

Supporting Information

Robust Metal Organic Frameworks with High Industrial Applicability in Efficient Recovery C₃H₈ and C₂H₆ from Natural Gas Upgrading

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1.1 Ideal adsorbed solution theory (IAST) selectivity calculations

IAST calculation is a common method to evaluate adsorption selectivities of binary or multinary mixtures from pure-component adsorption isotherms.[1, 2]

$$S = \frac{X_A/X_B}{Y_A/Y_B} \quad (S1)$$

Where S is the selectivity of component A relative to B. X_A and X_B are the molar fractions of components A and B in the adsorption phase, respectively. Y_A and Y_B are molar fractions of components A and B in the gas phase, respectively. Dual-site Langmuir-Freundlich (DSLFF) equation was used to simulate the isotherms of MOF-303, MIL-160, and CAU-23 shown as follows:[3, 4]

$$q = q_1 \frac{b_1 p^c}{1+b_1 p^c} + q_2 \frac{b_2 p^t}{1+b_2 p^t} \quad (S2)$$

Where p is the equilibrium pressure of the gas phase and adsorbed phase; q_a and q_b are the saturated capacity of site a and b, respectively; b_1 and b_2 are the affinity coefficients of site a and b, respectively; c and t are for the heterogeneity from an ideal homogeneous surface of site a and b, respectively.

1.2 Isostatic heat calculation

The isosteric heat (Q_{st}) was calculated by equation S4. Before the calculation, the isotherms tested at 303 K and 313 K were fitted by the Virial equation (equation S3). p is the pressure described in Pa, N is the adsorbed amount in mmol/g, T is the temperature in K, a_i and b_j are Virial coefficients, and m and n are the number of coefficients used to describe the isotherms, R is the universal gas constant.

$$\ln p = \ln N + \left(\frac{1}{T}\right) \sum_{i=0}^m a_i \times N^i + \sum_{j=0}^n b_j \times N^j \quad (S3)$$

$$Q_{st} = -R \times \sum_{i=0}^m a_i \times N^i \quad (S4)$$

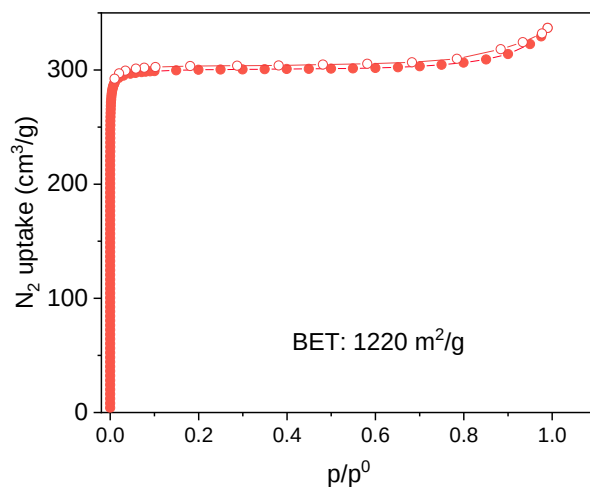


Fig. S1 N_2 adsorption-desorption isotherms of MOF-303 at 77 K.

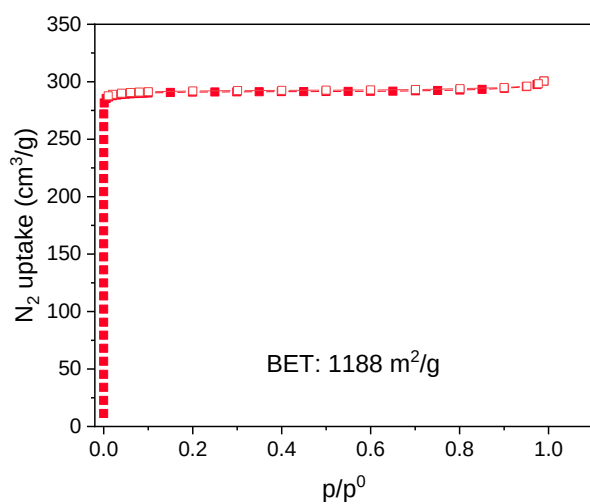


Fig. S2 N_2 adsorption-desorption isotherms of MIL-160 at 77 K.

