane (DCM), followed by vigorous stirring for 30 minutes. Subsequently, 1.0 g of dried PolyHIPE was immersed in the resulting solution. After 24 hours of soaking, 5.25 g of anhydrous aluminum chloride ($AlCl_3$) was added to the mixture under an ice bath, with nitrogen atmosphere maintained throughout the reaction. The hyper-crosslinking reaction was conducted under a stepwise temperature elevation protocol: the mixture was sequentially maintained at 0 °C for 4 h, 20 °C for 8 h, 40 °C for 12 h, 60 °C for 12 h, and finally 80 °C for 24 h. Upon completion of the reaction, the resulting monolith-TPP was collected and washed three times with ethanol and deionized water, respectively. The sample was then subjected to Soxhlet extraction with ethanol for 30 h to remove residual reagents and unreacted monomers. Finally, the material was dried in an oven at 60 °C for 48 h, yielding a purple-black monolithic column, designated as monolith-TPP.

Synthesis of monolith-TPP-SO_3H

A total of 200 mg of monolith–TPP was swollen in 40 mL of dichloromethane (DCM) for 24 hours. Subsequently, 300 μL of chlorosulfonic acid was slowly added dropwise under an ice bath, followed by continuous stirring at room temperature for 48 hours. Finally, the resulting monolith-TPP-SO_3H was collected by filtration, thoroughly washed with ethanol and water, and dried under vacuum.

Synthesis of monolith-TPP-SO_3H-Co

50 mg of cobalt acetate was dissolved in 40 mL of tetrahydrofuran (THF), followed by the addition of 100 mg of monolith-TPP-SO_3H. The mixture was allowed to swell for 24 hours. Subsequently, under a nitrogen atmosphere, the reaction mixture was heated to 80 °C and refluxed for 24 hours. The resulting product was then thoroughly washed several times with water and ethanol, followed by Soxhlet extraction with ethanol for 48 hours. Finally, the material was dried under vacuum to yield monolith-TPP-SO_3H-Co.

Synthesis of monolith-TPP-Co-HZ

Typically, 200 mg of monolith-TPP-SO_3H-Co was swollen in 40 mL of dichloromethane (DCM) for 12 h. Subsequently, 300 µL of hydrazine hydrate was added, and the mixture was heated to 50 °C under a nitrogen atmosphere and refluxed for 24 h. The resulting product was then washed three times each with ethanol and water, followed by vacuum drying in an oven at 60 °C for 48 h to obtain monolith-TPP-Co-HZ.

Characterization

The surface area and pore size distribution of the samples were determined using a Micromeritics ASAP 2020M surface area and porosity analyzer. Prior to each adsorption-desorption cycle, samples were degassed under vacuum at 100 °C for 8 h. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere using a PerkinElmer Pyris 1 TGA system, with the temperature ramping from ambient to 800 °C. The morphology of the samples was examined via field emission scanning electron microscopy (FE-SEM) using an FEI Sirion 200 instrument operating at 10 kV. Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were collected on a Bruker Avance II 400 MHz spectrometer equipped with a 2.5 mm MAS dual-resonance probe spinning at 12 kHz. Fourier transform infrared (FT-IR) spectra were recorded at room temperature using a Bruker VERTEX 70 spectrometer with KBr pellet technique. CO_2 adsorption behavior was analyzed using a Micromeritics ASAP 2460 system. X-ray photoelectron spectroscopy (XPS) data were obtained with a Kratos AXIS-ULTRA DLD-600 spectrometer. Elemental composition was quantified using a Vario Micro Cube elemental analyzer. The cobalt content in the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent 730 ICP-OES instrument. The reaction products from catalytic testing were characterized by ^1H NMR spectroscopy in $CDCl_3$, using a Bruker AV600 spectrometer.

General Catalysis Protocol

In a typical cycloaddition reaction, epoxide, monolith-TPP-Co-HZ, and TBAB were introduced into a 20 mL stainless-steel autoclave. To ensure thorough saturation with CO_2, the reactor was purged and refilled with carbon dioxide three times. The reaction was carried out at 25 °C under 0.1 MPa with gentle stirring for the designated time. After completion, the reaction mixture was dispersed in ethyl acetate, and the solid catalyst was removed by filtration. The conversion and selectivity were determined by GC, using 1,3,5-trimethylbenzene as the internal standard. The structure of the cyclic carbonate product was further confirmed by ^1H NMR spectroscopy.

For catalytic conversion under low CO_2 concentrations, a diluted gas mixture (15% CO_2/85% N_2) was introduced by balloon instead of pure CO_2, and the same reaction protocol was followed. To evaluate the recyclability of the catalyst, the recovered monolith-TPP-Co-HZ was thoroughly washed three times with ethyl acetate and ethanol, followed by vacuum drying at room temperature for 48 hours before being reused in subsequent catalytic cycles.

