Electronic Supplementary Material (ESI) for Green Chemistry.

Improved the Catalytic Performance of Co-MOF-74 by Nanostructure Construction

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1. Materials and Methods

Materials. $Co(NO_3)_2·6H_2O$ (99% purity), $Co(CH_3COO)_2·4H_2O$ (98 % purity), 1,2-dimethylimidazole (HMIm, 98%), 2,5-dihydroxyterephthalic acid (H_4DOBDC, 99% purity), methyl sulfoxide-d6 (DMSO-d6, 99.8% D) and Na_2SO_4 (99% purity) were supplied by Beijing InnoChem Science & Technology Co., Ltd. CO_2 (>99.95% purity) was purchased from Beijing Analysis Instrument Factory. Ethanol (A. R. grade), methanol (A. R. grade), N,N-dimethylformamide (DMF, A. R. grade) and CH_3CN (A. R. grade) were supplied by Beijing Chemical Works. Triethylamine (TEA, 98% purity) was bought from Aladdin Industrial Corporation. Benzaldehyde (99% purity), trimethylsilyl cyanide (97% purity), 4-nitrobenzaldehyde (98% purity), 4-methylbenzaldehyde (98% purity), 4-fluorobenzaldehyde (98% purity), 4-aminobenzaldehyde (>95% purity), thioanisole (98% purity) and 4-hydroxy-3-methylbenzaldehyde (98% purity) were brought from China National Medicines Co., Ltd. 4-Chlorothioanisole (98% purity), methyl p-tolyl sulfide (99% purity), 4-bromothioanisole (98% purity) and 4-fluorobenzaldehyde (98% purity) were purchased from J&K Scientific Co., Ltd. Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥0.92 meq g^{-1} exchange capacity) was purchased from Alfa Aesar China Co., Ltd.

ZIF-67 synthesis. For a typical experiment, $Co(NO_3)_2·6H_2O$ (1.4320 g), methanol (40 mL) and ethanol (40 mL) were added into a round-bottom flask under stirring. 40 mL methanol and 40 mL ethanol containing HMIm (1.6000 g) were poured into above solution under stirring for 30 s. The mixture was kept at 25 ^{o}C for 24 h. Then the solid was collected by centrifugation, followed by washing for 3 times with ethanol, and drying in vacuum at 80 °C for 12 h.

***h*-Co-MOF-74 synthesis.** ZIF-67 (40 mg) and H_4DOBDC (15 mg) were dissolved into 5 mL methanol. The above solution was stirred for 1 min, followed by the addition of 0.01 mL TEA. Then CO_2 was charged into the autoclave under stirring. The mixture was stirred at 6.80 MPa and 35 ^{o}C for 1 h. The precipitate was washed by DMF and ethanol twice and dried at 80 ^{o}C in vacuum for 8 h.

***s*-Co-MOF-74 synthesis.** It was prepared according to literature.[1] Typically, 0.1800 g H_4DOBDC, 0.8910 g $Co(NO_3)_2·6H_2O$, 25 mL H_2O, 25 mL DMF and 25 mL ethanol were added in a 100 mL Teflon-sealed autoclave. The mixture was stirred until homogeneous, followed by heating to 150 ^{o}C and keeping for 36 h. After the solution was cooled to room temperature, the solid was collected by centrifugation and washed for 3 times with methanol. Finally, the product was dried in vacuum at 80 °C for 12 h.

Co-MOF-74 nanoparticles synthesis. It was prepared according to literature.[2] A yellow solution of 0.1300 g of H_4DOBDC in 2.5 mL of DMF was added dropwise over another solution of 2.5 mL DMF solution containing 0.3120 g $Co(CH_3COO)_2\cdot4H_2O$ under stirring. The mixture was stirred at 25 ^{o}C for 20 h. The precipitate was washed by DMF and ethanol twice and dried at 80 ^{o}C in vacuum for 8 h.

Characterizations. The morphologies of the samples were characterized by SEM (HITACHI S-4800) and TEM (JEOL-1010) operated at 100 kV. EDS spectrum and EDS elemental mapping were performed on JEOL-2100F operated at 200 kV. XRD was performed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV and 200 mA. XPS was determined by VG Scientific ESCALab220i-XL spectrometer using Al Ka radiation. FT-IR spectra were performed on a Bruker Tensor 27 spectrometer. Liquid ^{1}H NMR spectra were recorded on Bruker 400 spectrometer. XAFS experiment was carried out at Beamline 1W2B at Beijing Synchrotron Radiation Facility. Small-angle X-ray scattering (SAXS) was carried out at Beamline 1W2A at Beijing Synchrotron Radiation Facility. UV-Vis diffuse reflectance spectra were carried out on a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan) with $BaSO_4$ as a reference. PL spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer.

