Electronic Supplementary Material (ESI) for Dalton Transactions.

A hydrostable cage-based MOF with open metal sites and Lewis basic sites immobilized in pore surface for efficient separation and purification of natural gas and C_2H_2

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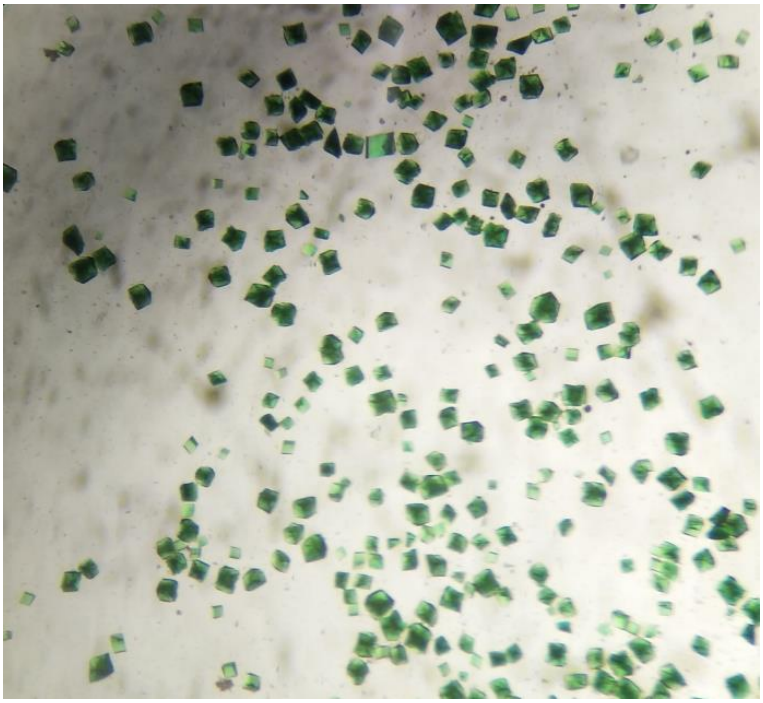


Fig. S1 The electronic photograph of as-synthesized **ZJNU-15**.

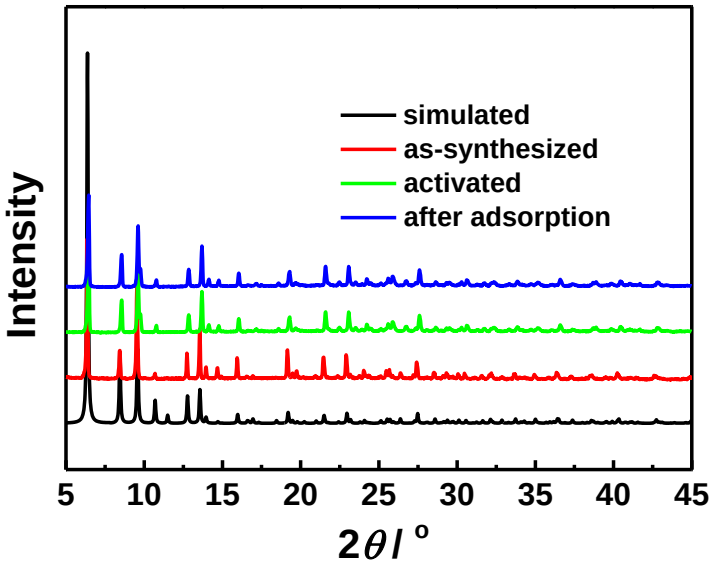


Fig. S2 Comparison of experimental and simulated PXRD patterns of **ZJNU-15**.