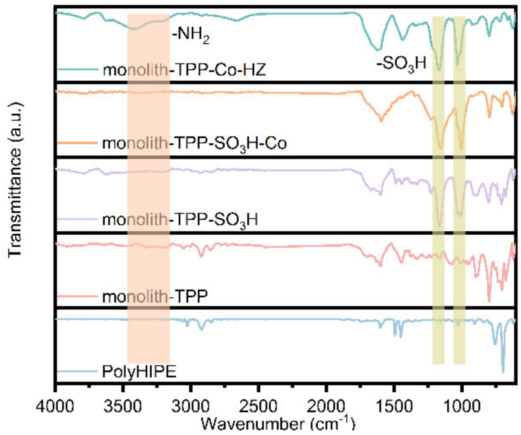

Fig. S1 FT-IR spectra of PolyHIPE, monolith-TPP, monolith-TPP-SO_3H, monolith-TPP-SO_3H-Co and monolith-TPP-Co-HZ.

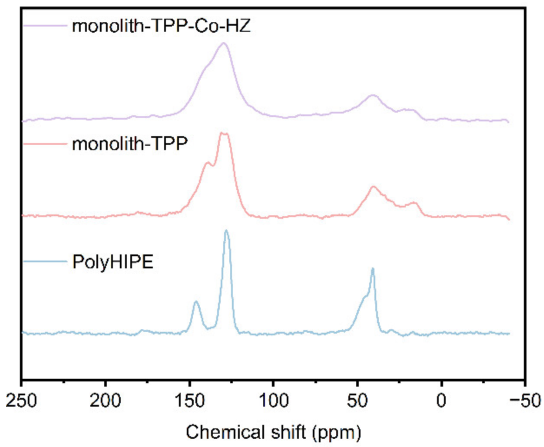

Fig. S2 Solid-state ^{13}C NMR spectra of PolyHIPE, monolith-TPP and monolith-TPP-Co-HZ.

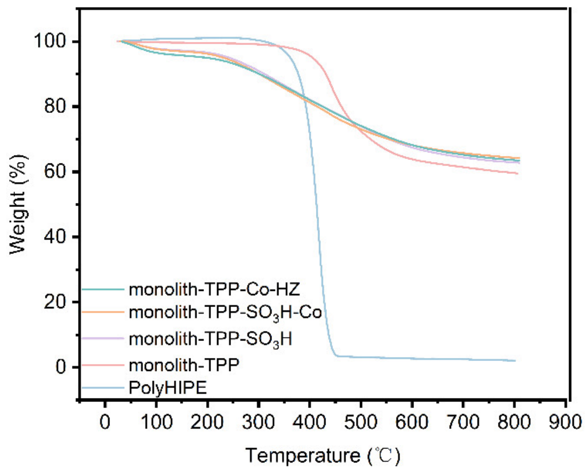

Fig. S3 TGA curves of PolyHIPE, monolith-TPP, monolith-TPP-SO_3H, monolith-TPP-SO_3H-Co and monolith-TPP-Co-HZ recorded under N_2 atmosphere.

Tab. S1 Elemental analysis of samples.

Sample	C %	H %	N %	S %
monolith-TPP	84.1	5.4	4.1	-
monolith-TPP-SO_3H	60.3	4.7	2.3	5.7
monolith-TPP-Co-HZ	57.6	5.8	6.7	4.3

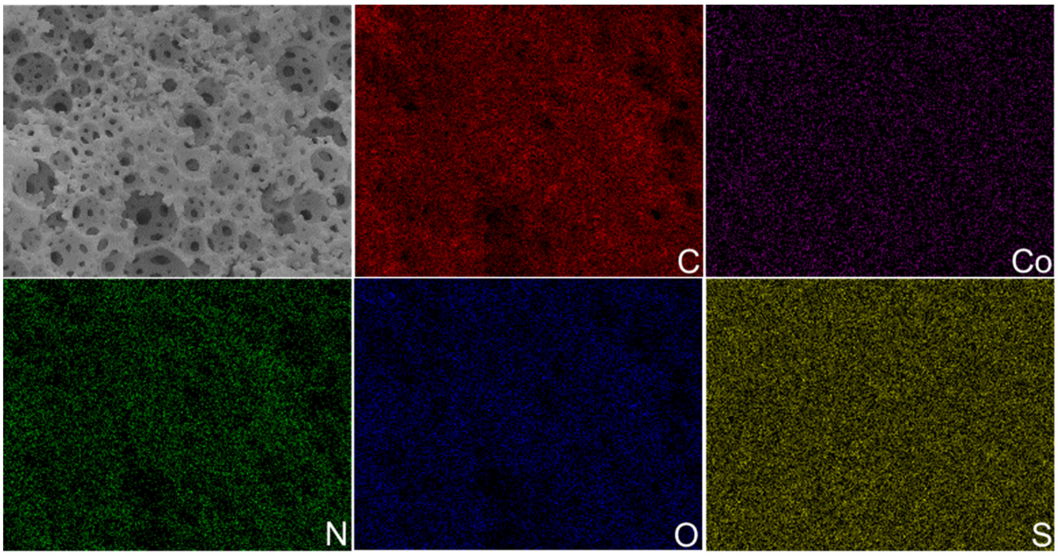

Fig. S4 Element mapping spectra for monolith-TPP-Co-HZ.

