Supplementary Material

A commercially scalable MOF adsorbent Cu-BTC for helium recovery from natural gas: Performance and mechanism studies at room temperature and lower temperatures

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Table S1. Atomic charges and bond length data of adsorbate molecules CO_2, CH_4, and N_2

Adsorbate	Parameter	Value
CO_2	C atomic charge	0.6512
	O atomic charge	-0.3256
	C=O bond length (Å)	1.196
CH_4	C atomic charge	-0.24
	H atomic charge	0.06
	C-H bond length (Å)	1.109
N_2	N atomic charge	0
	N≡N bond length (Å)	1.12

Table S2. Fitting parameters of single-component gas adsorption isotherms of CO_2, CH_4, N_2, and He on Cu-BTC

Adsorbate	Temperature (K)	Parameter	Simulation data	Experimental data
CO_2	298	n_m (mmol·g^{-1})	17.4858	13.7039
		b (kPa^{-1})	0.0017	0.0042
		R^2 (%)	99.773	99.967
CH_4	298	n_m (mmol·g^{-1})	14.6315	15.7576
		b (kPa^{-1})	0.0008	0.0006
		R^2 (%)	99.949	99.985
	200	n_m (mmol·g^{-1})	18.287	15.3146
		b (kPa^{-1})	0.0102	0.0147
		R^2 (%)	99.71	99.647
N_2	298	n_m (mmol·g^{-1})	12.4195	13.5074
		b (kPa^{-1})	0.0004	0.0002
		R^2 (%)	99.965	99.994
	200	n_m (mmol·g^{-1})	16.3225	13.0877
		b (kPa^{-1})	0.0025	0.0029
		R^2 (%)	99.855	99.945
He	298	k_H (mmol·g^{-1}·kPa^{-1})	0.00027	0.00035
		R^2 (%)	99.992	99.985
	200	k_H (mmol·g^{-1}·kPa^{-1})	0.00045	0.00045
		R^2 (%)	99.985	99.981