Electrochemical measurements. Electrochemical measurement was conducted with a CHI660e electrochemical station in a typical three electrode cell, using a Pt mesh as the counter electrode and a saturated Ag/AgCl as the reference electrode. The working electrode was prepared by spreading the ethanolic slurry of photocatalyst (50 μL) over ITO plate with an area of 1 cm^2. The suspension was prepared by dispersing the photocatalyst (2 mg) into a mixed solution containing 0.2 mL ethanol and 20 μL 5 wt% Nafion. The electrolyte was an aqueous solution of Na_2SO_4 (0.5 M), which was purged with nitrogen for 1 h before measurement.

Photocatalysis study. Typically, the photocatalyst (10 mg) was dispersed in 5 mL acetonitrile, which contained 25 μL thioanisole, under ultrasonication. Then the suspension was illuminated under a xenon lamp (300 W, simulated sunlight) for different time at 25 °C under air atmosphere. After reaction for a certain time, the heterogeneous mixture was separated by centrifugation. ^{1}H NMR was applied to detect the liquid supernatant in DMSO-d6. The production rate of methyl phenyl sulfoxide was obtained by the follow formula:

$$\textit{Production rate of methyl phenyl sulfoxide} \ (\mu mol \ g - 1 \ h - 1) = \frac{\textit{the mole number of the product}}{\textit{the mass of the catalyst} \ * \ \textit{time}}$$

Thermocatalysis study. Aldehyde (2 mmol, 1 equiv) and catalyst (1.6 mol % based on Co(II)) were added into trimethylsilyl cyanide (6 mmol, 3 equiv). Then the suspension was stirred at 60 °C for a certain time. The heterogeneous mixture was separated by centrifugation. ^{1}H NMR was applied to detect the liquid supernatant in DMSO-d6. The TOF value was obtained by the follow formula:

$$TOF \ (h - 1) = \frac{\textit{the mole number of the product}}{\textit{the mole number of the Co in catalyst} \ * \ \textit{time}}$$

2. Results and Discussion

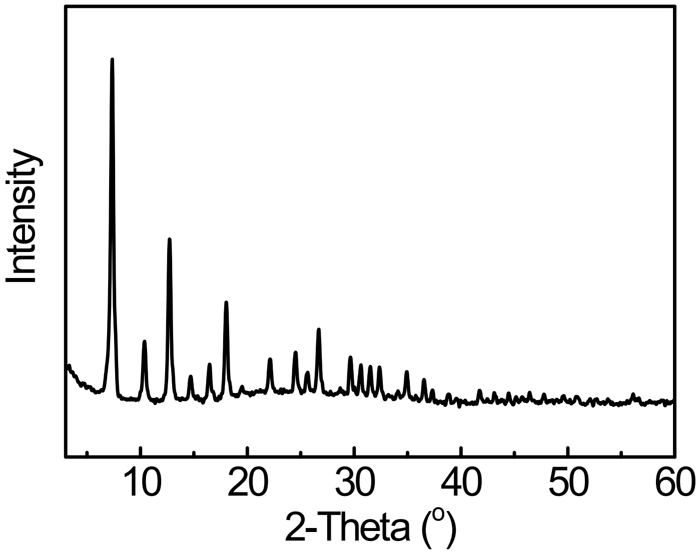

Fig. S1. XRD pattern of ZIF-67.

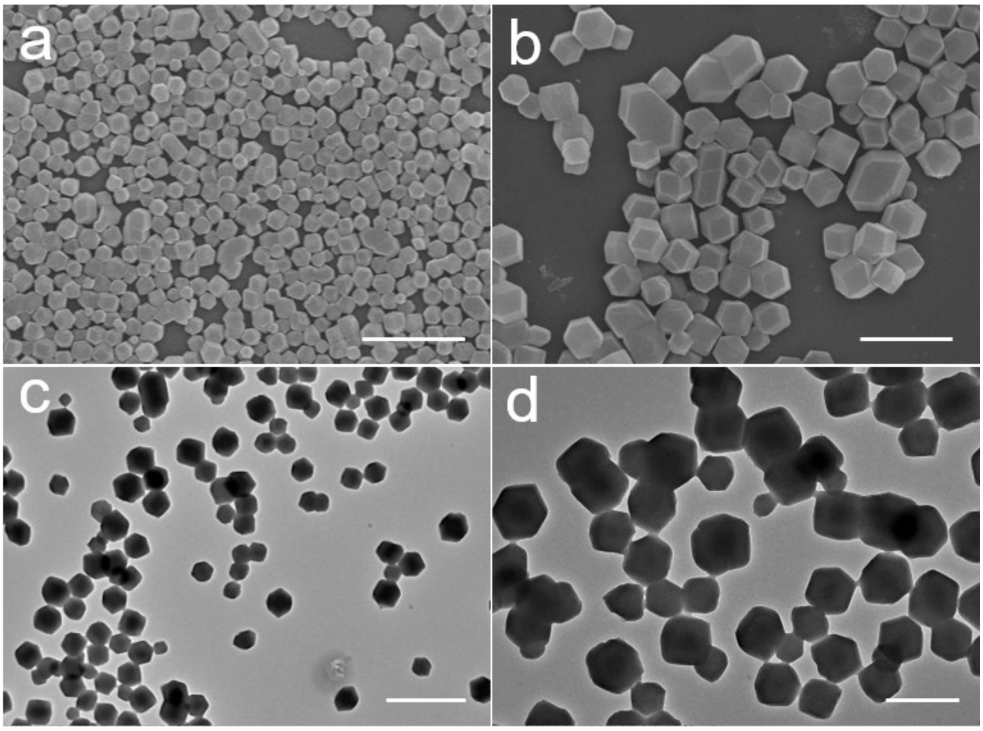

Fig. S2. SEM and TEM images of ZIF-67. Scale bars: 2 μm in a, 1 μm in b and c, 500 nm in d.