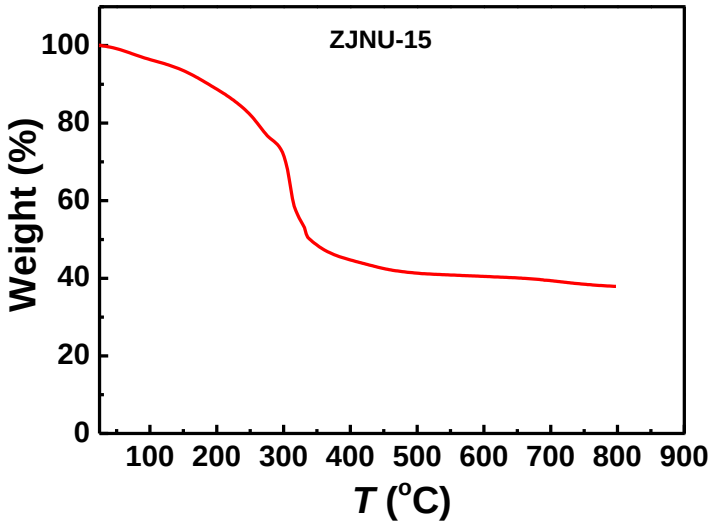


Fig. S3 TGA profile of as-synthesized **ZJNU-15** under N_2 atmosphere.

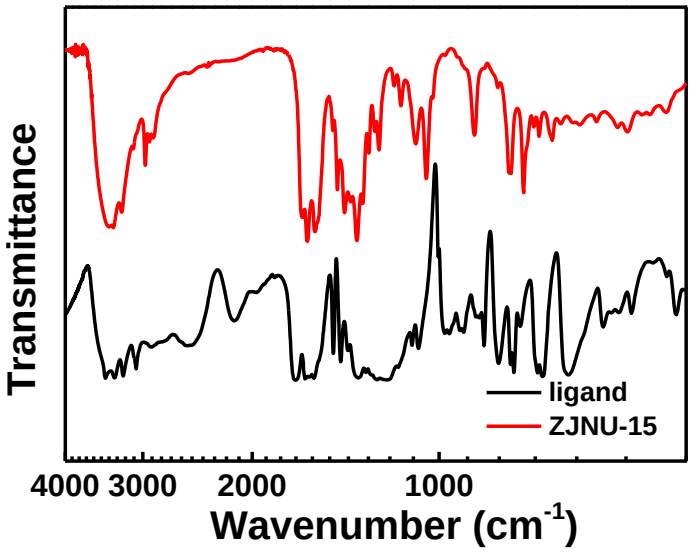
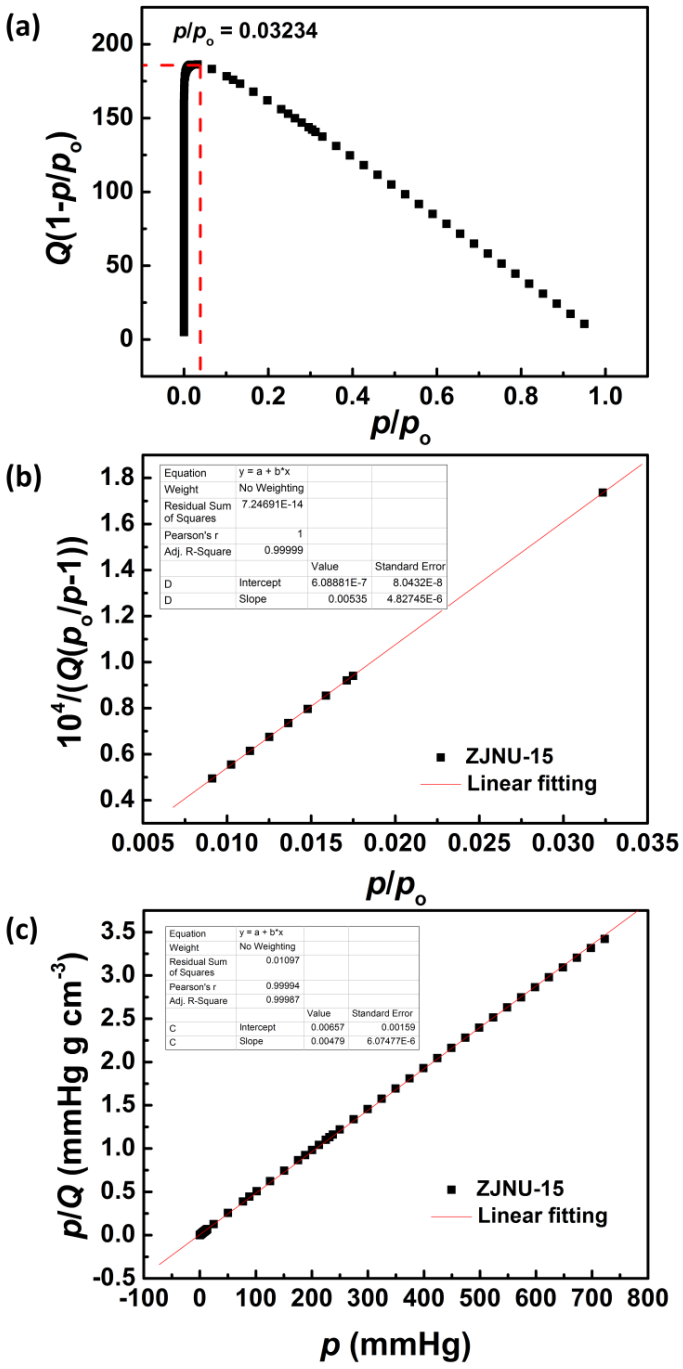