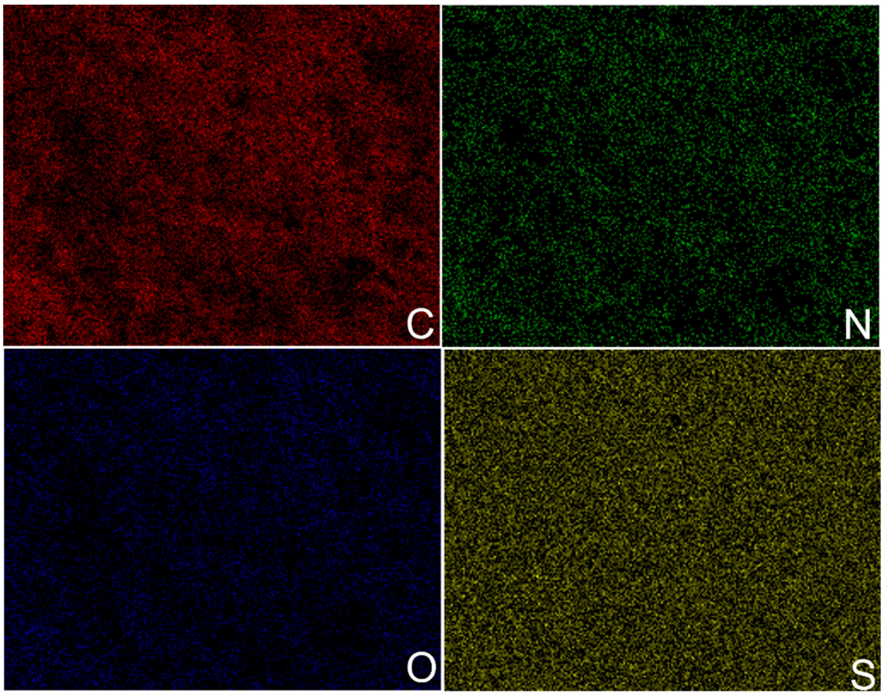

Fig. S5 Element mapping (C, N, O and S) spectra for monolith-TPP-SO_3H.

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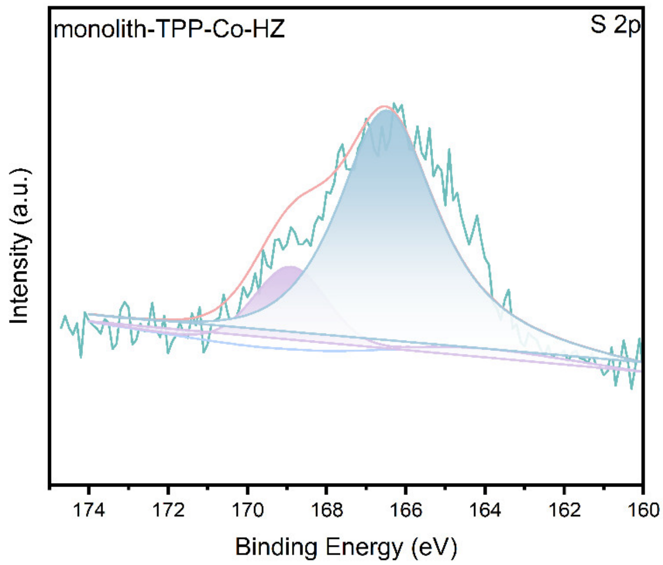

Fig. S6 High-resolution S 2p XPS spectrum of monolith-TPP-Co-HZ.