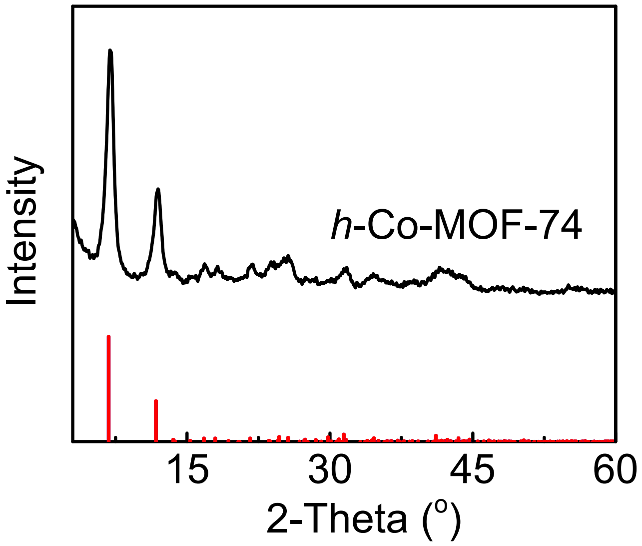

Fig. S3. XRD pattern of *h*-Co-MOF-74 synthesized in CO_2/methanol solution at 6.80 MPa and 35 ^{o}C for 1 h. The bottom lines are the simulated XRD pattern of Co-MOF-74.

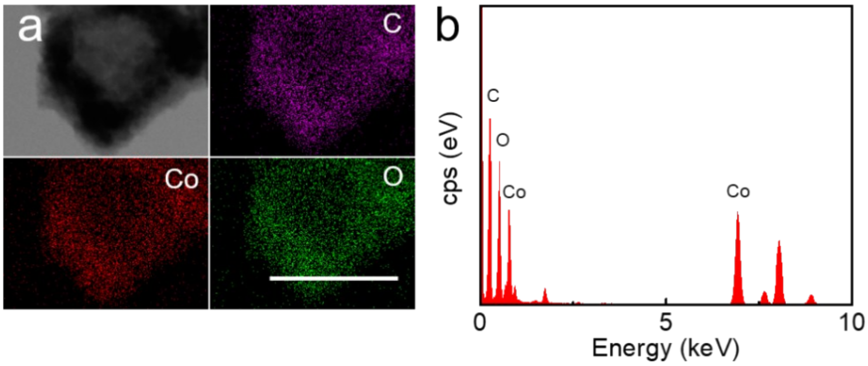

Fig. S4.. EDS mapping images (a) and EDS spectrum (b) of *h*-Co-MOF-74 synthesized in CO_2/methanol solution at 6.80 MPa and 35 °C for 1 h. Scale bar: 300 nm in a.

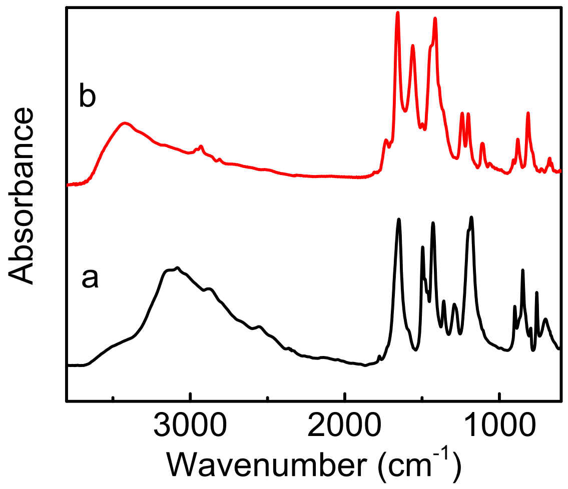

Fig. S5. FT-IR spectra of H_4DOBDC (a) and *h*-Co-MOF-74 (b) synthesized in CO_2/methanol solution at 6.80 MPa and 35 ^oC for 1 h.