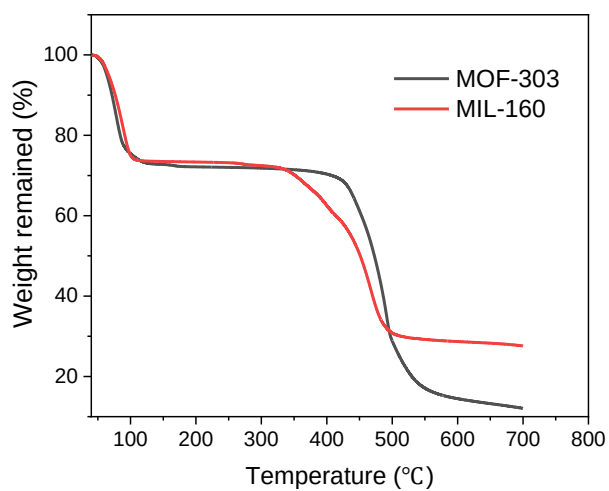


Fig. S3 TGA curves for MOF-303 and MIL-160.

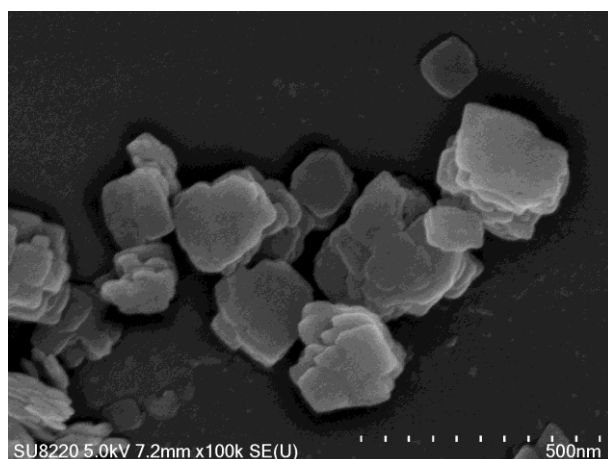


Fig. S4 SEM image of MOF-303.

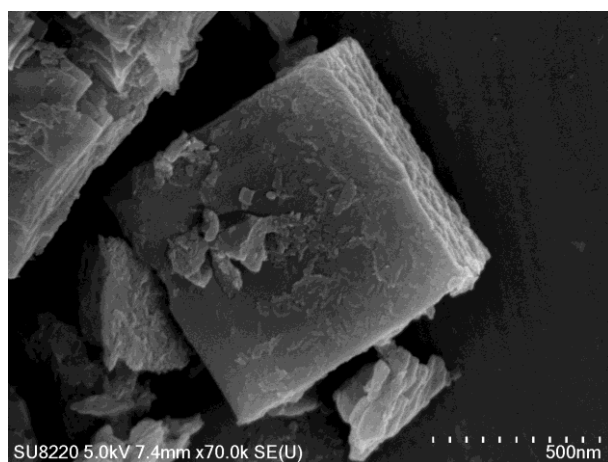


Fig. S5 SEM image of MIL-160.

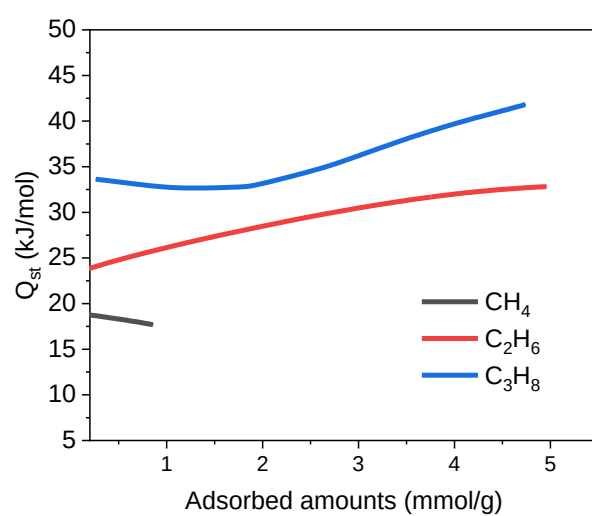


Fig. S6 Isothermic heats of adsorption for C_3H_8 , C_2H_6 and CH_4 on MOF-303.

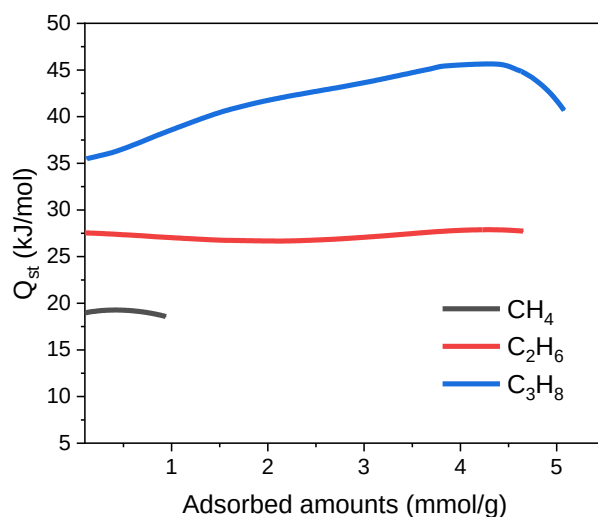


Fig. S7 Isosteric heats of adsorption for C_3H_8 , C_2H_6 and CH_4 on MIL-160.