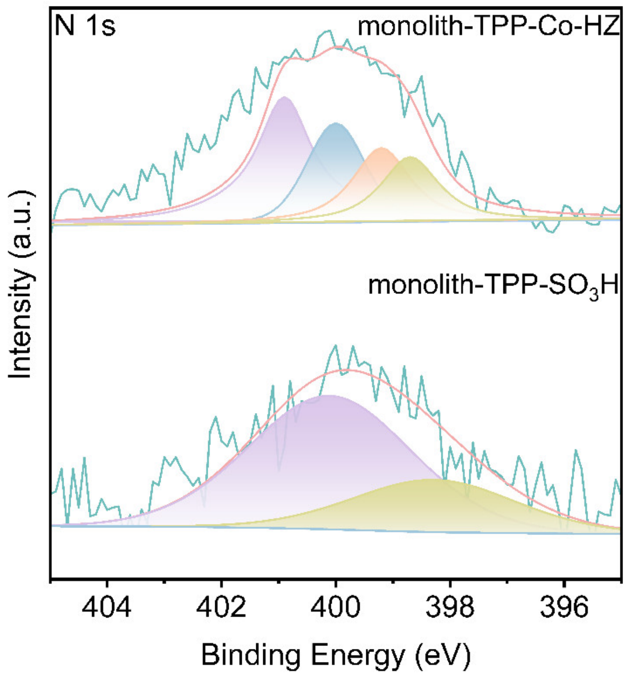

Fig. S7 XPS spectra for N 1s of monolith-TPP-SO_3H and monolith-TPP-Co-HZ.

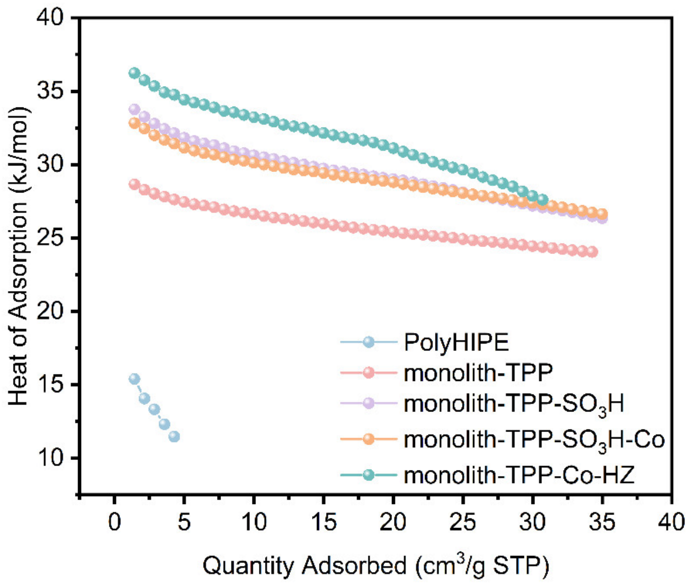

Fig. S8 Isosteric heats of CO_2 adsorption for all samples.

Tab. S2 Porosity properties and gas uptake capacities.

Sample	S_{BET}[a] ($m^2\ g^{-1}$)	S_L[b] ($m^2\ g^{-1}$)	PV[c] ($cm^3\ g^{-1}$)	MPV[d] ($cm^3\ g^{-1}$)	CO_2 uptake[e] (wt%)	CO_2 uptake[f] (wt%)	Qst[g] ($kJ\ mol^{-1}$)	Selectivity[h] (CO_2/N_2)
PolyHIPE	3	1	0	0	1.3	0.9	15.4	-
monolith-TPP	761	1164	0.43	0.18	11.1	6.8	28.6	29
monolith-TPP-SO_3H	462	631	0.23	0.13	10.9	7.3	33.7	35
monolith-TPP-SO_3H-Co	411	555	0.20	0.12	10.5	7.0	32.8	38
monolith-TPP-Co-HZ	255	346	0.11	0.07	9.2	6.1	36.3	55

[a] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using the BET equation. [b] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using the Langmuir equation.[c] Pore volume calculated from the nitrogen isotherm at $P/P_0 = 0.995$ and 77.3 K. [d] Micropore volume calculated from nitrogen isotherm at $P/P_0 = 0.050$. [e] Volumetric CO_2 uptake measured with a Micromeritics ASAP 2020 M analyzer at 1.00 bar and 273 K. [f] Volumetric CO_2 uptake measured with a Micromeritics ASAP 2020 M analyzer at 1.00 bar and 298 K. [g] Isosteric heat of adsorption of polymers determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 273 K and 298 K. [g] Adsorption selectivity of CO_2/N_2 by Henry law at 298 K.

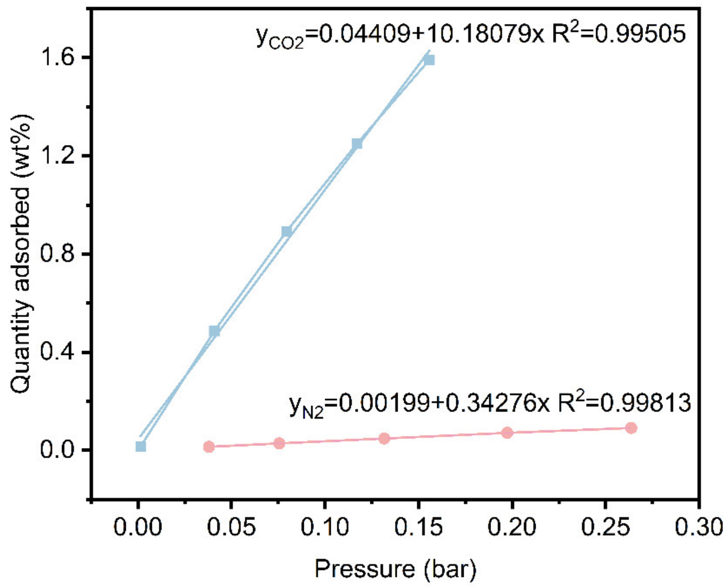

Fig. S9 CO_2/N_2 selectivity of monolith-TPP calculated by Henry's law constants at low pressure and 298 K.