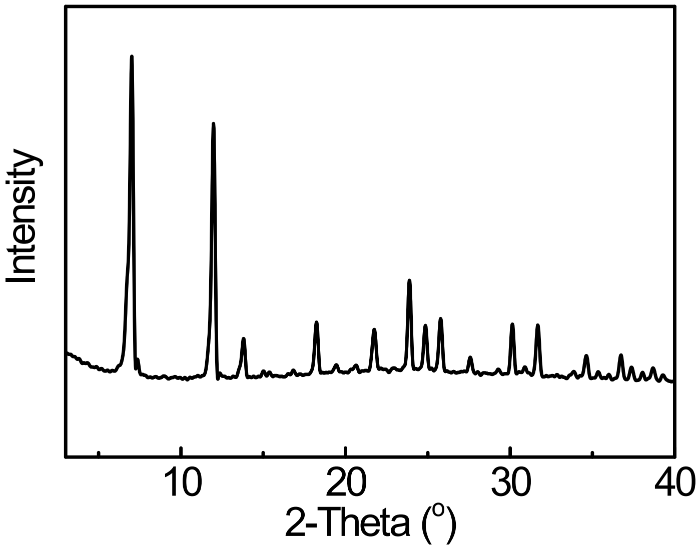

Fig. S6. XRD pattern of *s*-Co-MOF-74.

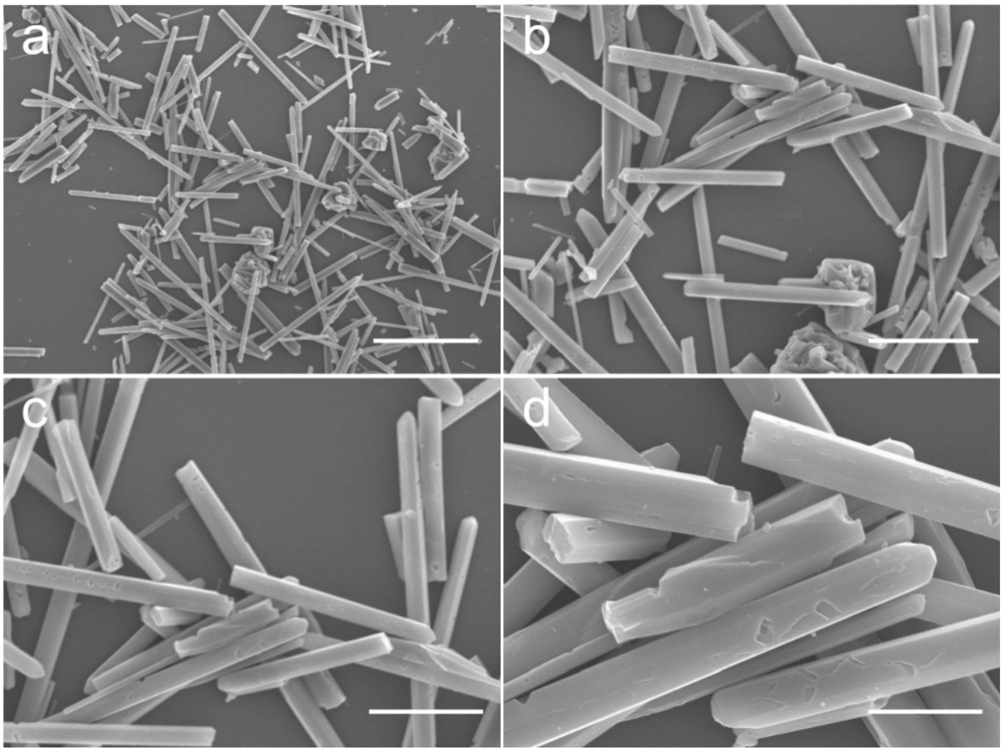

Fig. S7. SEM images of *s*-Co-MOF-74. Scale bars: 50 μm in a, 20 μm in b, 15 μm in c, 6 μm in d.

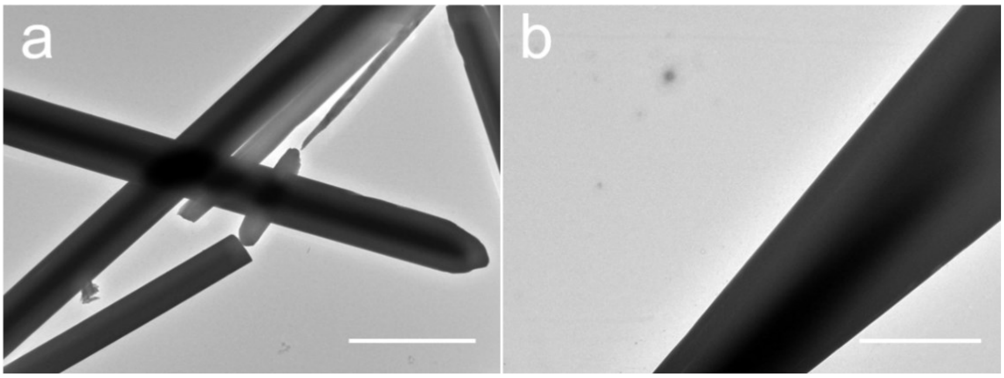

Fig. S8. TEM images of *s*-Co-MOF-74. Scale bars: 5 μm in a and 2 μm in b.

