

Supporting Information

Superhydrophobic MOFs with Enhancing Catalytic Activity for Chemical Fixation of CO₂

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1. EXPERIMENTAL SECTION

1.1. General Information. All chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (XRD) patterns were collected by a Bruker D8 ADVANCE instrument with 0.02° of step sizes in the 2θ range of 5 to 40° . Fourier transform infrared (FT-IR) spectra of samples were recorded at room temperature on a PerkinElmer. The average spectra were scanned sixteen times in the range of 4000 - 400 cm^{-1} . The size and morphology details of the materials were determined by scanning electron microscopy (SEM) on a Hitachi 3030 equipped with an energy dispersive X-ray detector (EDX). Thermogravimetric (TG) analysis was performed on a PerkinElmer/Pyris1 machine in the temperature range of room temperature to $750\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C min}^{-1}$ under a N_2 atmosphere. The wetting properties of the as-prepared samples were characterized by obtaining their contact angles with liquid water using a Biolin Attension Theta. Nitrogen adsorption isotherm measurements were measured using a 3H-2000PS1 analyser (Beishide Instrument Co., China) at 77 K to determine the surface area of the samples, and the pore size distribution was calculated using NLDFT models. X-ray photoelectron spectroscopy (XPS) was obtained by monochromated X-rays (Quantum 2000, USA) using $\text{Al K}\alpha$ radiation. The products of the catalysis reaction were monitored by gas chromatography (GC).

1.2. Synthesis and Preparation.

1.2.1 Preparation of MIL-101(Cr)-NH₂. In a typical experiment, 3.2 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.44 g of 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$) were added slowly into 60 mL of H_2O solution, containing 0.8 g NaOH . The mixture stirred at room temperature for 30 min was then transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at $150\text{ }^\circ\text{C}$ for 12 h . After natural cooling, the obtained mixture was collected by centrifugation at 7000 rpm for 2 min . The obtained green powder was washed several times with water, DMF and methanol and dried at $100\text{ }^\circ\text{C}$ overnight. Then, activated NH_2 -MIL-101(Cr) was obtained.

1.2.2 Preparation of MIL-101(Al)-NH₂. In detail, aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 0.51 g) and $\text{H}_2\text{BDC-NH}_2$ (0.56 g) were dissolved in 30 mL of DMF, followed by ultrasonic stirring for 30 min . The mixed solution was then transferred into a 50 mL Teflon-lined autoclave for solvothermal treatment at $130\text{ }^\circ\text{C}$ for 72 h . After being cooled to room temperature, the resultant yellow precipitate was separated by centrifugation and washed three times with DMF and absolute methanol. Finally, the obtained yellow powder was dried under vacuum at $60\text{ }^\circ\text{C}$ overnight.

1.2.3 Preparation of UiO-66(Zr)-NH₂ In a typical procedure of UiO-66(Zr)-NH_2 , 15.0 g (64.4 mmol) ZrCl_4 , 11.7 g (64.4 mmol) $\text{H}_2\text{BDC-NH}_2$ and 440 mL (7.73 mol) acetic acid were dissolved in 1 L DMF in a 2 L three-necked flask, and then 75 mL H_2O was added. The resulting homogeneous solution was heated in an oil bath under stirring at $120\text{ }^\circ\text{C}$ for 15 min before it was cooled to room temperature. The product was separated via centrifugation at 10 000 rpm for 3 minutes and further purified with ethanol several times.

1.2.4 Preparation of UiO-66(Hf)-NH₂. In a typical procedure, 1.5 g (4.7 mmol) HfCl_4 , 0.85 g (4.7 mmol) $\text{H}_2\text{BDC-NH}_2$ and 36 mL acetic acid were dissolved in 200 mL

DMF in a 500 mL three-necked flask, and then 5 mL H₂O was added. The resulting homogeneous solution was heated in an oil bath under stirring at 120 °C for 15 min before it was cooled to room temperature. The product was separated *via* centrifugation at 10000 rpm for 3 minutes and further purified with ethanol several times.

1.2.5 Preparation of MOF-CF₃. To modify MOF-NH₂ with 4-(trifluoromethyl)benzaldehyde (4-TFMB), 0.40 g of MOF-NH₂ was first dispersed into 30 mL of toluene in a flask under ultrasound, and 0.62 mL of 4-TFMB was then added to the mixture. Then, the solution was refluxed at 120 °C for 12 h. Afterwards, the precipitate was washed with abundant ethanol three times and dried under vacuum at 40 °C overnight. The obtained product was MOF-CF₃ by the reaction.