Fig. S4 Comparison of FTIR spectra of as-synthesized **ZJNU-15** and its organic ligand



S_{BET} = 1/(6.08881×10^{-7}+ 0.00535)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 814 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00479)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 909 m^2 g^{-1}

BET constant C = 1 + 0.00535/6.08881×10^{-7} = 8788

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.010555$$

Fig. S5 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-15**.

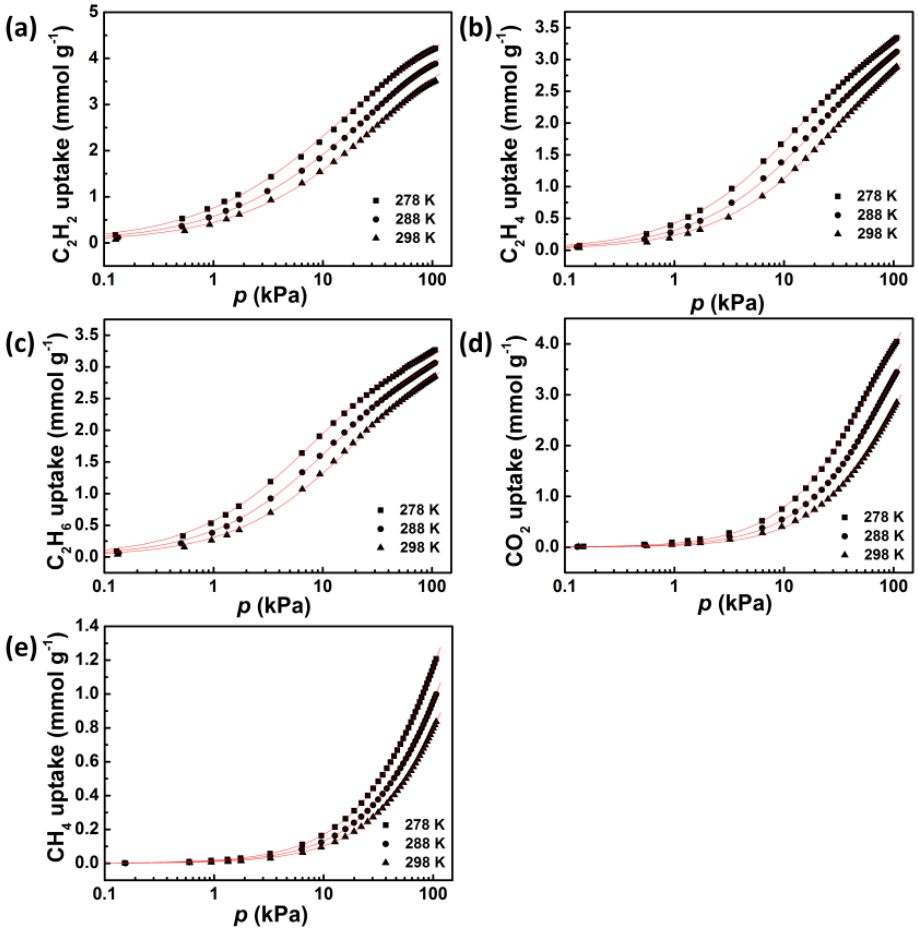
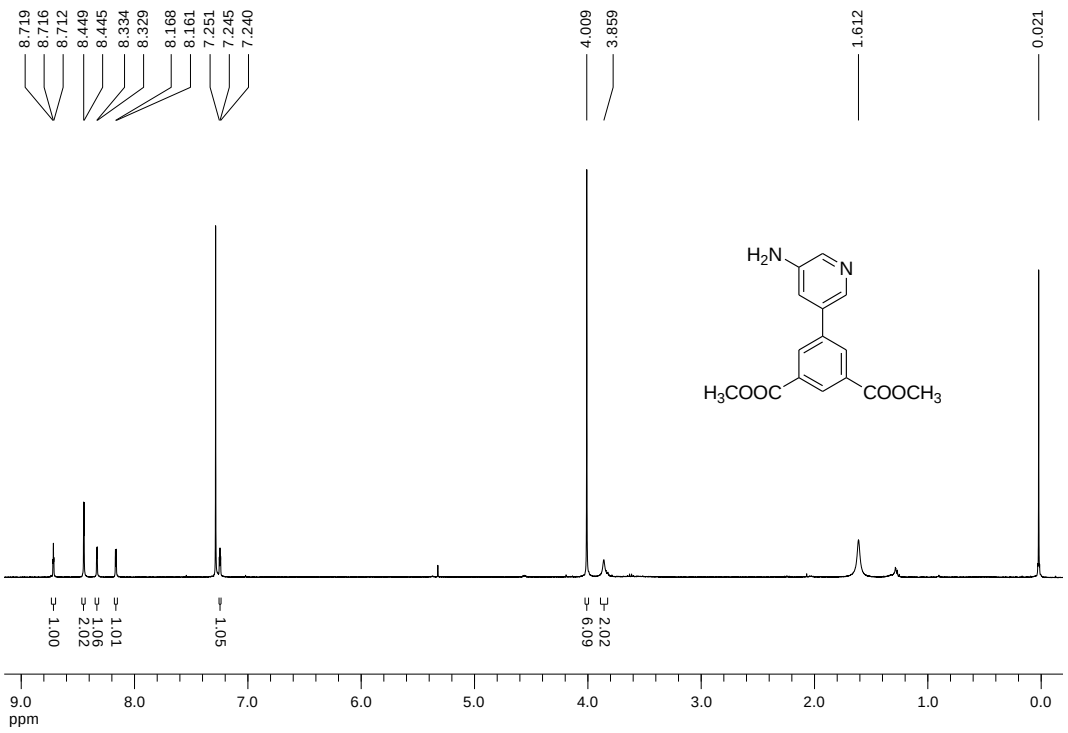