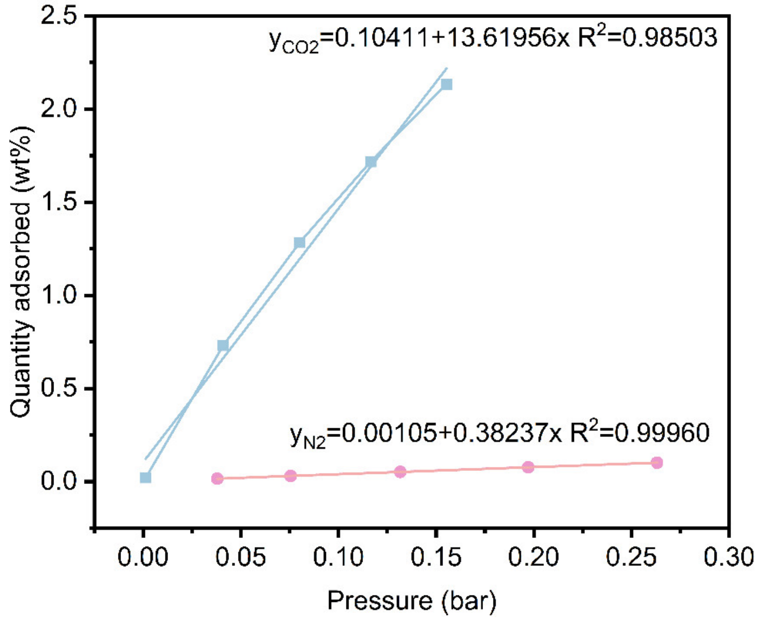

Fig. S10 CO_2/N_2 selectivity of monolith-TPP-SO_3H calculated by Henry's law constants at low pressure and 298 K.

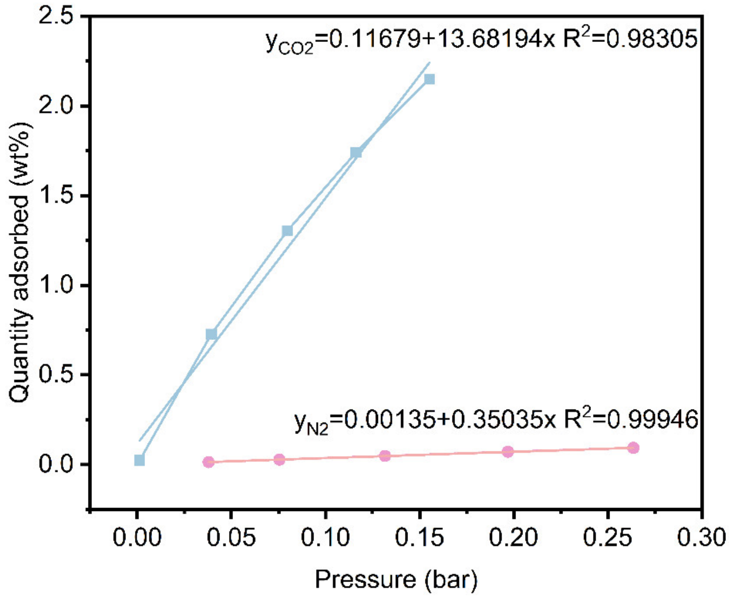

Fig. S11 CO_2/N_2 selectivity of monolith-TPP-SO_3H-Co calculated by Henry's law constants at low pressure and 298 K.

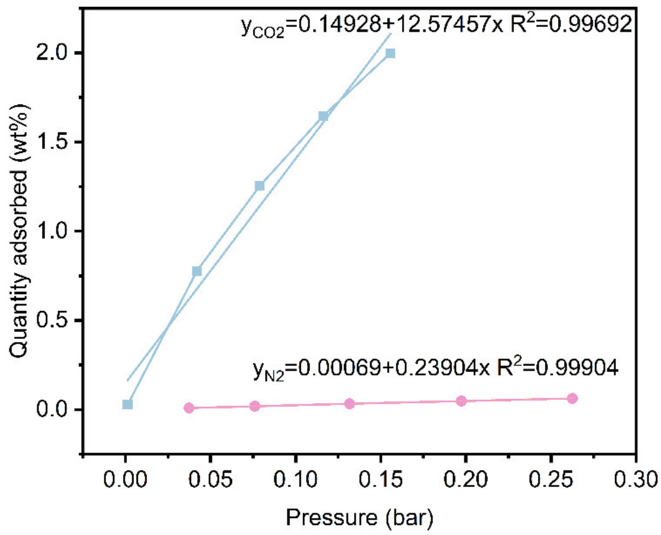

Fig. S12 CO_2/N_2 selectivity of monolith-TPP-Co-HZ calculated by Henry's law constants at low pressure and 298 K.