1.3. Catalytic Performance Evaluation. A 10 mL stainless steel autoclave was charged under a protective atmosphere with catalyst (0.05 mmol), TBABr (0.1 mmol) and epoxide (10 mmol) at 25 °C. CO₂ was added until the internal pressure in the system reached 1.0 MPa at 25 °C. The solution was mechanically stirred at 600 rpm. The temperature of the reactor was then raised to 60 °C. After catalytic reactions, the catalysts were separated by filtration, and the samples of the reaction mixture were analysed by GC to determine the conversions. The catalysts were washed abundantly with MeOH and CH₂Cl₂, placed in a vial and soaked in MeOH for at least 6 h and subsequently dried under vacuum at room temperature.

1.4. Theoretical calculation method Based on the adsorption isotherms of pure gas at 298 K and 273 K, Using the Clausius-Clapeyron equation, the Isothermic Heat of Adsorption (Q_{st}) were computed as follows:¹

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad \text{Equation (S1)}$$

where P denotes the pressure; N gives the amount of uptake; T refers to the temperature and m and n connote the number of words necessary to fully explain the isotherm.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad \text{Equation (S2)}$$

Here R means the universal gas constant. The coverage dependence of the Q_{st} values was derived by fitting the adsorption data at various temperatures for two MOFs.

1.5. Breakthrough tests. Breakthrough experiments of MIL-101(Cr)-CF₃ for CO₂/N₂ mixtures of 15/85 and 50/50 were purged into a packed column with a total inlet flow rate of 2.0 mL/min at 298 K.

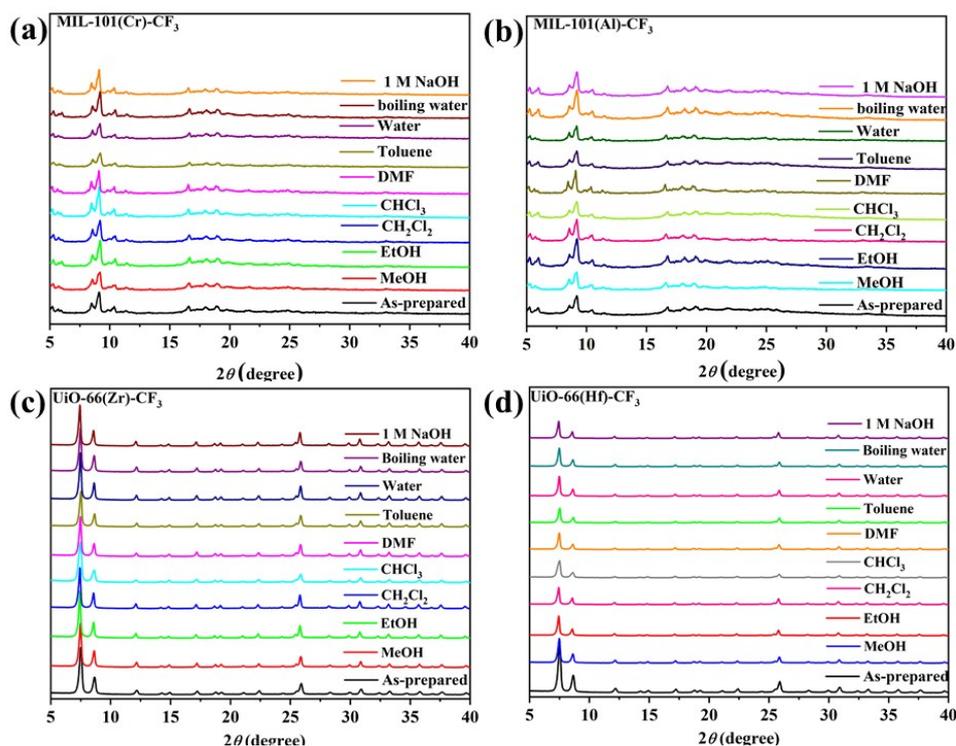


Fig. S1 Chemical stability tests of MOF-CF₃ immersed in MeOH, CH₂Cl₂, CHCl₃, toluene, and MeCN, even in boiling water for 24 h.

