Supplementary Material

Suitability of Hydrophilic and Hydrophobic Metal–Organic Frameworks as Porous Matrices for CO_2 Hydrate Formation

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S1. Synthesis of HKUST-1 and ZIF-8

S1.1. Synthesis of HKUST-1

HKUST-1 was prepared by a modified solvothermal procedure. The reagents were $Cu(NO_3)_2 \cdot 3H_2O$ (99%, Shanghai Macklin Biochemical Co., Ltd.), 1,3,5-benzenetricarboxylic acid (98%, Shanghai Energy Chemical Technology Co., Ltd.), N,N-dimethylformamide (DMF, 99.5%, Xilong Scientific Co., Ltd.), anhydrous ethanol (99.5%, Shanghai Lingfeng Chemical Reagent Co., Ltd.), and deionized water.

$Cu(NO_3)_2 \cdot 3H_2O$ (2.6 g) was dissolved in deionized water (30 mL), and 1,3,5-benzenetricarboxylic acid (0.68 g) was dissolved separately in ethanol (30 mL). The solutions were combined and stirred at room temperature for 1 h. DMF (2 mL) was added, and stirring continued for 10 min. The mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 353 K for approximately 20 h. After cooling to room temperature, the precipitate was centrifuged, washed with ethanol and deionized water 3–5 times, and oven-dried to obtain HKUST-1 (Figure S1) [35].

S1.2. Synthesis of ZIF-8

ZIF-8 was prepared by stirring at room temperature using $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Xilong Scientific Co., Ltd.), 2-methylimidazole (99%, Shanghai Macklin Biochemical Co., Ltd.), and methanol (99.5%, Shanghai Lingfeng Chemical Reagent Co., Ltd.) [32,36].

2-Methylimidazole (3.3 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 g) were separately dissolved in methanol (35 mL each). The solutions were mixed and stirred at room temperature for 24 h. The precipitate was centrifuged, washed with methanol 3–5 times, and dried at 353 K for 12 h to obtain ZIF-8 (Figure S1).

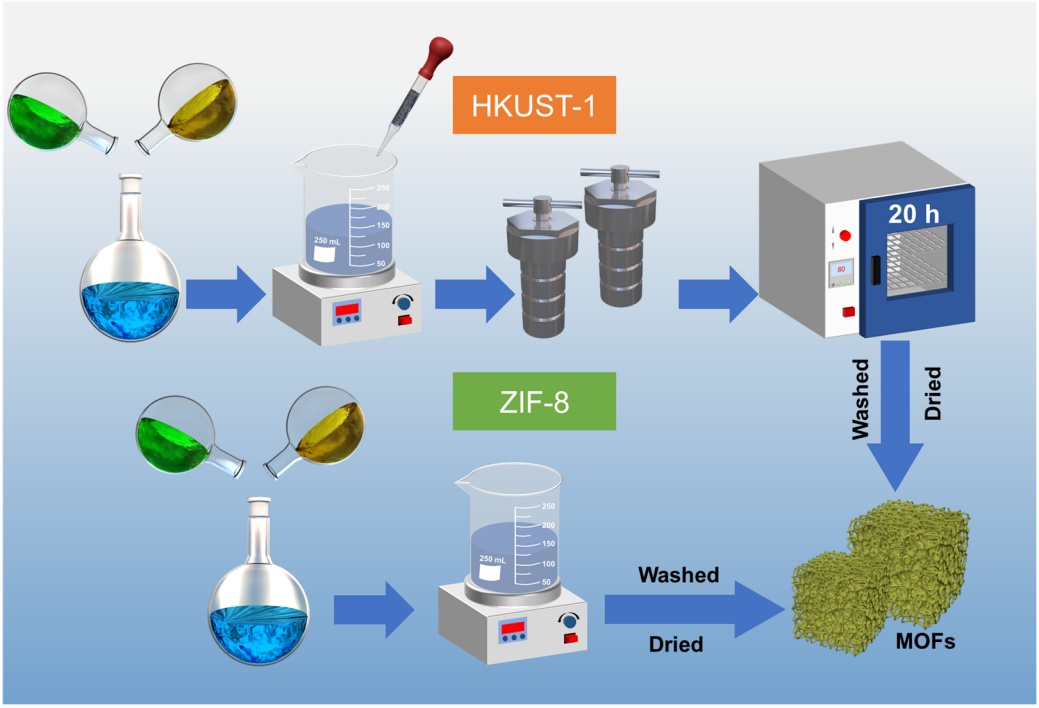


Figure S1. Schematic of the HKUST-1 and ZIF-8 preparation procedures.