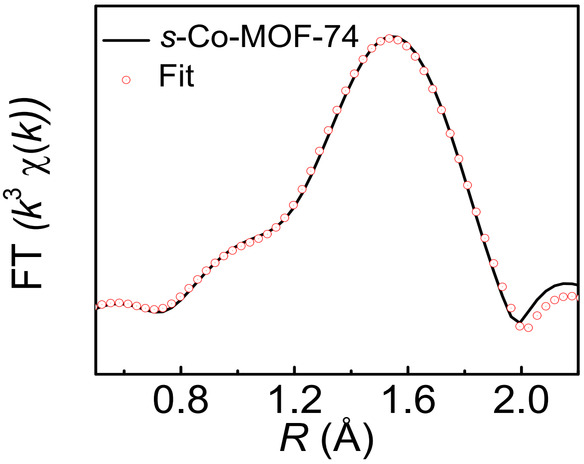

Fig. S9. Experimental EXAFS spectrum and fitting curve of *s*-Co-MOF-74.

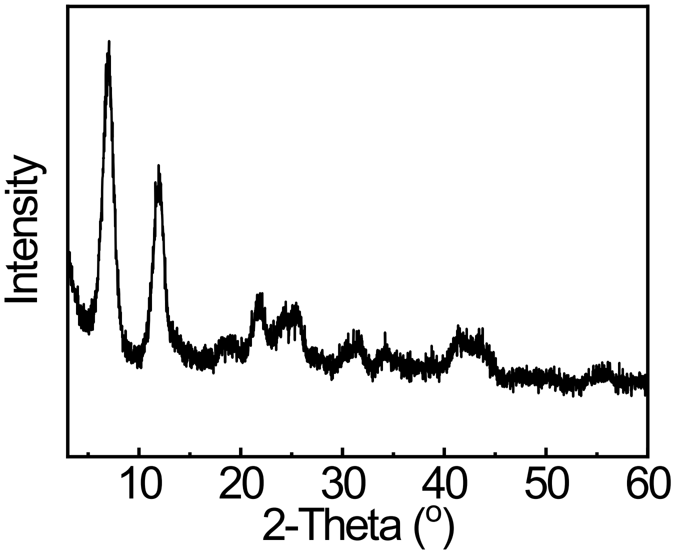

Fig. S10. XRD pattern of *n*-Co-MOF-74.

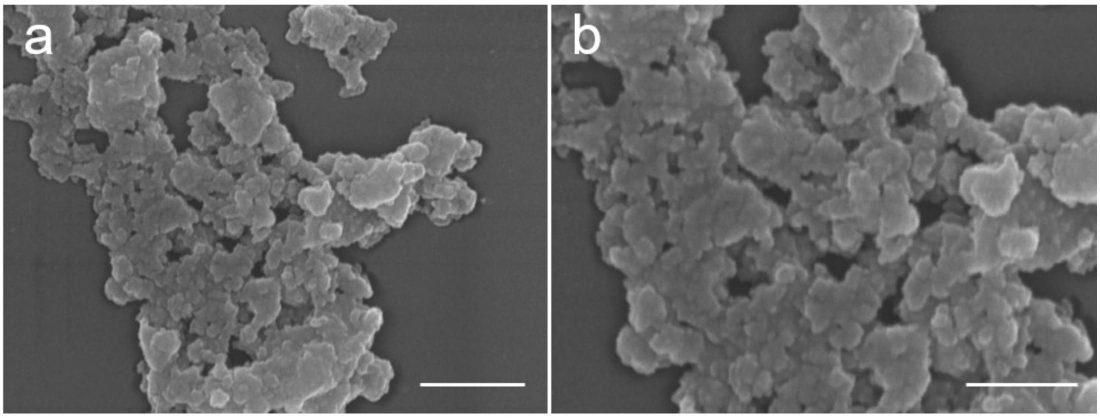

Fig. S11. SEM images of *n*-Co-MOF-74. Scale bars: 500 nm in a and 300 nm in b.

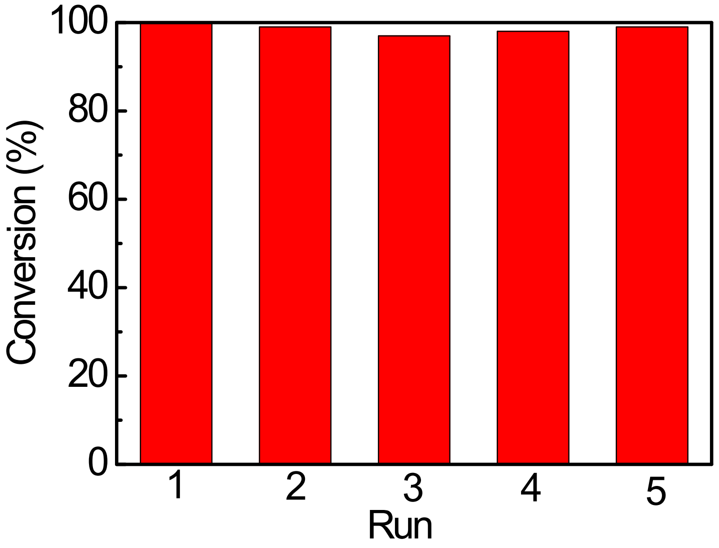

Fig. S12. Reusability of *h*-Co-MOF-74 synthesized in CO_2/methanol solution at 6.80 MPa and 35 ^oC for 1 h for catalyzing the thioanisole to methyl phenyl sulfoxide.