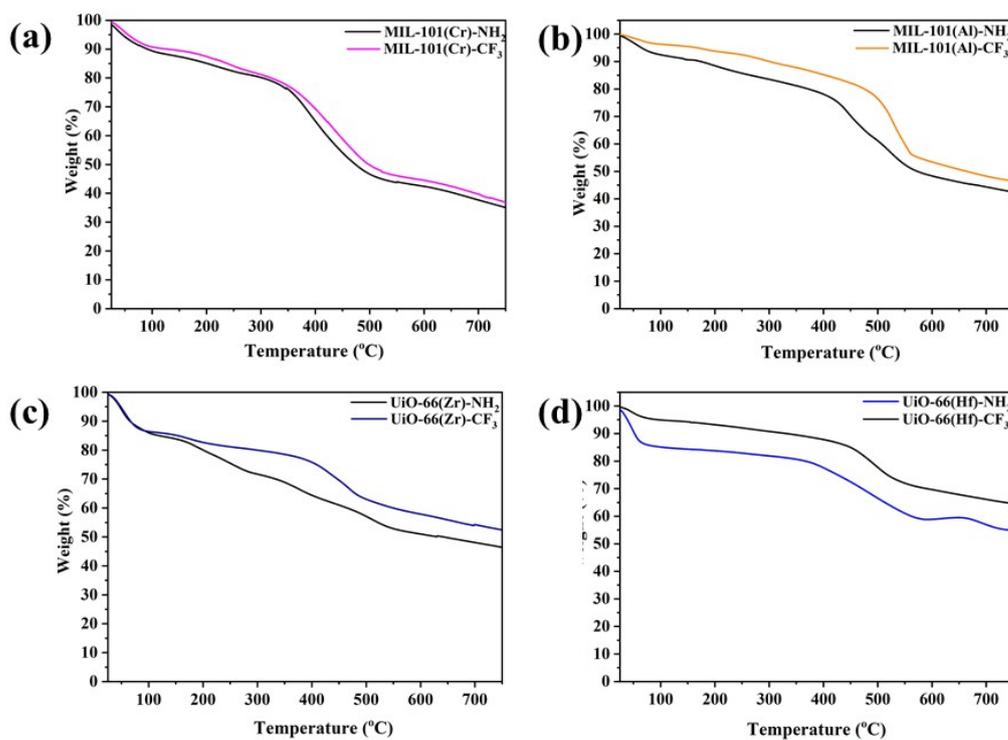


Fig. S2 Thermogravimetric analyses of MOF-NH₂ and MOF-CF₃.

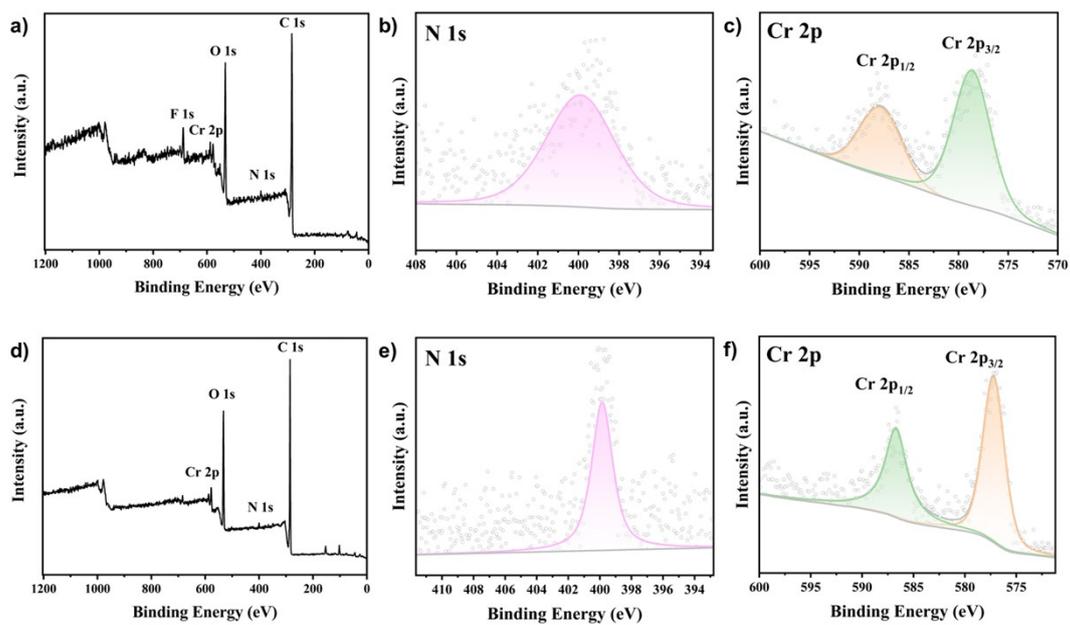


Fig. S3 X-ray photoelectron spectroscopy (XPS) for MIL-101(Cr)-CF₃ (a-c) and MIL-101(Cr)-NH₂ (d-e).