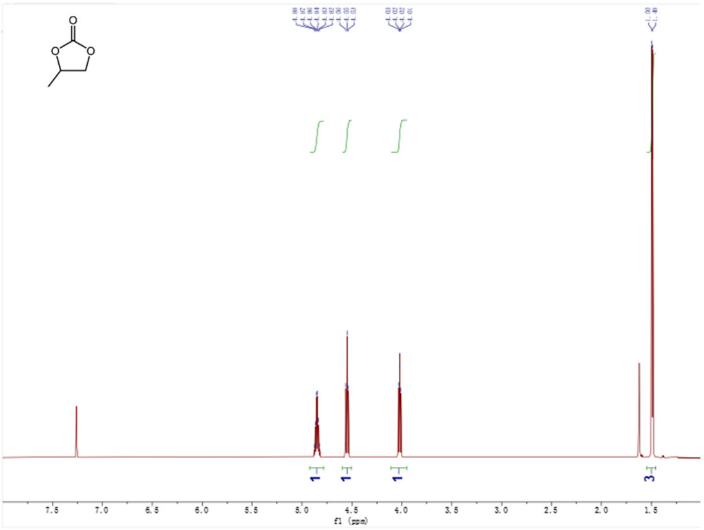

Fig. S13 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4-methyl-1,3-dioxolan-2-one.

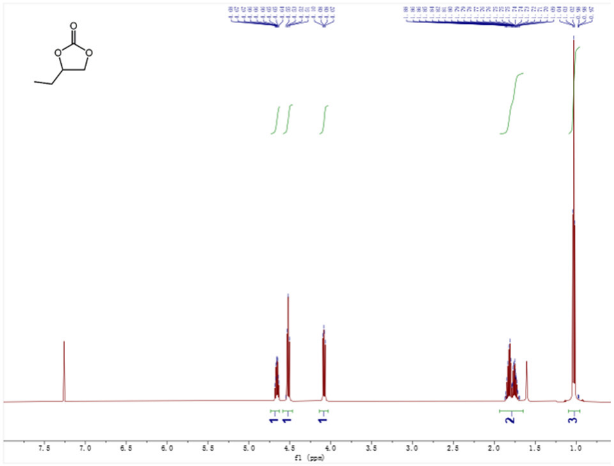

Fig. S14 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4-ethyl-1,3-dioxolan-2-one.

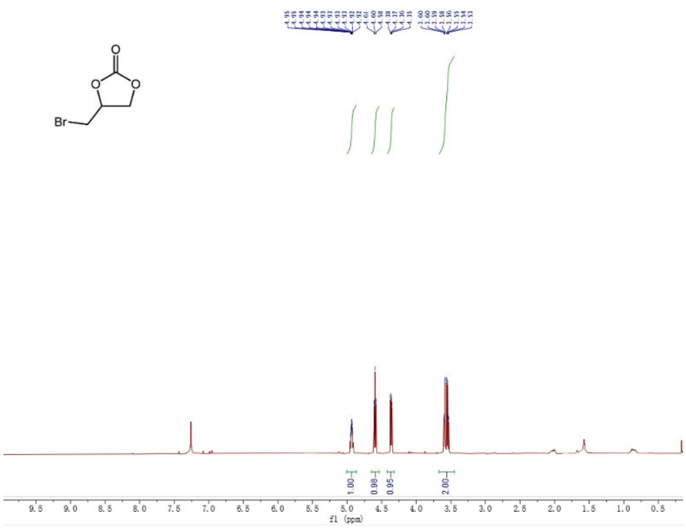

Fig. S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4-(bromomethyl)-1,3-dioxolan-2-one.