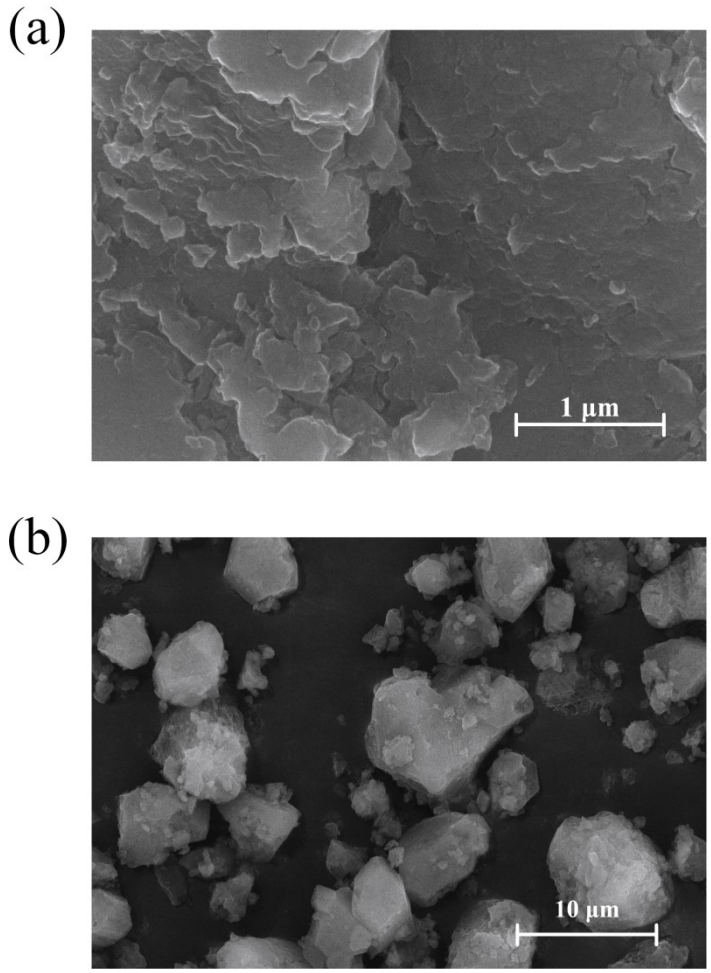

Fig. S1. SEM images of Cu-BTC powder

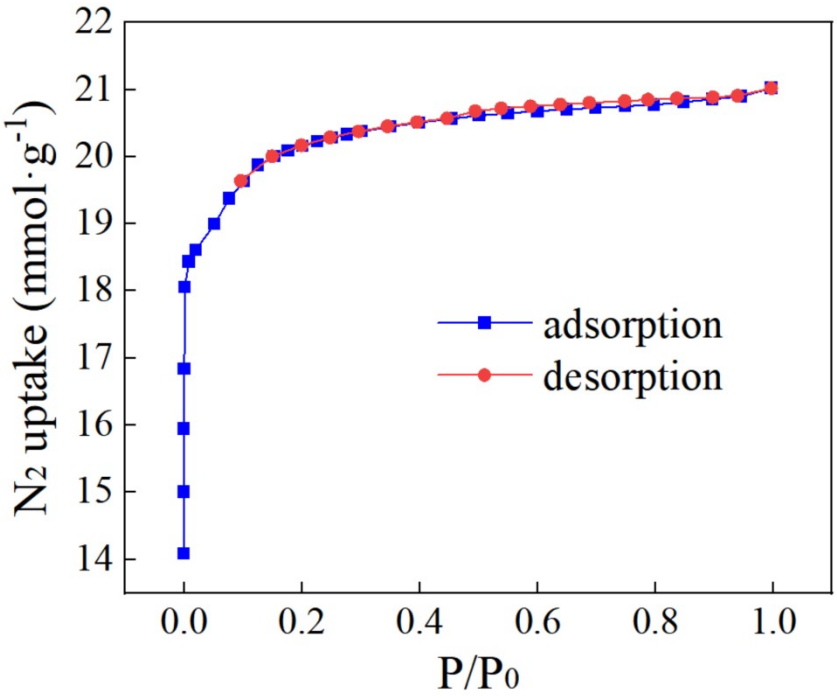

Fig. S2. Adsorption-desorption isotherms of N_2 on Cu-BTC sample at 77.3 K, used for calculating the BET specific surface area, where P is the equilibrium pressure after adsorption and P_0 is the saturation vapor pressure of the adsorbate at the adsorption temperature.

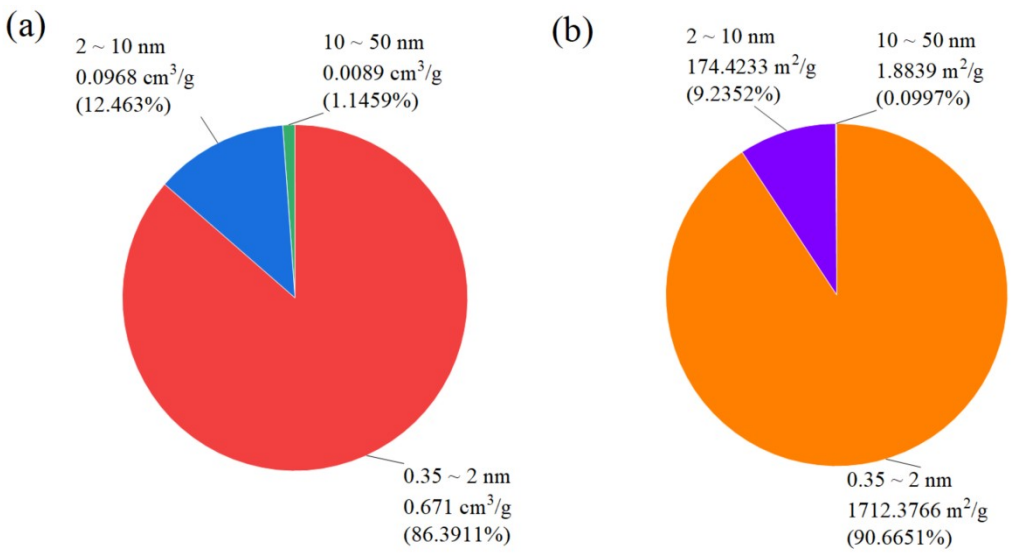

Fig. S3. Pore size distribution of Cu-BTC sample based on (a) pore volume and (b) pore area.