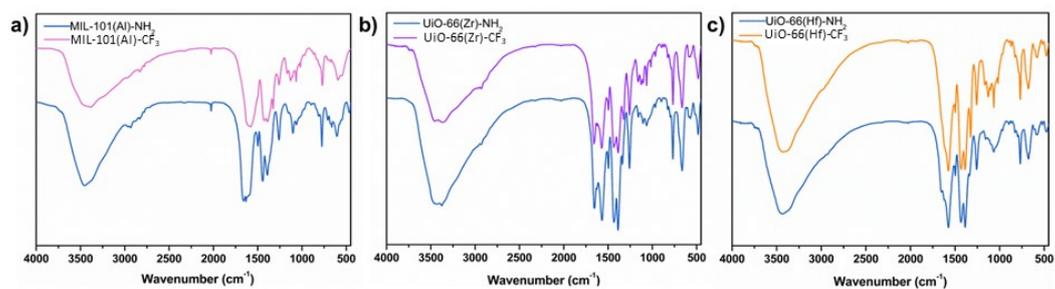


Fig. S4 FT-IR spectra analyses of MOF-NH₂ and MOF-CF₃.

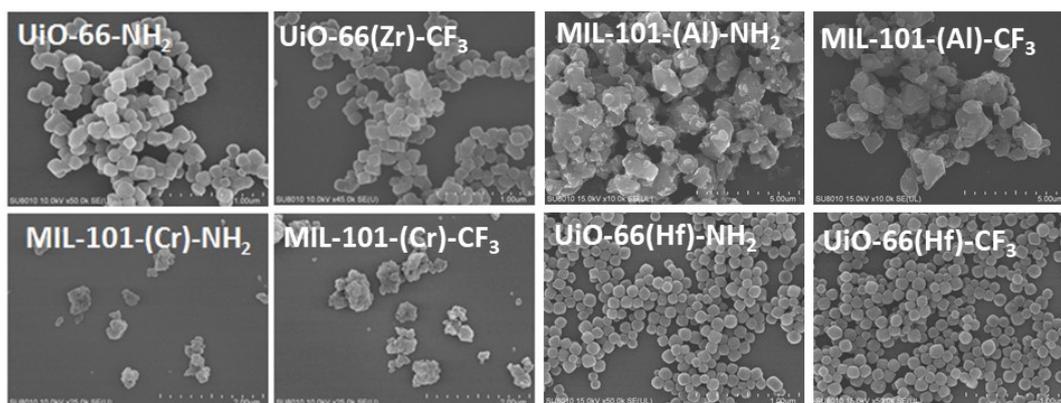


Fig. S5 SEM images of pristine MOF-NH₂ and MOF-CF₃.