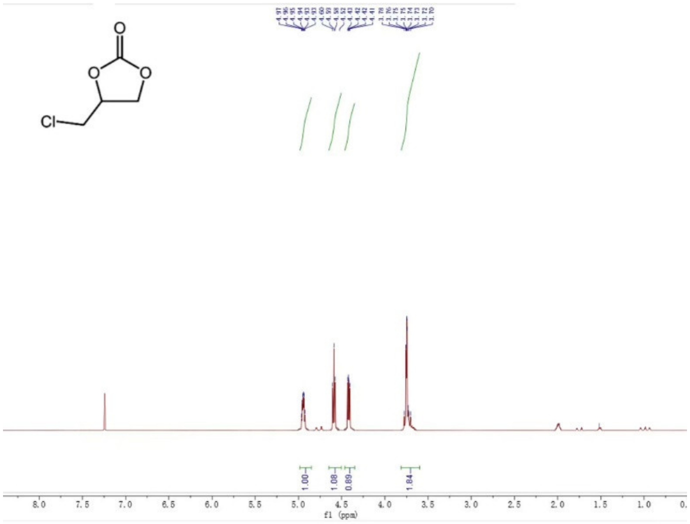

Fig. S16 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4-(chloromethyl)-1,3-dioxolan-2-one.

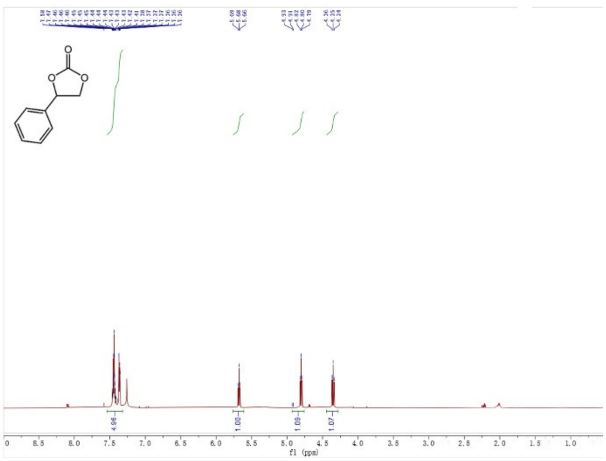

Fig. S17 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4-phenyl-1,3-dioxolan-2-one.

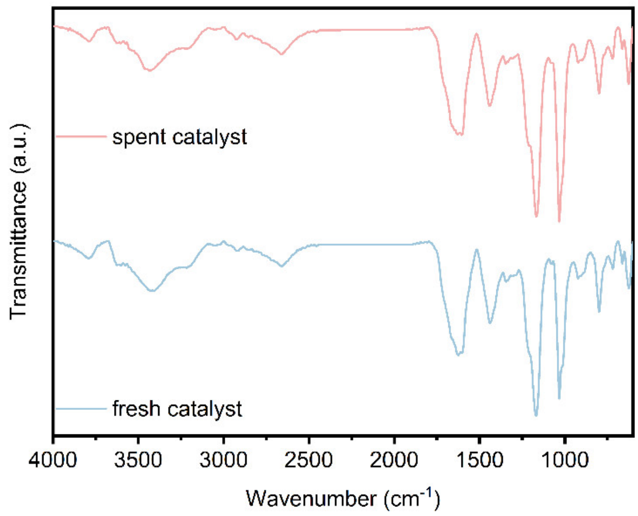

Fig. S18 FTIR spectra of fresh and spent monolith-TPP-Co-HZ after ten catalytic cycles.

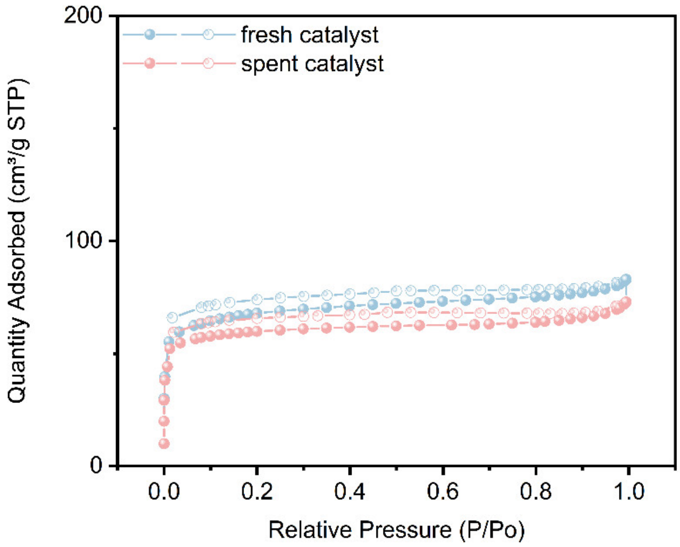

Fig. S19 N_2 adsorption-desorption isotherms of fresh and spent monolith-TPP-Co-HZ measured at 77 K.