S2. Characterization methods

N_2 adsorption–desorption measurements were performed using an ASAP 2460 surface-area and porosity analyzer (Micromeritics, USA) to determine accessible surface area, pore volume, and model-derived pore-size distributions. X-ray diffraction (XRD) was measured using an Empyrean diffractometer (Malvern Panalytical, Netherlands) at 45 kV and 40 mA over 2θ = 5–40°, with a step size of 0.01°. Particle-size distributions were measured using an SZ-100V2 analyzer (HORIBA Scientific, France). The initial micropore-size distributions were analyzed using the Horváth–Kawazoe method (main-text Figure 1). The larger pore-width distributions shown in main-text Figure 11 were obtained from N2 sorption data; their calculation model and fitting settings should be verified against the instrument analysis records before quantitative comparison.

S3. High-pressure DSC measurements

High-pressure differential scanning calorimetry (DSC) was used to examine ice- and CO_2 hydrate-associated thermal transitions in MOF–water powder samples at different nominal water loadings, CO_2 charging pressures, and minimum temperatures. The selected initial charging pressures were 1.9, 2.1, 2.5, 2.8, and 3.1 MPa; the usual minimum temperature was 261 K. Selected experiments employed a lower minimum temperature of 253 K or a higher initial charging pressure of 5 MPa. Dynamic DSC peak temperatures are treated as apparent transition conditions rather than independently established phase-equilibrium points. Experimental materials are summarized in Table S1.

For each measurement, a MOF powder sample was placed in the DSC sample cell, and deionized water was added by micropipette according to the target nominal pore-volume-based loading. The DSC chamber was purged with Ar as a protective gas; after evacuation, CO_2 was charged using a high-pressure pump. Figure S2 shows the experimental apparatus and a representative temperature and heat-flow program. Initial CO_2 charging pressure should be distinguished from the pressure recorded at a particular thermal transition.

Samples were held at 293 K for 0.5 h, cooled to the selected minimum temperature at 0.05 K min^{-1}, held for 5–6 h, and reheated to 293 K at the same rate, followed by a further 0.5 h hold. Heat-flow events during cooling and heating were examined for features consistent with crystallization, ice melting, and hydrate dissociation. Assignment of any individual peak requires consideration of the simultaneous pressure–temperature path and possible overlapping transitions; a heat-flow event alone does not uniquely identify a phase.

The DSC peak area was evaluated using the instrument calibration relationship:

$$\Delta H = K(\mathrm{T}) \times A \tag{S1}$$

Here, K(T) is the temperature-dependent instrument calibration factor and A is the integrated peak area. The equation gives the calibrated peak integral. Conversion to a mass-specific enthalpy (J g−1) additionally

requires a defined sample-mass denominator. The mass basis and baseline-integration settings for the reported data must be checked against the original measurement files before absolute enthalpy comparisons. Nominal water loading was calculated as:

$$S_v = (V_{water} / V_{p,total}) \times 100\% \quad \text{(S2)}$$

where Vwater is the volume of added water and Vp,total is the estimated total dry-MOF pore volume. The pore-volume estimate is given by:

$$V_{p,total} = m_{MOF} \times v_p \quad \text{(S3)}$$

where mMOF is the dry MOF mass and vp is its measured specific pore volume. Thus, Sv is a nominal preparation ratio, not a direct measurement of water occupancy within individual micropores; values above 100% are possible because added water can also occupy external and interparticle regions.

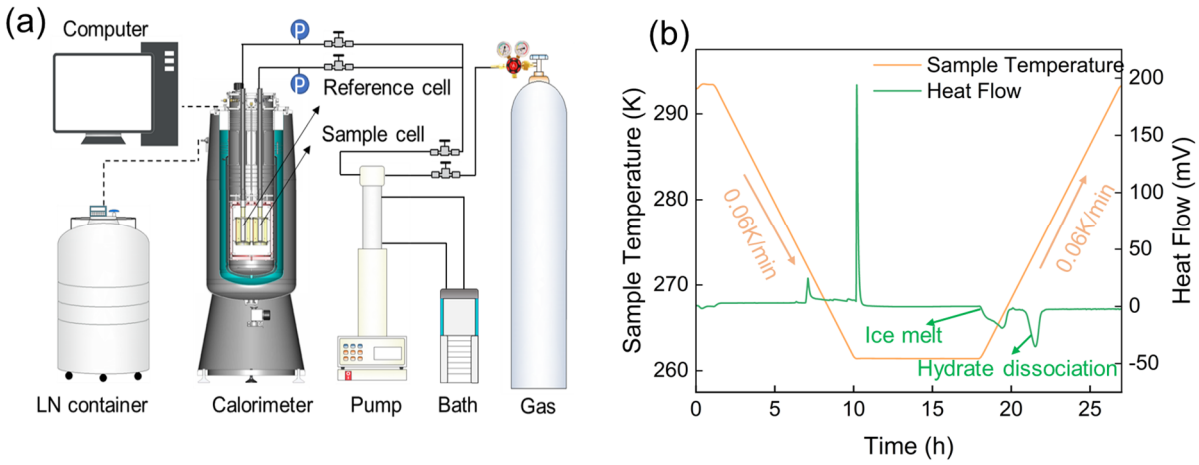


Figure S2. (a) High-pressure DSC apparatus and (b) representative temperature program and heat-flow response. Thermal-event labels indicate tentative peak assignments, not independently verified phase equilibria.