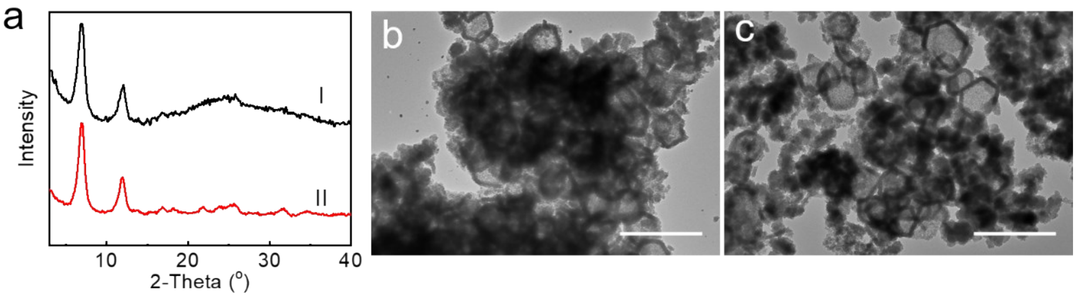

Fig. S13. (a) XRD pattern of the *h*-Co-MOF-74 after 5 catalysis runs (I) and fresh *h*-Co-MOF-74 (II); (b, c) TEM images of *h*-Co-MOF-74 after 5 catalysis runs. Scale bar: 500 nm in b and c.

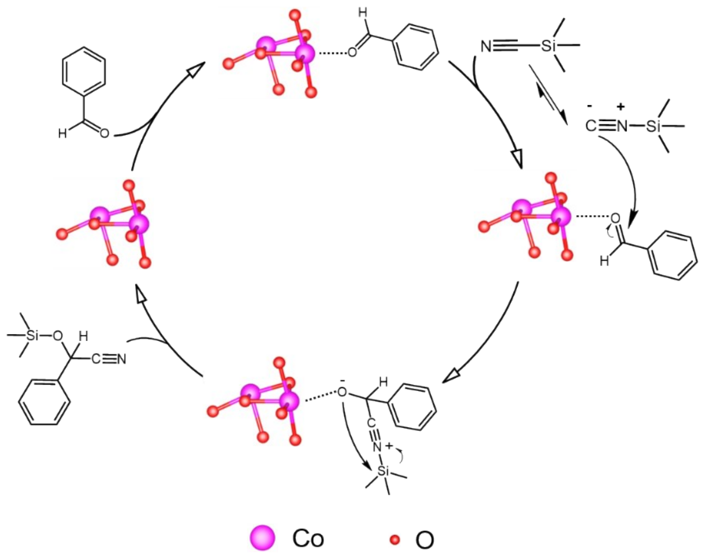

Fig. S14. A proposed mechanism for the cyanosilylation reaction of carbonyl compounds catalyzed by *h*-Co-MOF-74.[8]

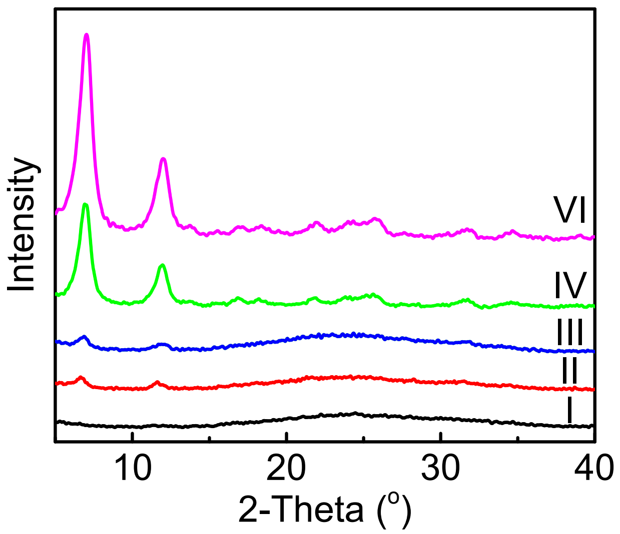

Fig. S15. XRD patterns of the products synthesized at different pressures (I CO_2-free; II 2.40 MPa; III 4.50 MPa; IV 6.80 MPa; V 8.60 MPa). The reaction time was fixed at 1 h.