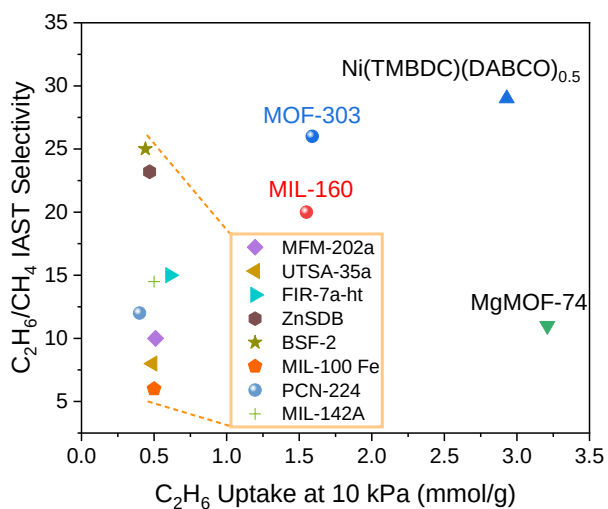


Fig. S8 The uptake amounts of C_2H_6 and IAST selectivities of C_2H_6/CH_4 at 298 K and 10 kPa for MOF-303, MIL-160 and some previously reported top-performing MOFs.

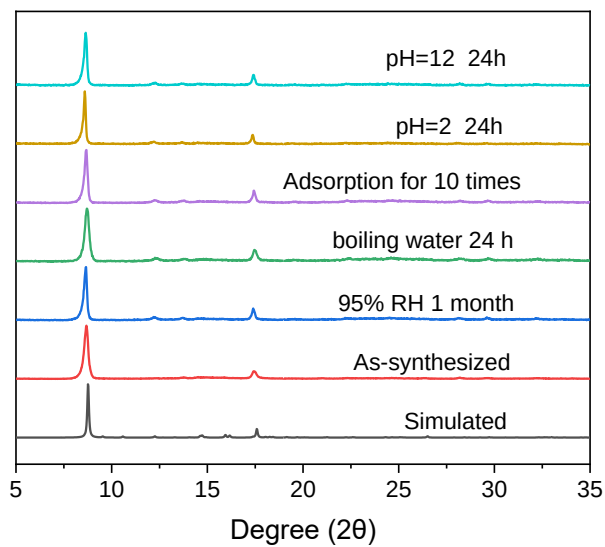


Fig. S9 PXRD patterns of MOF-303 after being treated under different extreme conditions.

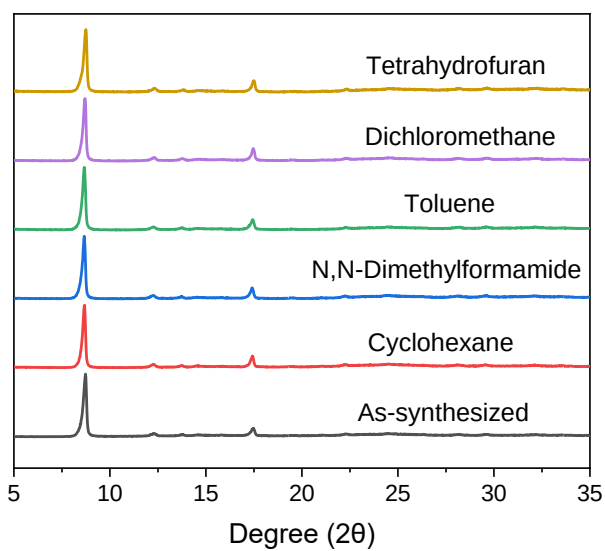


Fig. S10 PXRD patterns of MOF-303 after being treated in different solvents for 48 h.

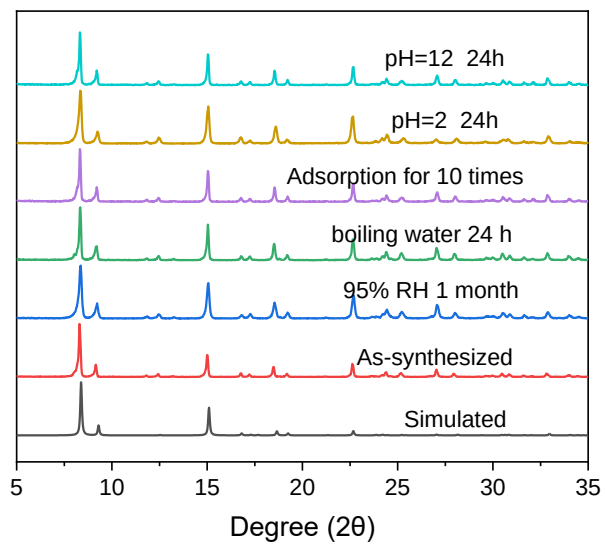


Fig. S11 PXRD patterns of MIL-160 after being treated under different extreme conditions.