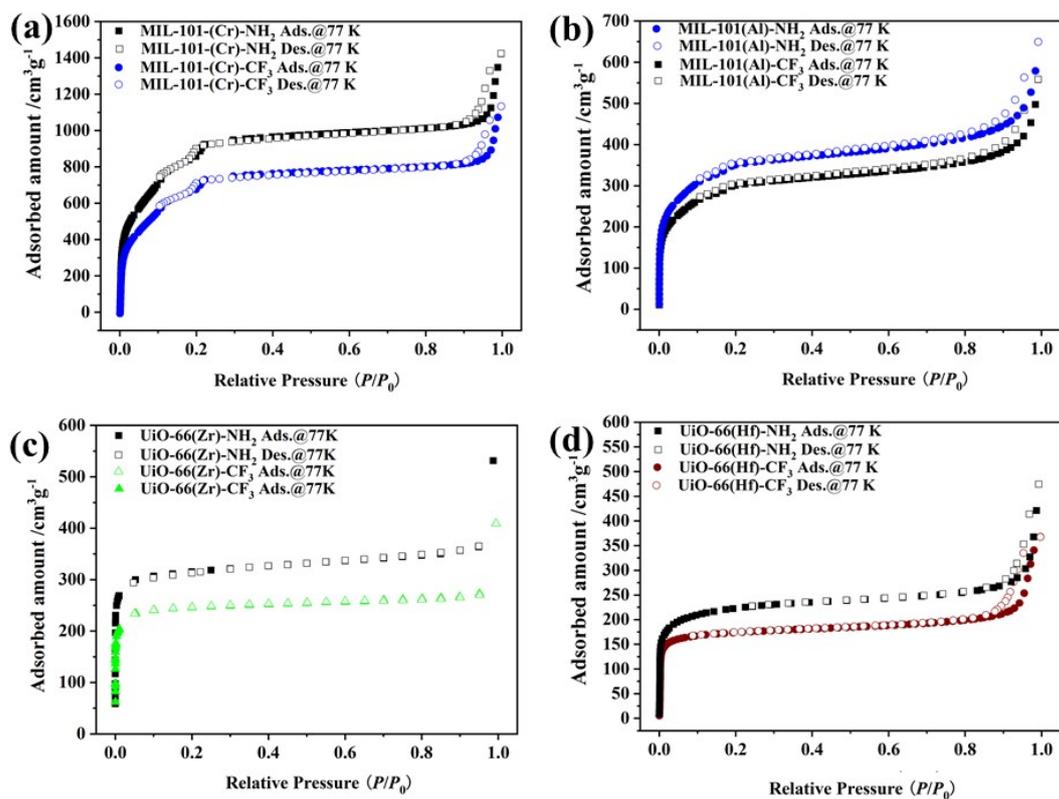


Fig. S6 N_2 adsorption/desorption isotherms of MOFs-NH₂ and MOF-CF₃ at 77 K.

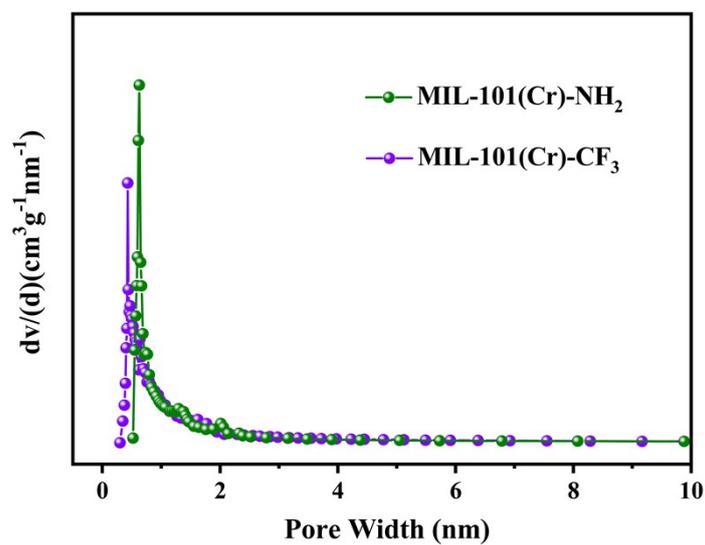


Fig. S7 Pore size distribution for the MOFs-NH₂ and MOF-CF₃.

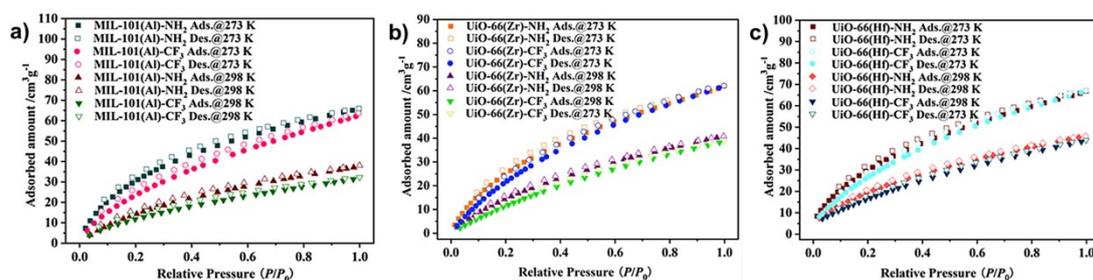


Fig. S8 CO₂ adsorption/desorption isotherms of MOF-NH₂ and MOF-CF₃ at 273 K and 298 K.