Fig. S6 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) C_2H_4, (c) C_2H_6, (d) CO_2, and (e) CH_4 in **ZJNU-15** with the fitted isotherms at 278 K, 288 K, and 298 K.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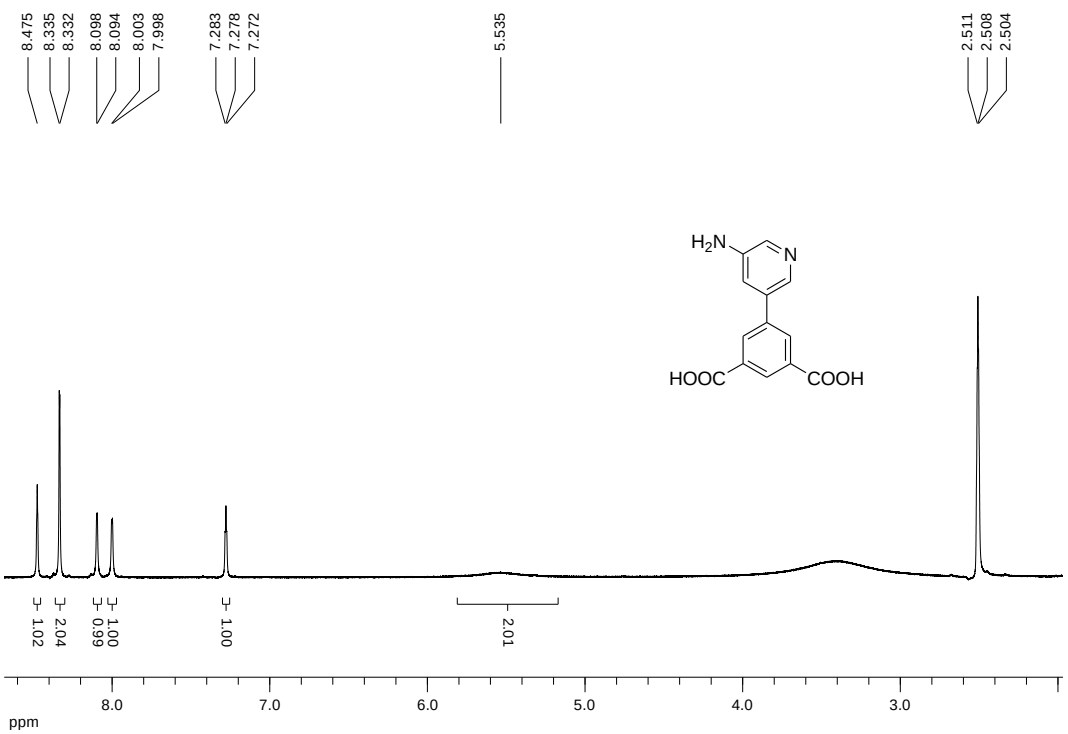
8.716
8.712
8.449
8.445
8.334
8.329
8.168
8.161
7.251
7.245
7.240
4.009
3.859
1.612
0.021
H2N
N
H3COOC
COOCH3
1.00
2.02
1.09
1.01
1.05
6.09
2.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