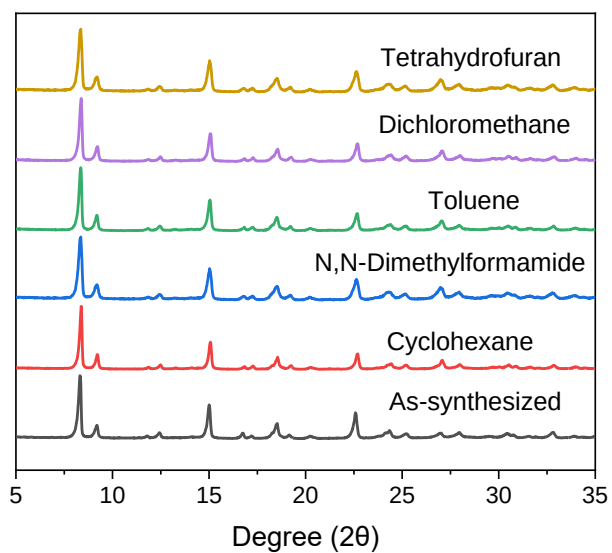


Fig. S12 PXRD patterns of MIL-160 after being treated in different solvents for 48 h.

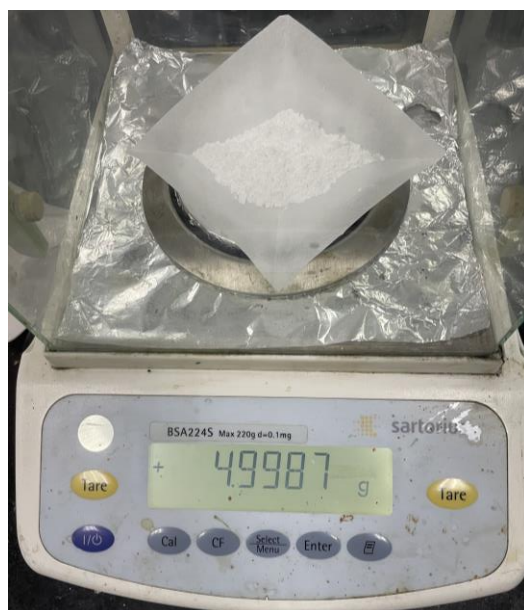


Fig. S13 MOF-303 product of 5 g synthesis.

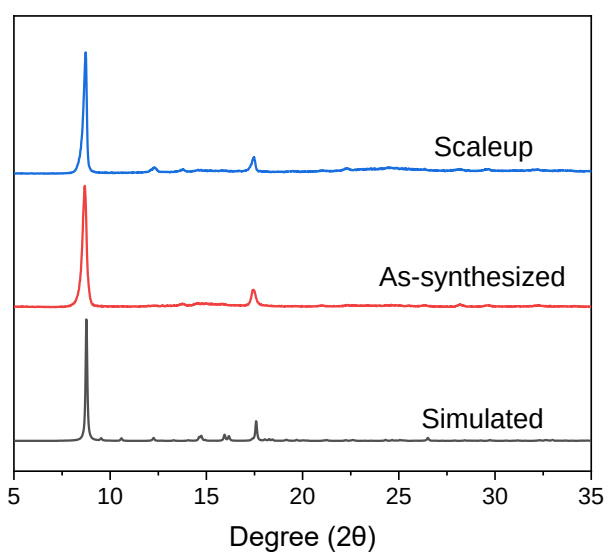


Fig. S14 PXRD patterns of simulated, as-synthesized, and scaled up MOF-303.

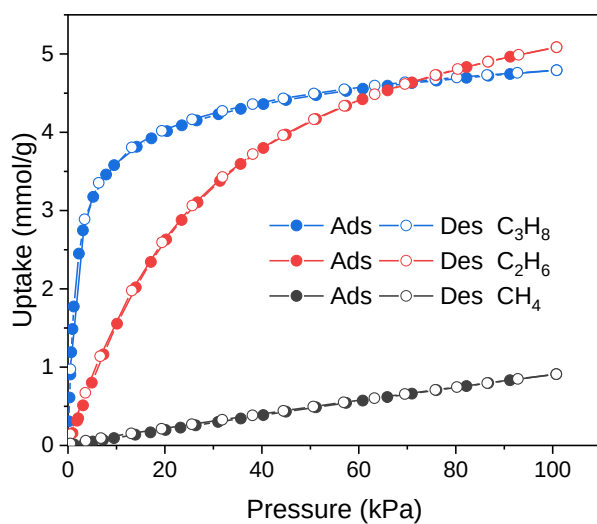


Fig. S15 Adsorption-desorption isotherms of C_3H_8 , C_2H_6 and CH_4 for scaled up MOF-303 at 298K.