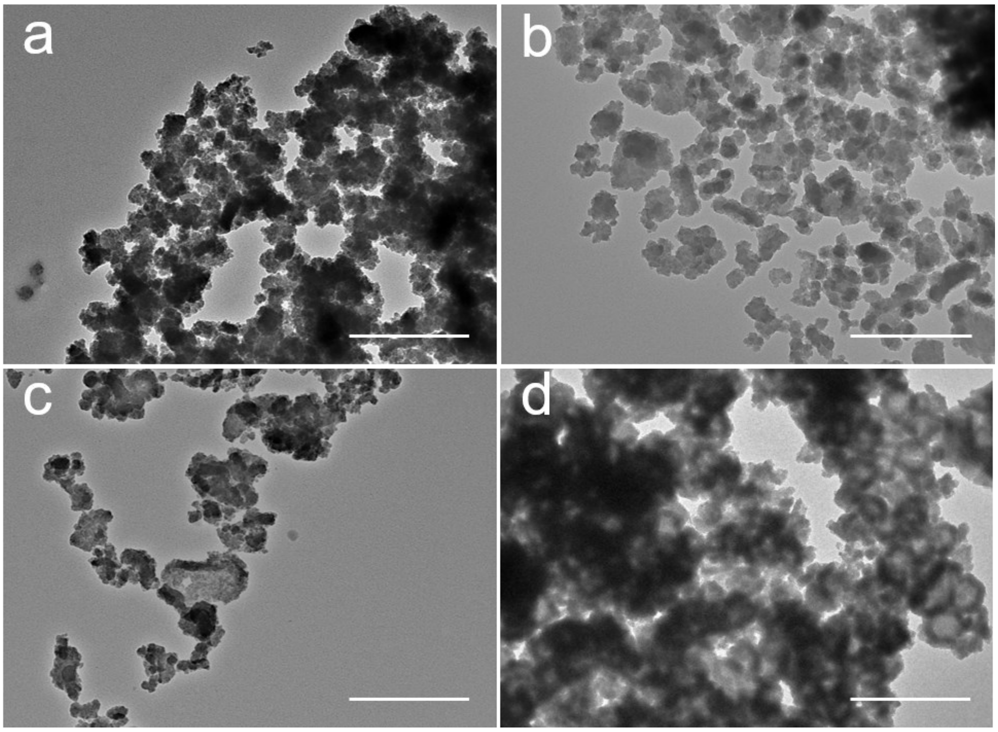

Fig. S16. TEM images of the products synthesized at different pressures. (a) CO_2-free, (b) 2.40 MPa, (c) 4.50 MPa, (d) 8.60 MPa. The reaction time was fixed at 1 h. Scale bars: 500 nm in a and c, 400 nm in b, 1 μm in d.

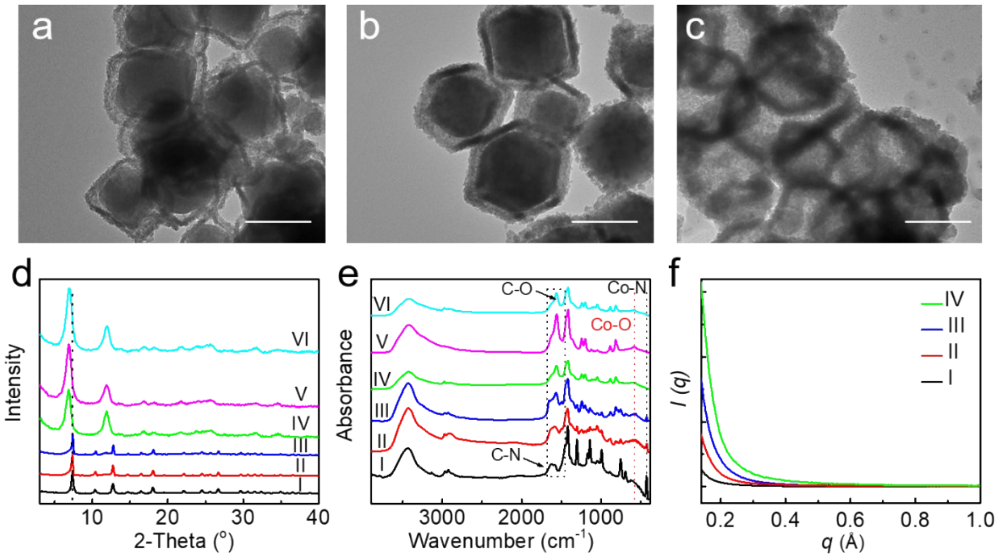

Fig. S17. (a-c) TEM images of the products synthesized at 6.80 MPa and time of 5, 10 and 30 min, respectively; (d-f) XRD patterns, FT-IR spectra and SAXS patterns of ZIF-67 (I) and the products synthesized at 6.80 MPa and different time (II 5 min; III 10 min; IV 30 min; V 1 h; VI 5 h). Scale bar: 200 nm in a, b and c.