8.475
8.335
8.332
8.098
8.094
8.003
7.998
7.283
7.278
7.272
5.535
2.511
2.508
2.504
H2N
N
HOOC
COOH
1.02
2.04
0.99
1.00
1.00
2.01
8.0
7.0
6.0
5.0
4.0
3.0
ppm

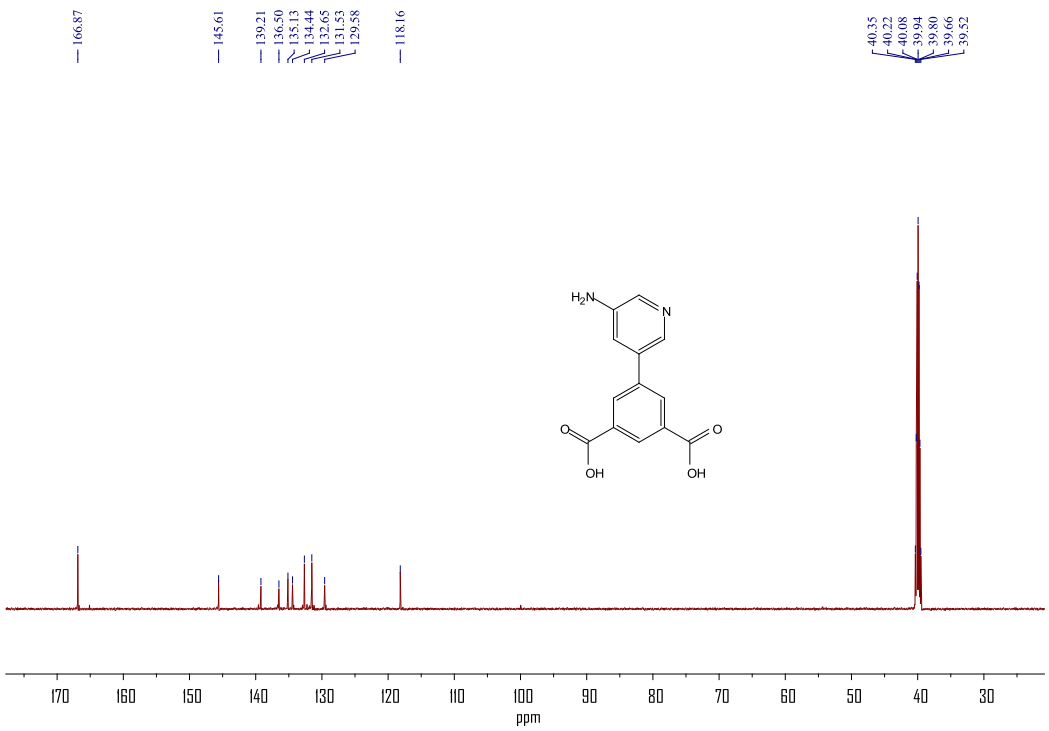


Fig. S7 ^{1}H and ^{13}C NMR spectra

Table S1 Summary of physical parameters of C_2H_2, C_2H_4, C_2H_6, CO_2, and CH_4