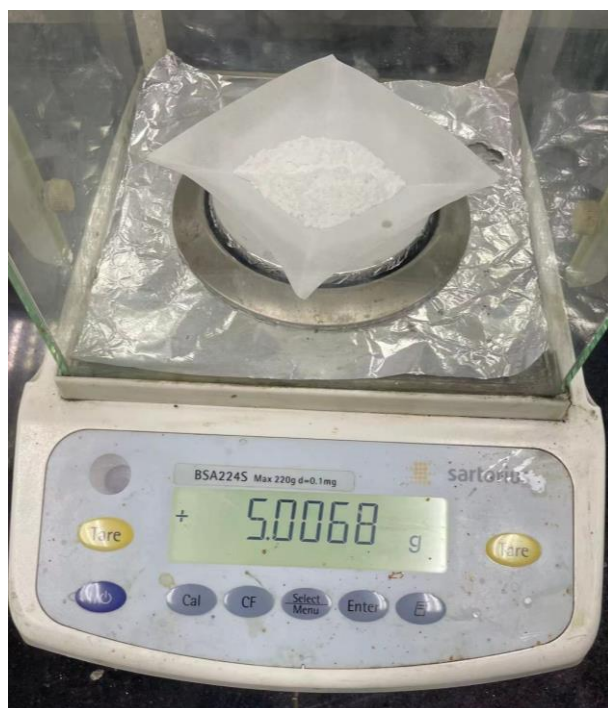


Fig. S16 MIL-160 product of 5 g synthesis.

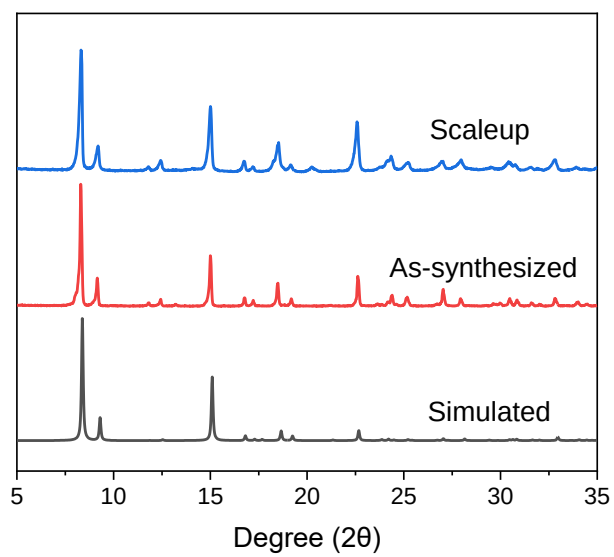


Fig. S17 PXRD patterns of simulated, as-synthesized, and scaled up MIL-160.

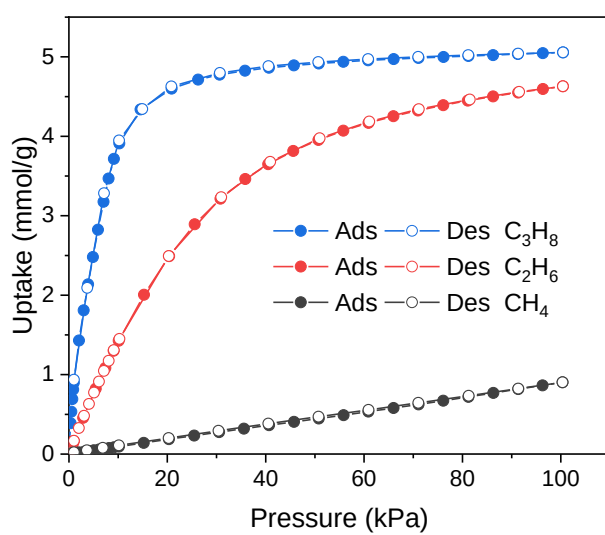


Fig. S18 Adsorption-desorption isotherms of C_3H_8 , C_2H_6 and CH_4 for scaled up MIL-160 at 298K.