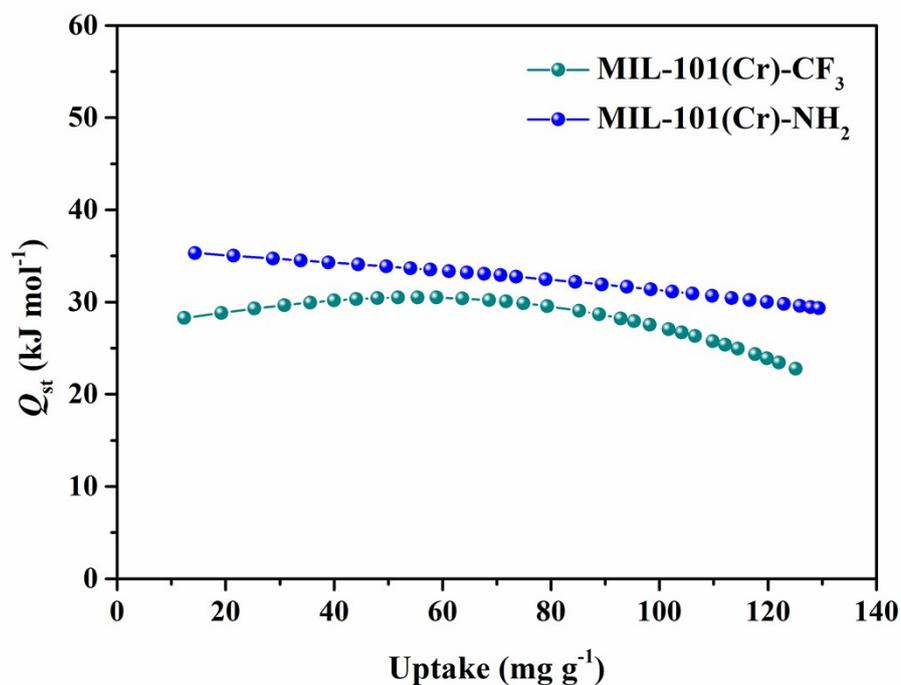


Fig. S9 The isosteric heat of CO₂ adsorption (Q_{st}) of MOF-NH₂ and MOF-CF₃.

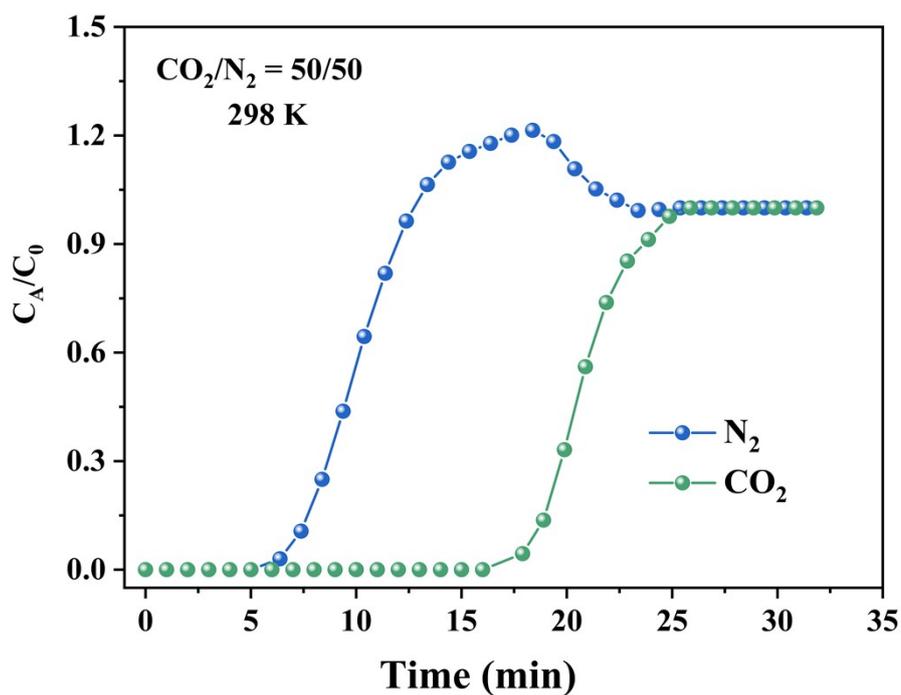


Fig. S10 Breakthrough curve in MIL-101(Cr)-CF₃ for CO₂/N₂ separation (composition: 50/50) at 298 K.