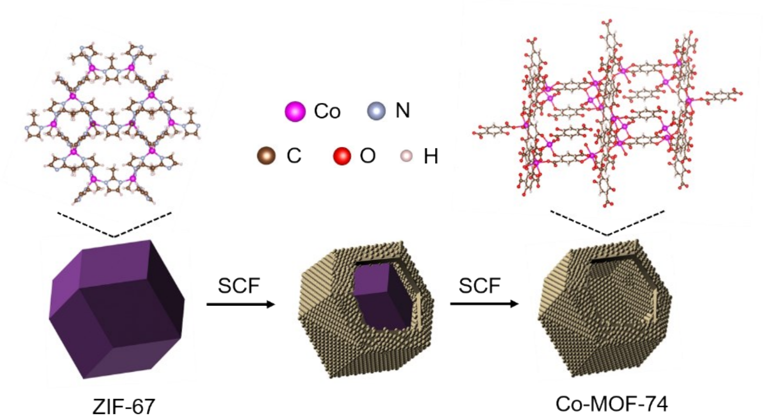

Fig. S18. Diagram illustrating the formation process of *h*-Co-MOF-74.

Table S1 EXAFS fitting parameters at the Co K-edge for various samples.

Sample	Shell	*N*	*R* (Å)	σ^2 (Å^2·10^3)	ΔE_0 (eV)	*R* factor (%)
s-Co-MOF-74	Co-O	5.0	2.05	8.3	-2.5	0.1
h-Co-MOF-74	Co-O	4.2	2.05	7.3	-2.1	0.6

N: coordination numbers; R: bond distance; σ^2: Debye-Waller factors; ΔE_0: the inner potential correction; R factor: goodness of fit. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N ± 20%; R ± 1%; σ^2 ± 20%; ΔE_0 ± 20%.

Table S2 Photo-oxidation of thioanisole to methyl phenyl sulfoxide over different catalysts.

Entry	Catalyst	Conditions	Time (h)	Conversion	Selectivity	Production rate of methyl phenyl sulfoxide (μmol g^{-1} h^{-1})	Ref.
1	TiO_2	CH_3CN 500 W Hg lamp Ag_2SO_4	4	30%	10%	17	3
2	TiO_2	aqueous-acetonitrilic 400 W Hg lamp O_2	24	58%	69%	450	4
3	P25 TiO_2	CH_3OH/TEA 300W Xe lamp >400 nm O_2	10	84%	92%	580	5
4	UiO-66	CH_3OH-benzotrifluoride 300 W Xe lamp, >360 nm O_2	8	8%	95%	95	6

5	DUT-67 (Zr)	CH_3OH-benzotrifluoride 300 W Xe lamp, >360 nm air	8	46.6%	95%	553	6
6	DUT-67 (Zr)	CH_3OH-benzotrifluoride 300 W Xe lamp, >360 nm O_2	8	95%	98%	1163	6
7	*s*-Co-MOF-74	CH_3CN 300 W Xe lamp simulated sunlight air	10	30%	98%	637	This work
8	*h*-Co-MOF-74	CH_3CN 300 W Xe lamp simulated sunlight air	10	99%	100%	2124	This work

Table S3 Photocatalytic performance of *h*-Co-MOF-74 synthesized in CO_2/methanol solution at 6.80 MPa and 35 ^{o}C for 1 h for oxidation of different substrates.

Entry	R in reactant	Time (h)	Conversion (%)	Selectivity (%)	TOF (μmol g^{-1} h^{-1})
1	CH_3	10	100	97	1908
2	F	10	100	98	1841
3	Cl	10	100	97	1656
4	Br	10	100	99	1297

Table S4 Cyanosilylation of different aldehydes to corresponding cyanohydrins over different catalysts.

Entry	Catalyst	Temperature °C	Substrate	Time (h)	Conversion (%)	Selectivity (%)	TOF (h^{-1})	Ref.
1	$\{[Co_2(1,4\text{-}NDC)_2(L)(H_2O)_2(\mu_2\text{-}H_2O)]\cdot(DMF)_2(H_2O)\}_n$	60	benzaldehyde	6	96	/	32	7
2	$\{[Co(fma)(L)\text{-}(H_2O)_2]\cdot S\}_n$	60	benzaldehyde	6	81	/	27	7
3	*s*-Co-MOF-74	60	benzaldehyde	1.5	62	98	26	This work
4	*h*-Co-MOF-74	60	benzaldehyde	1.5	97	100	40	This work
5	*h*-Co-MOF-74	60	4-fluorobenzaldehyde	0.5	75	100	94	This work
6	*h*-Co-MOF-74	60	4-nitrobenzaldehyde	0.5	64	100	80	This work
7	*h*-Co-MOF-74	60	4-methylbenzaldehyde	0.5	28	100	35	This work
8	*h*-Co-MOF-74	60	4-aminobenzaldehyde	0.5	25	100	31	This work
9	*h*-Co-MOF-74	60	4-hydroxy-3-methylbenzaldehyde	0.5	17	100	21	This work

1,4-NDC=1,4-naphthalene dicarboxylic acid; fma=fumaric acid; L=3,3′-azobis pyridine; S=disordered solvents.

References

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