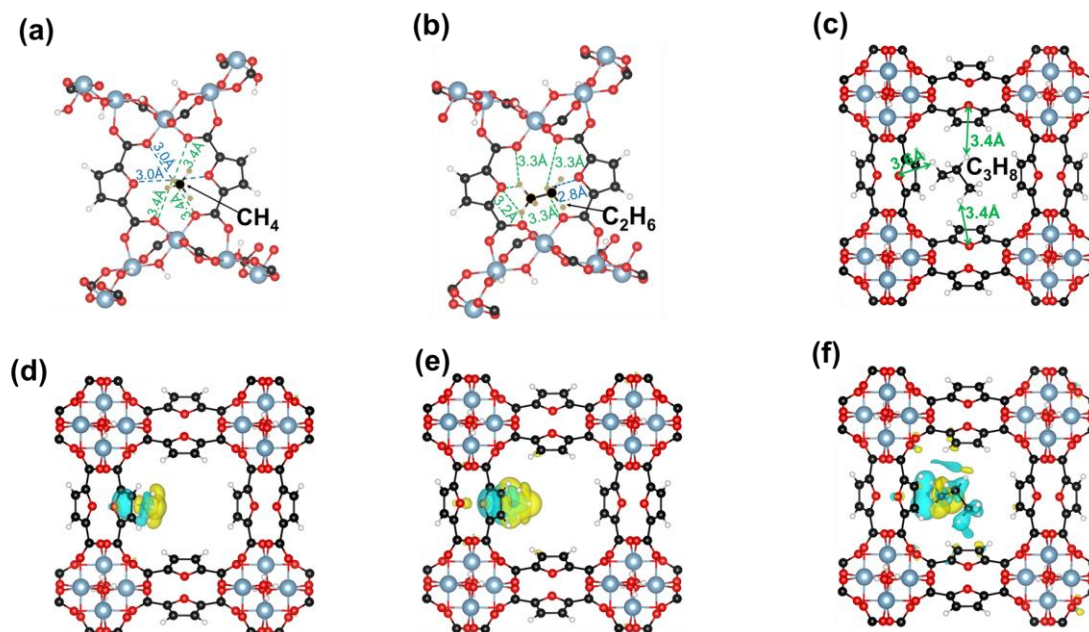


Fig. S19 MIL-160 structure showing (a) CH_4 , (b) C_2H_6 and (c) C_3H_8 binding at their primary site, interacting with the O atoms of the linkers with distances shown. Induced charge densities for (d) CH_4 , (e) C_2H_6 and (f) C_3H_8 (iso-level = 0.0005 electrons/ $\text{\AA}^3$). Blue highlighted areas represent a depletion of charge and yellow areas an increase in charge after the guest molecule occupies a binding site.

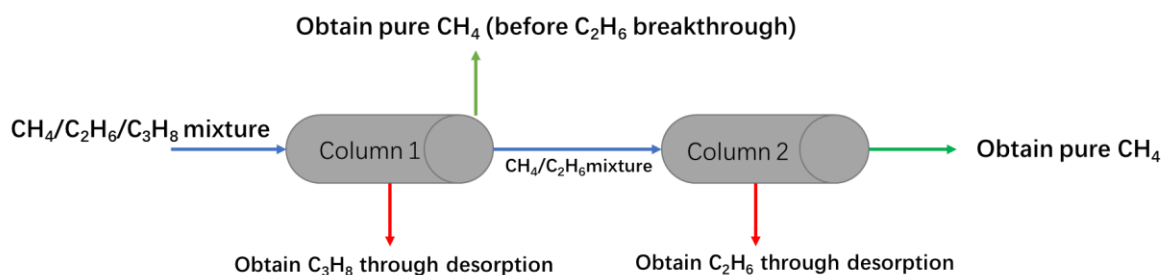


Fig. S20 Individual recovery C_3H_8 and C_2H_6 from natural gas through two separated adsorbent columns.

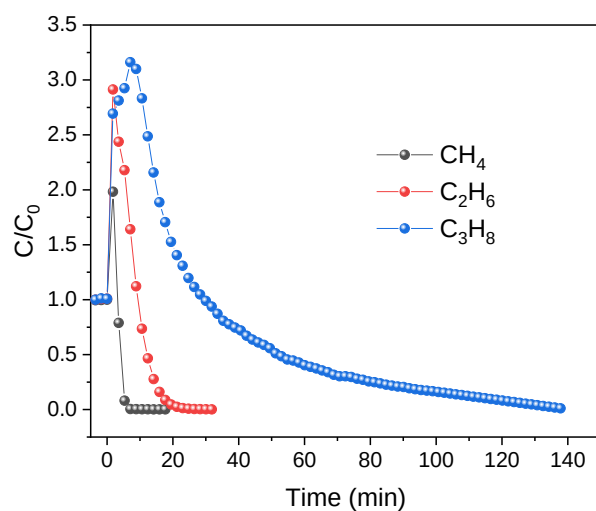


Fig. S21 Desorption curves of MIL-160 packed column at 333 K under 2 mL/min N₂ flow.