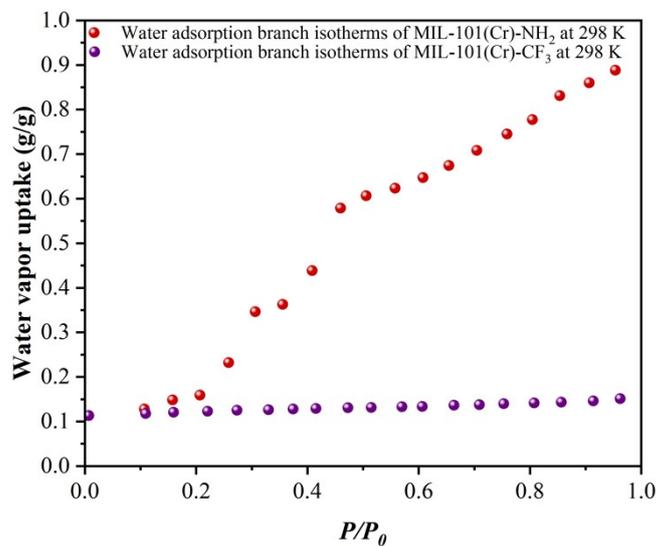


Fig. S11 Water adsorption branch isotherms measured at 298 K for MIL-101(Cr)-NH₂ and MIL-101(Cr)-CF₃.

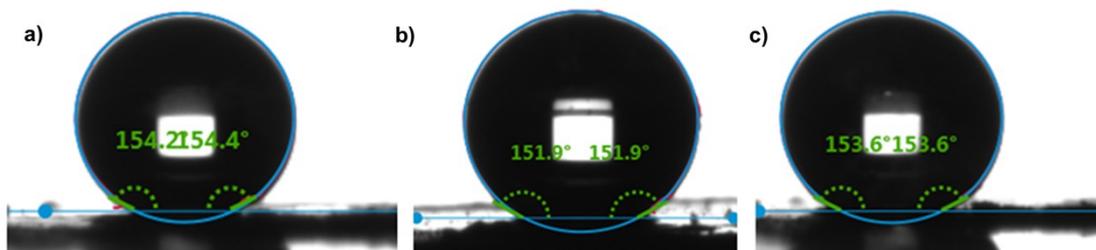


Fig. S12 The WCAs of a) MIL-101(Cr)-CF₃; b) MIL-101(Al)-CF₃; c) UiO-66(Zr)-CF₃; and d) UiO-66(Hf)-CF₃.

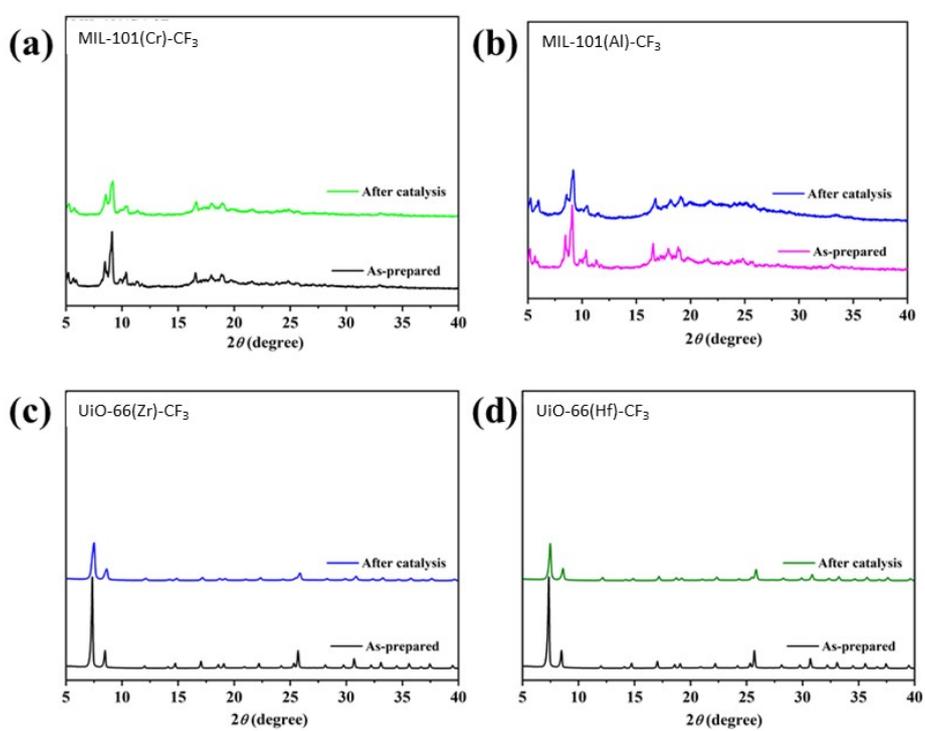


Fig. S13 Stability tests of MOF-CF₃ for the cycloaddition of CO₂ with propylene oxide.