Adsorbates	BP (K)	T_c (K)	p_c (bar)	Kinetic diameter (Å)	Molecular dimension (Å)	Polarizability ($\times10^{25}$ cm^3)	Dipole moment ($\times10^{18}$ esu cm)	Quadruple moment ($\times10^{26}$ esu cm^2)
C_2H_2	188.40	308.30	61.14	3.3	3.3×3.3×5.7	33.3-39.3	0	+7.5
C_2H_4	169.42	282.34	50.41	4.163	3.3×4.2×4.8	42.52	0	+1.50
C_2H_6	184.55	305.32	48.72	4.443	3.8×4.1× 4.8	44.4-44.7	0	+0.65
CO_2	216.55	304.12	73.74	3.3	3.2×3.3×5.4	29.11	0	-4.3
CH_4	111.66	190.56	45.99	3.758	3.7×3.7×3.7	25.93	0	0

BP: normal boiling point; T_c: critical temperature; p_c: critical pressure

Table S2 Crystal data and structure refinement for **ZJNU-15**.

MOF	**ZJNU-15**
Empirical formula	$C_{49.50}H_{50.50}Cu_4N_{9.50}O_{17.50}$
Formula weight	1312.65
Temperature (K)	150(2)
λ (Å)	0.71073
Crystal system	Trigonal
Space group	*R-3c :H*
Unit cell dimensions	a = 18.4889(6) Å b = 18.4889(6) Å c = 55.2602(18) Å α = 90° β = 90° γ = 120°
V (Å^3)	16359.3(12)
Z	12
D_c (g cm^{-3})	1.599
μ (mm^{-1})	1.619
F(000)	8040
θ range for data collection (°)	2.465 to 27.486
Limiting indices	$-24 \le h \le 24$ $-23 \le k \le 24$ $-71 \le l \le 70$
Reflections collected / unique	46837 / 4170
R_{int}	0.0379
Max. and min. transmission	0.851 and 0.823
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4170 / 0 / 190
Goodness-of-fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0458 wR_2 = 0.2036
R indices (all data)	R_1 = 0.0495 wR_2 = 0.2129
Largest diff. peak and hole (e·Å^{-3})	0.949 and -3.245
CCDC	1981353

Table S3 Langmuir-Freundlich fitting parameters for adsorption of C_2H_2, C_2H_4, C_2H_6, CO_2, and CH_4 in **ZJNU-15**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	5.43508	2.148×10^{-5}	20.64	0.66069	0.99944
C_2H_4	3.98376	9.18412×10^{-6}	21.89	0.79632	0.99976
C_2H_6	3.64972	5.45569×10^{-6}	24.11	0.78982	0.9995
CO_2	6.60789	1.37095×10^{-7}	26.32	1.04849	0.99984
CH_4	3.35002	2.00532×10^{-6}	18.28	0.99161	0.99995

Table S4 Summary of gas adsorption properties of **ZJNU-15**

ZJNU-15		298 K	288 K	278 K
Uptake capacity[a] ($cm^3\ g^{-1}$, STP)	C_2H_2	78.7	87.1	94.5
	C_2H_4	64.7	70.0	74.9
	C_2H_6	63.9	68.7	73.3
	CO_2	63.8	77.2	90.7
	CH_4	18.7	22.4	27.1
IAST adsorption selectivitiy[a]	C_2H_2/CH_4	37.7	46.9	60.9
	C_2H_4/CH_4	17.7	19.9	22.9
	C_2H_6/CH_4	23.2	26.9	31.9
	CO_2/CH_4	5.0	5.9	7.3
	C_2H_2/CO_2	4.4	4.2	4.1
	C_2H_4/CO_2	2.5	2.3	2.0
	C_2H_6/CO_2	3.0	2.8	2.6
Q_{st}[b] ($kJ\ mol^{-1}$)	C_2H_2	33.6		
	C_2H_4	28.4		
	C_2H_6	30.5		
	CO_2	23.4		
	CH_4	21.0		

[a] at 1 atm; [b] at near zero surface coverage