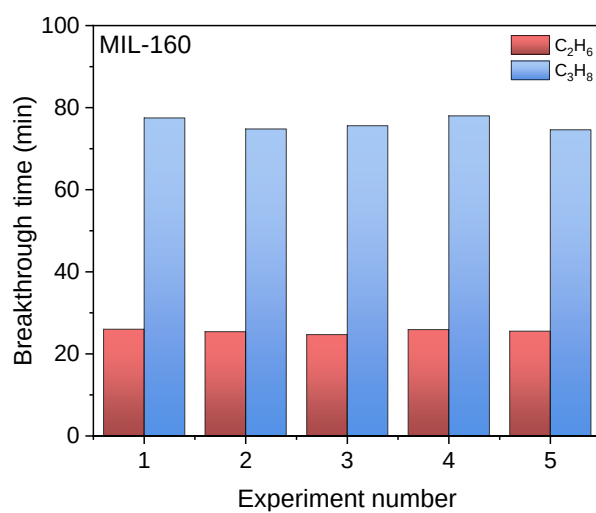


Fig. S22 C₃H₈ and C₂H₆ breakthrough times of MIL-160 in consecutive five cycles of breakthrough experiments (298 K and 100 kPa).

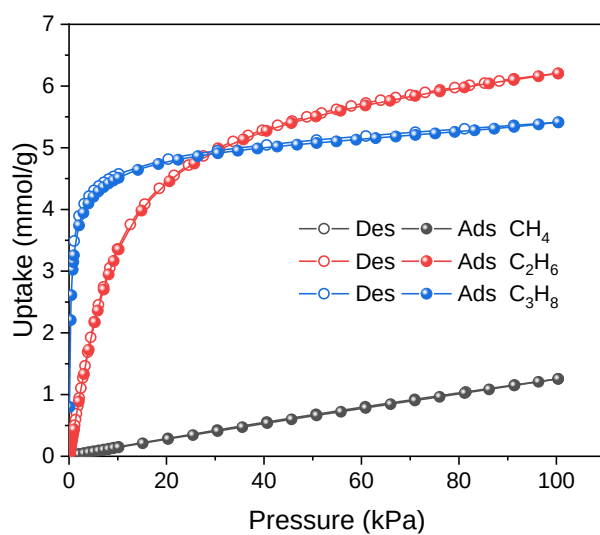


Fig. S23 Adsorption-desorption isotherms of C₃H₈, C₂H₆, and CH₄ in MOF-303 at 273K.

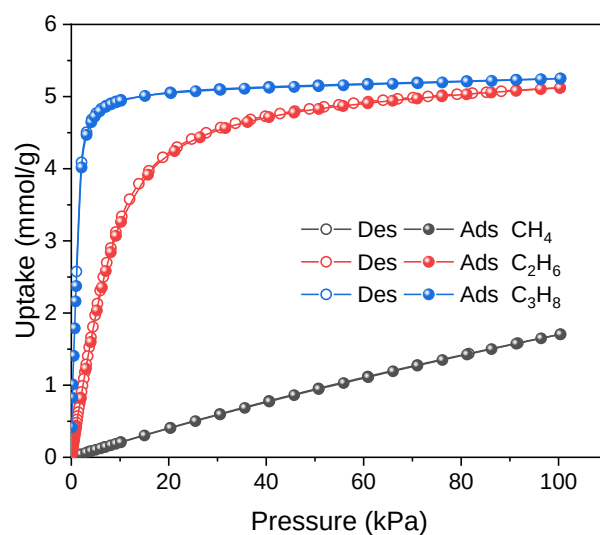


Fig. S24 Adsorption-desorption isotherms of C₃H₈, C₂H₆, and CH₄ in MIL-160 at 273K.

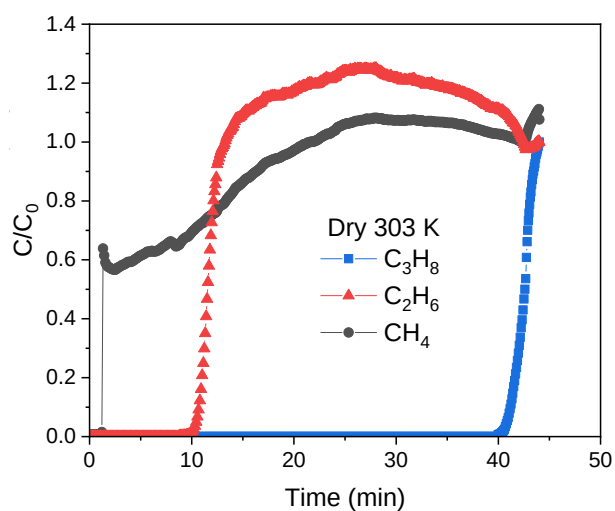


Fig. S25 Ternary breakthrough curves ($\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$, 85:10:5, v/v/v) of 100 mg MOF-303 sample at dry condition and 298 K with flow rate of 3 ml/min.