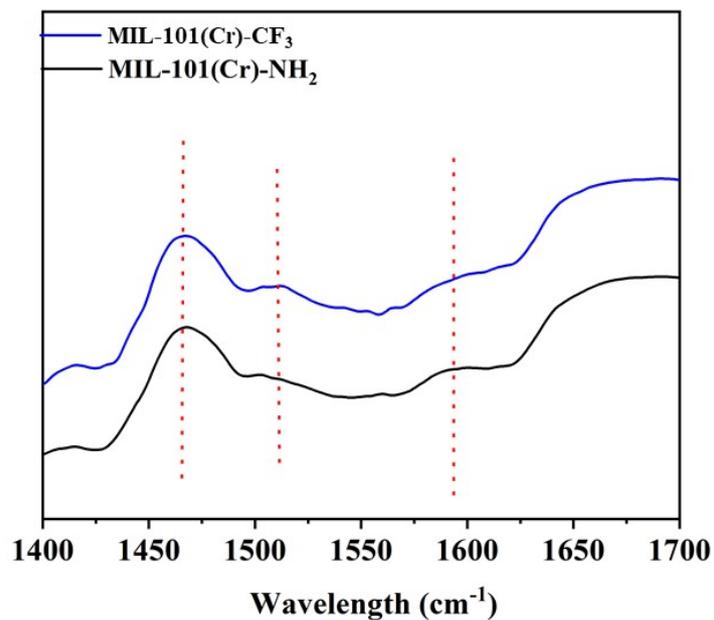


Fig. S14 Py-IR spectra of MIL-101(Cr)-NH₂ and MIL-101(Cr)-CF₃ at 150 °C.

Table S1 CO₂ uptake values of MOF-NH₂ and MOF-CF₃.

MOF	CO ₂ -uptake value at 273 K/cm ³ g ⁻¹	CO ₂ -uptake value at 298 K/cm ³ g ⁻¹
MIL-101(Cr)-NH ₂	75.8	45.1
MIL-101(Cr)-CF ₃	73.5	42.3
MIL-101(Al)-NH ₂	65.9	38.0
MIL-101(Al)-CF ₃	63.7	32.8
UiO-66(Zr)-NH ₂	61.9	40.9
UiO-66(Zr)-CF ₃	62.2	38.9
UiO-66(Hf)-NH ₂	67.2	45.9
UiO-66(Hf)-CF ₃	67.0	43.9

Table S2 Cycloaddition of CO₂ with propylene oxide catalyzed by various catalysts.

Entry	R	catalyst	Conversion (%)
1	Me	UiO-66(Zr)-NH ₂	70.8
2	Me	UiO-66(Zr)-3F	84.3
3	Me	UiO-66(Hf)-NH ₂	73.9

4	Me	UiO-66(Hf)-3F	86.8
5	Me	MIL-101(Al)-NH ₂	74.4
6	Me	MIL-101(Al)-3F	86.6

Reaction conditions: epoxides (10 mmol), catalyst (0.05 mmol), TBABr (0.1 mmol, 1 mol%) under CO₂ (1.0 MPa), 60 °C and 12 h. The conversions were determined by GC.

Table S3. Comparison of the catalytic activity of MIL-101(Cr)-CF₃ with literature-reported MOFs for cycloaddition of CO₂ with epoxypropane under similar conditions.

Entry	Catalyst	<i>T</i> (°C)	<i>P</i> (MPa)	<i>t</i> (h)	Yield (%) ^b	Ref.
1	CoMOF-1	100	2.5	8	99	[2]
2	Ti-ZIF	100	3.0	8	95	[3]
3	ZIF-90	100	1.2	8	88	[4]
4	{MgL(H ₂ O) ₂ } _n	70	1.0	12	99	[5]
5	[In ₂ (dpa) ₃ (1,10-phen) ₂]·H ₂ O	50	1.2	12	91	[6]
8	MIL-101(Cr)-CF ₃ ^a	60	1.0	12	97.5	This work

Reaction conditions: ^a epoxide (10 mmol), catalyst (0.05 mmol), TBABr (0.1 mmol, 1 mol%) under CO₂ pressure (1.0 MPa), temperature (60 °C), time (12 h). ^b Determined by GC. ^c Epoxide (10 mmol), catalyst (40 μmol), CO₂ pressure (0.1 MPa), temperature (298 K), time (48 h). ^d Epoxide (10 mmol), CO₂ pressure (0.5 MPa), temperature (353 K), time (10 h). ^e Epoxide (30 mmol), catalyst (0.27 mmol).⁵

Reference

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