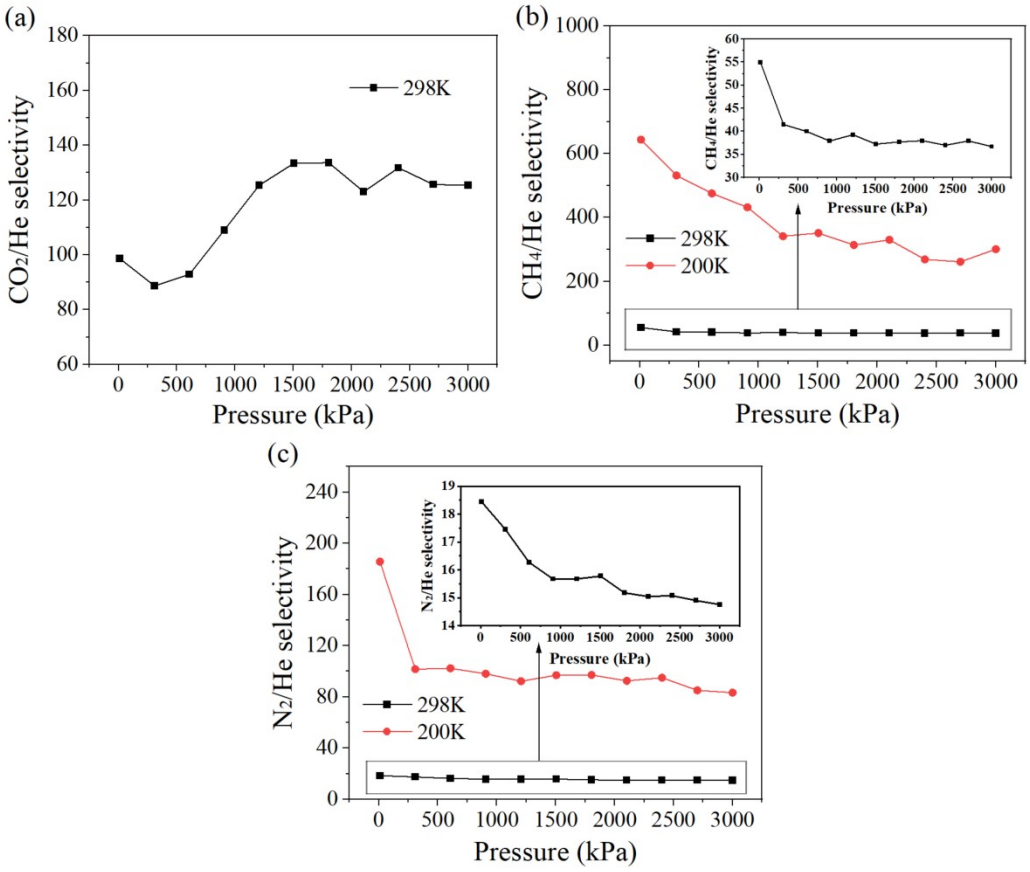

Fig. S4. The GCMC simulation-derived selectivity adsorption coefficients of Cu-BTC for CO_2/He (50:50) (a) at 298 K, CH_4/He (50:50) (b) at 298 K and 200 K, and N_2/He (50:50) (c) mixed gases at 298 K.