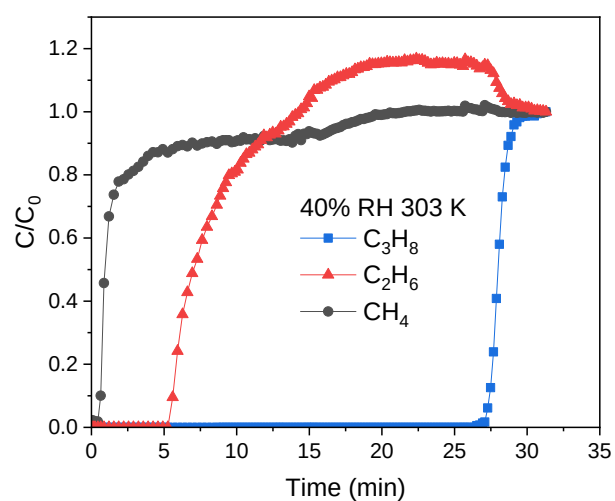


Fig. S26 Ternary breakthrough curves ($\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$, 85:10:5, v/v/v) of 100 mg MOF-303 sample at 40% RH and 298 K with flow rate of 3 ml/min.

Table S1. Virial fitting parameters of MOF-303 for CH₄, C₂H₆, and C₃H₈.

parameters	CH ₄	C ₂ H ₆	C ₃ H ₈
a0	-2272.32392	-2788.86971	-4041.42364
a1	0.57756	-14.0571	-2.45369
a2	2.13032	0.10145	0.23258
a3	-0.20128	-0.00106	-0.00357
a4	0.00923	6.38925E-6	1.75719E-5
a5	-1.46518E-4	-1.30439E-8	-2.90127E-8
b0	11.56895	9.7908	11.29752
b1	-0.00855	0.039	-0.02238
b2	-0.00165	-3.16784E-5	2.64246E-4
R²	0.9998	0.99991	0.9991

Table S2. Virial fitting parameters of MIL-160 for CH₄, C₂H₆, and C₃H₈.

parameters	CH ₄	C ₂ H ₆	C ₃ H ₈
a0	-2248.56281	-3314.68682	-4253.38993
a1	-22.73086	0.95676	0.79444
a2	2.39089	0.07284	-0.35785
a3	-0.10065	-0.00118	0.00518
a4	0.00391	2.69031E-6	-2.94497E-5
a5	-5.45086E-5	1.16064E-8	5.92653E-8
b0	11.3583	11.7228	11.90864
b1	0.07344	-0.0183	0.0465
b2	-0.00469	1.9203E-4	-1.11724E-4
R²	0.99994	0.99979	0.99972

Table S3. DSLF fitting parameters of MOF-303 for CH₄, C₂H₆, and C₃H₈ at 298K.

Gas	q1	b1	c	q2	b2	t	R ²
CH ₄	0.55642	5.8121E-9	4.24108	0.62131	0.00748	1.332	0.9995
C ₂ H ₆	4.12416	0.03485	1.21655	1.55931	0.00117	1.69236	0.9998
C ₃ H ₈	3.47401	1.10116	1.11095	2.05609	0.07394	0.66395	0.9994

Table S4. DSLF fitting parameters of MIL-160 for CH₄, C₂H₆, and C₃H₈ at 298K.

Gas	q1	b1	c	q2	b2	t	R ²
CH ₄	1.01126	6.16358E-6	2.64412	0.42715	0.01453	1.34278	0.9997
C ₂ H ₆	0.78666	2.72423E-4	2.71681	4.47389	0.03534	1.12915	1
C ₃ H ₈	3.74521	0.30535	0.93083	1.48055	8.87804E-4	3.54412	0.99999

References

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- [2] Y. Lin, C. Kong, Q. Zhang, L. Chen, Metal-organic frameworks for carbon dioxide capture and methane storage, *Advanced Energy Materials* 7(4) (2017) 1601296.
- [3] Y. Ye, Z. Ma, R.-B. Lin, R. Krishna, W. Zhou, Q. Lin, Z. Zhang, S. Xiang, B. Chen, Pore space partition within a metal–organic framework for highly efficient C₂H₂/CO₂ separation, *Journal of the American Chemical Society* 141(9) (2019) 4130-4136.
- [4] B. Liang, X. Zhang, Y. Xie, R.-B. Lin, R. Krishna, H. Cui, Z. Li, Y. Shi, H. Wu, W. Zhou, An ultramicroporous metal–organic framework for high sieving separation of propylene from propane, *Journal of the American Chemical Society* 142(41) (2020) 17795-17801.