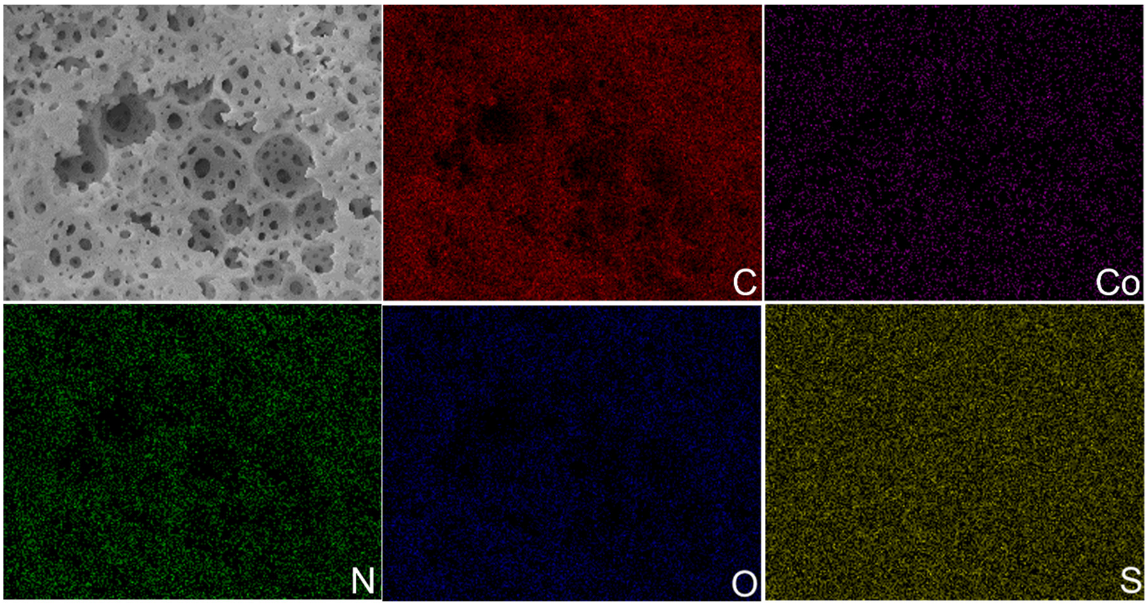

Fig. S20 FE-SEM image and elemental mapping (C, N, Co, O, S) spectra of monolith-TPP-Co-HZ after ten catalytic cycles.

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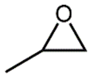
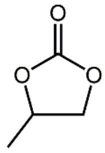
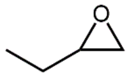
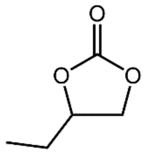
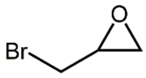
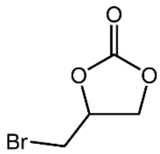
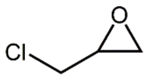
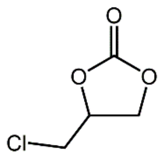
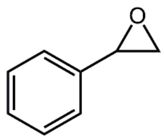
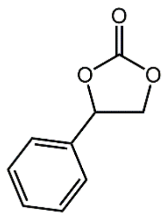
Tab. S3 Different substituted epoxides coupled with CO_2 catalyzed by monolith-TPP-Co-HZ at room temperature and low CO_2 concentration (15% CO_2/85% N_2) [a].

Entry	Epoxides	Products	Time (h)	Yields (%) [b]	TON(TOF)
1			48	76	1141(24)
2			48	69	1036(22)
3			48	72	1081(23)
4			48	74	1111(23)
5			48	62	930(19)

[a] Reaction conditions: epoxide (25 mmol) with monolith-TPP-Co-HZ (45 mg), n-Bu_4NBr (1.2 mmol), at room temperature under 0.1 MPa 15% CO_2/85% N_2, balloon. [b] Isolated yields determined by GC and ^1H NMR.

Tab. S4 The catalytic performance for chemical conversion of CO_2 cycloaddition with PO over various metal-based catalytic systems at low concentration of CO_2 (15% CO_2/85% N_2).

Catalyst	T (K)	P (MPa)	Time (h)	Yield (%)	TOF (h^{-1})	Ref.
Co/POP-TPP	302	1.0	48	45.4	436	1
Cu/POP-Bpy	302	0.1	72	77.5	2.15	2
Co@PDVB-VP-0.5	373	1.0	0.75	98.9	1034	3
Ag@Co-PIN-NH_2	298	0.1	14	95	27.14	4
Al-HCP	313	3.0	1	99	396	5
TBB-Bpy-Co	298	0.1	72	76.5	3.79	6
Bp-Zn@MA	373	2.0	6	99	1580	7
CoTPP-PiP(Br)	353	3.0	12	99	41.2	8
ZnTPP/QA-azo-PiP1	353	3.0	15	99	33	9
Zn-PPTF15	333	0.1	24	83	0.47	10
monolith-TPP-Co-HZ	298	0.1	48	76	24	This work

Tab. S5 Comparison of nitrogen content in the monolith-TPP-Co-HZ before and after the cycle.

Sample	fresh catalyst (wt%)	spent catalyst (wt%)
monolith-TPP-Co-HZ	6.7	6.5

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