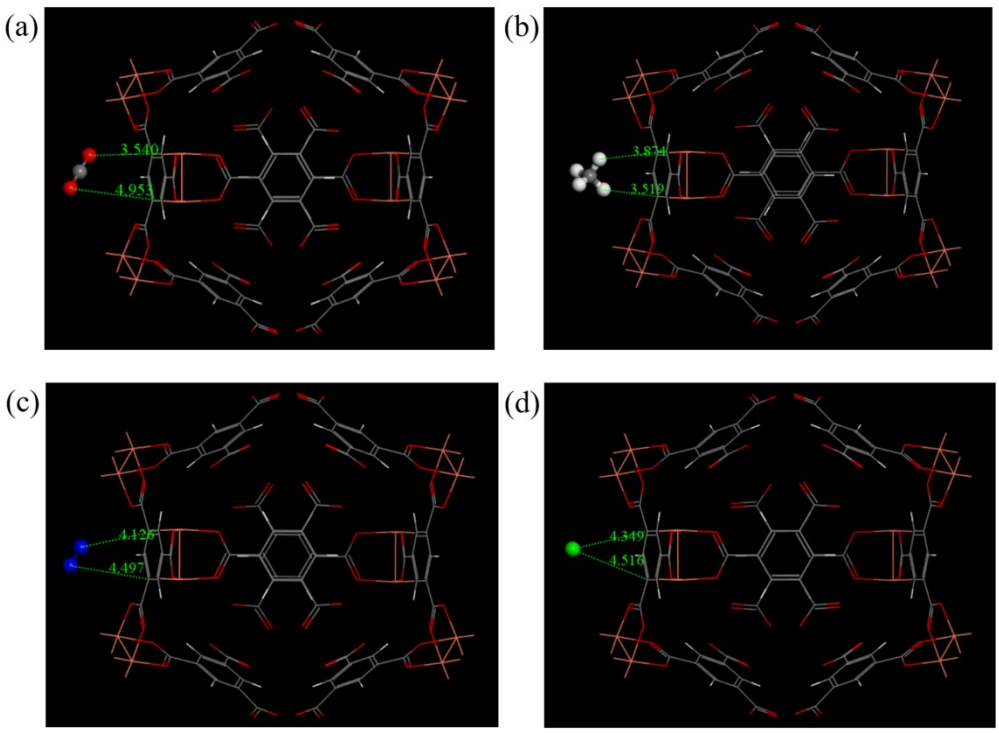

Fig. S5. Adsorption configurations of CO_2 (a), CH_4 (b), N_2 (c), and He (d) at the B site in Cu-BTC; atom colors: C (gray), O (red), N (blue), H (white), Cu (orange), He (green).

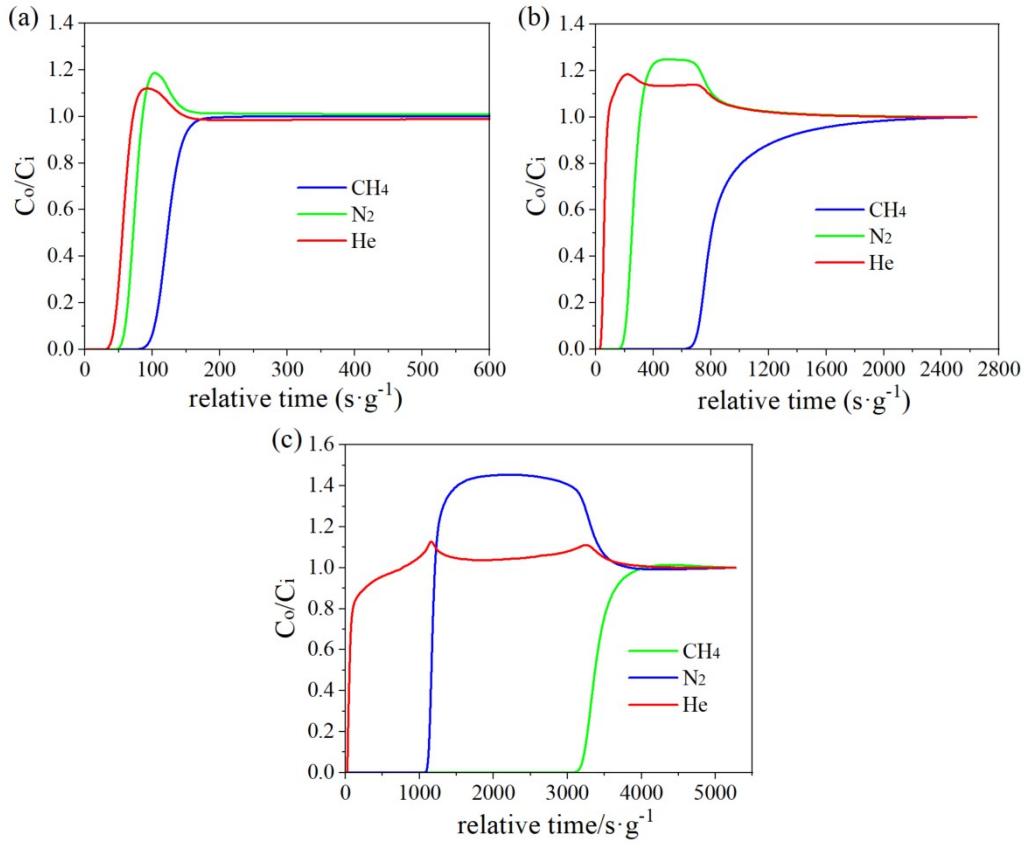

Fig. S6. Adsorption breakthrough curves of CH_4/N_2/He (33:33:33) ternary mixed gas in Cu-BTC at 298 K (a), 200 K (b), and 150 K (c). The test pressure is 101.324 kPa, with the x-axis representing the ratio of time to sample mass and the y-axis representing the ratio of outlet to inlet concentration for each component.