Table S1 Materials.

Experimental Material	Purity	Source
HKUST-1	---	Laboratory-synthesized
ZIF-8	---	Laboratory-synthesized
CO_2 gas	99.99%	Shenzhen Huatepeng Special Gas Co., Ltd.
Ar gas	99.99%	Shenzhen Huatepeng Special Gas Co., Ltd.
Deionized water	18.2 MΩ·cm	Laboratory ultrapure water system

S4. Cyclic stability tests

Repeated cooling–heating exposure of HKUST-1 and ZIF-8 was investigated in a high-pressure CO_2–water reactor (Figure S3). Both materials were prepared at the same nominal pore-volume-based water loading, Sv = 190%, using 500 mg dry MOF in a 10 mL reactor. The volume of added deionized water was calculated from the corresponding dry-material pore volume; thus, equal nominal loadings do not necessarily require identical water volumes for HKUST-1 and ZIF-8. The reactor was charged to an initial CO_2 pressure of 2.8 MPa at 296 K.

After a 30 min initial hold at 296 K, the bath was cooled to 275 K and held for 10–11 h, followed by reheating to 296 K and a 4 h hold. One cooling–heating sequence was defined as one cycle. Samples recovered after selected numbers of cycles were dried and characterized by N_2 sorption, particle-size analysis, and XRD, and compared with the as-prepared materials. For the N_2 sorption measurements of recovered samples, the main text specifies drying and degassing at 393 K for 7 h. These tests establish structural changes after exposure to

hydrate-forming temperature–pressure conditions, but do not confirm that hydrate formed and dissociated in every cycle for either material.

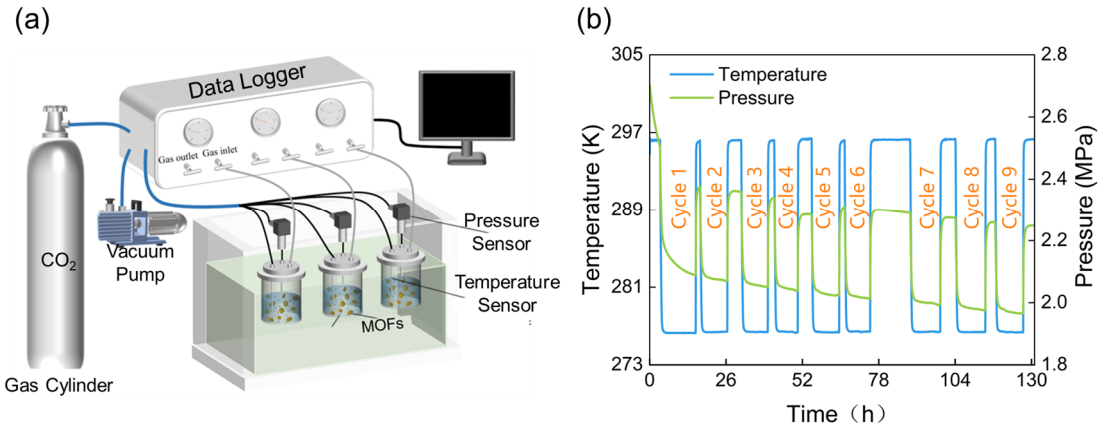


Figure S3. (a) Experimental apparatus for repeated CO_2–water thermal cycling and (b) representative temperature and pressure profiles during cycling.

References

32. Liu, X.; Chen, H.; Yuan, J.; Li, X.; Yu, J., Evaluation and screening of metal-organic frameworks for the adsorption and separation of methane and hydrogen. *Mater. Today Commun.* **2022,** 33, 104602.

35. Jeong, N. C.; Samanta, B.; Lee, C. Y.; Farha, O. K.; Hupp, J. T., Coordination-Chemistry Control of Proton Conductivity in the Iconic Metal–Organic Framework Material HKUST-1. *Journal of the American Chemical Society* **2012,** 134, (1), 51-54.

36. Venna, S. R.; Jasinski, J. B.; Carreon, M. A., Structural Evolution of Zeolitic Imidazolate Framework-8. *Journal of the American Chemical Society* **2010,** 132, (51), 18030-18033.