BET specific surface area calculation method:

Based on the adsorption-desorption isotherm data in Fig. S2, select multiple adsorption equilibrium points. Plot a scatter diagram with P/P_0 on the x-axis and $P/P_0/[V(1-P/P_0)]$ on the y-axis, and perform a linear fit for all data points. Here, V is the adsorption capacity of the adsorbate on the adsorbent at equilibrium pressure P ($cm^3 \cdot g^{-1}$). According to the BET adsorption model, the equation of the fitted line can be derived as shown in Equation (1):

$$\frac{P/P_0}{V\left(1-P/P_0\right)}=\frac{1}{V_m \times C}+\frac{C-1}{V_m \times C}\times\frac{P}{P_0} \quad \text{* MERGEFORMAT (1)}$$

Where V_m is the monolayer saturated adsorption capacity of the adsorbent for the adsorbate, and C is a constant related to the adsorption performance of the adsorbent. The value of V_m can be determined from the slope a and intercept b of the fitted line. The calculation formula is given by Equation (2):

$$V_m=\frac{1}{a+b} \quad \text{* MERGEFORMAT (2)}$$

The calculation formula for the BET specific surface area S is shown in Equation (3):

$$S=N_A \times a_m / 22414 \times V_m \quad \text{* MERGEFORMAT (3)}$$

Where N_A is Avogadro's constant, 6.02×10^{23} mol^{-1}; a_m is the cross-sectional area of the adsorbate molecule.

Calculation method for the IAST selectivity adsorption coefficient:

IAST draws on Raoult's law and introduces surface spreading pressure to study adsorption phase equilibrium. The partial pressure P_i of gas component *i* is:

$$P_i = P_i^0(\pi_i)x_i \qquad \text{* MERGEFORMAT (4)}$$

Where x_i and π_i are the mole fraction and surface spreading pressure of component i in the adsorbed phase, respectively. P_i^0 is the pure gas pressure when it has the same surface spreading pressure as the mixture. At adsorption phase equilibrium, the normalized spreading pressure π^* of all components should be equal:

$$\pi_i^* = \frac{\pi_i A}{RT} = \int_0^{P_i^0} \frac{q_i^0(P)}{P} dP \qquad \text{* MERGEFORMAT (5)}$$

$$\pi_1^* = \pi_2^* = \pi_3^* = \cdots = \pi_n^* \qquad \text{* MERGEFORMAT (6)}$$

Where $q_i^0(P)$ is the equilibrium uptake of the pure gas, A is the specific surface area of the adsorbent, and the total adsorption amount n_t is:

$$n_t = 1 \Big/ \sum_{i=1}^{n} \frac{x_i}{q_i^0(P_i^0)} \qquad \text{* MERGEFORMAT (7)}$$

$$\sum_{i=1}^{n} x_i = 1 \qquad \text{* MERGEFORMAT (8)}$$

For a binary mixture composed of components 1 and 2, applying IAST requires satisfying the following conditions:

$$Py_1 = P_1 x_1 \qquad \text{* MERGEFORMAT (9)}$$

$$Py_2 = P_2 x_2 \qquad \text{* MERGEFORMAT (10)}$$

$$x_1 + y_1 = 1 \qquad \text{* MERGEFORMAT (11)}$$

$$x_2 + y_2 = 1 \qquad \text{* MERGEFORMAT (12)}$$

Where P is the total pressure, P_i (i=1, 2) is the pressure of components 1 and 2 when they have the same surface spreading pressure as the mixture, and x_i and y_i (i=1, 2) represent the mole fractions in the adsorbed phase and gas phase, respectively. According to Equation (13), the selectivity adsorption coefficient $S_{1/2}$ can be calculated:

$$S_{1/2} = \frac{x_1/x_2}{y_1/y_2} \qquad \text{* MERGEFORMAT (13)}$$