Supporting Information for the manuscript

Enhanced CO_2 Sorption and Selectivity by Functionalization of a NbO-type Metal-Organic Framework with Polarized Benzothiadiazole Moieties

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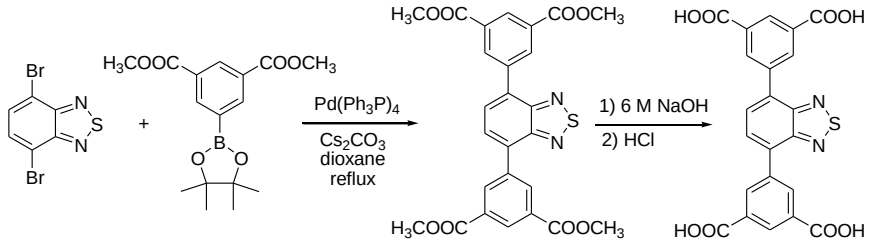
General remarks

All starting materials and reagents for synthesis were commercially available and used as received. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruke Avance 600 spectrometer. Fourier transform infrared (FTIR) spectrum was recorded using a Nicolet 5DX FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out using a Netzsch STA 449C thermal analyzer with a heating rate of 5 ^{o}C min^{-1} in a flowing nitrogen atmosphere (10 mL min^{-1}). Powder X-ray diffraction (PXRD) patterns were recorded on a Philips PW3040/60 automated powder diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.542 Å) with a 2θ range of 5–45°. The elemental analyses were performed with Perkin–Elmer 240 CHN analyzers. The crystal data were collected on a Bruker APEX II diffractometer equipped with a graphite-monochromatized Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by direct methods and expanded with difference Fourier techniques. All calculations were performed using SHELXS-97 and SHELXL-97 program packages. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To have a guest-free framework, the fresh sample was guest-exchanged with dry acetone at least 10 times, filtered and vacuumed at 373 K until the outgas rate was 6 μmHg min^{-1} prior to measurements. A sample of 113.7 mg was used for the sorption measurements and was maintained at 77 K with liquid nitrogen, and at 273 K with an ice–water bath. As the center-controlled air conditioner was set up at 23 ^{o}C, a water bath was used for adsorption isotherms at 296 K.

Synthesis and characterization of the organic building block (H_4L)



Scheme 1 Synthetic route to the organic linker used to construct **ZJNU-40**.

To a mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.50 g, 1.70 mmol), dimethyl 5-(pinacolboryl)isophthalate (1.20 g, 3.74 mmol), Cs_2CO_3 (1.66 g, 5.10 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) were added dry dioxane (40 mL). The resulting mixture was stirred under reflux under a nitrogen atmosphere for 72 hr. After removal of the solvents, CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The mixture was filtered, washed with water and CH_2Cl_2 sequentially, and dried under vacuum. The solid was hydrolyzed with 6 M NaOH, filtered and acidified with concentrated HCl to afford the target compound as a yellow solid in 66% yield (0.52 g, 1.12 mmol). ^{1}H NMR (DMSO-d_6, 600.1 MHz) δ (ppm): 13.50 (s, br, 4H), 8.81 (d, J = 1.8 Hz, 4H), 8.57 (t, J = 1.8 Hz, 2H), 8.15 (s, 2H); ^{13}C NMR (DMSO-d_6, 150.9 MHz) δ (ppm): 166.41, 152.95, 137.32, 133.66, 131.67, 130.97, 129.63, 128.89; selected FTIR (KBr, cm^{-1}): 1732, 1709, 1601, 1554, 1441, 1404, 1304, 1271, 1215, 1161, 1124, 916, 895, 854, 802, 756, 708, 685, 667, 548, 519.

Synthesis and characterization of ZJNU-40

A mixture of the organic linker H_4L (5.0 mg, 10.7 μmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (15.0 mg, 62.1 μmol) was dissolved into a mixed solvent of *N*,*N*-diethylformamide (DEF) and H_2O (1.5 mL / 0.08 mL) in a screw-capped vial (20 mL). 50 μL of 6 M HCl were then added. The vial was capped and heated at 353 K for 96 h. Blue rhombic crystals were obtained in 67% yield. **ZJNU-40** can be best formulated as $[Cu_2L(H_2O)_2]{\cdot}4DEF{\cdot}6H_2O$ on the basis of single-crystal X-ray diffraction structure determination, TGA and microanalysis. Selected FTIR (KBr, cm^{-1}): 1660, 1591, 1568, 1495, 1444, 1417, 1381, 1093, 1049, 879, 777, 754, 729; TGA data for loss of $4DEF+8H_2O$, calcd: 46.6%, found: 48.0%; anal. for $C_{42}H_{64}Cu_2N_6O_{18}S$, calcd: C, 45.85%, H, 5.86%, N, 7.64%; found: C, 48.59%, H, 5.90%, N, 7.55%.

Fitting of pure-component isotherms

The measured experimental data on *excess* loadings, q^{excess}, of the pure components CO_2, CH_4, and N_2 in **ZJNU-40a** and **NOTT-101**, were first converted to absolute loadings, q, using

$$q = q^{excess} + \frac{pV_{pore}}{ZRT} \quad (1)$$

where Z is the compressibility factor. The Peng-Robinson equation of state was used to estimate Z. The accessible pore volume for **ZJNU-40a** and **NOTT-101** are 0.8806 $cm^3\ g^{-1}$ and 1.0485 $cm^3\ g^{-1}$, respectively.

The absolute component loadings were fitted with the Langmuir model

$$q = q_{sat}\frac{bp}{1+bp} \quad (2)$$

with T-dependent parameter b

$$b = b_0 \exp\left(\frac{E}{RT}\right) \quad (3)$$

The Langmuir parameters for adsorption of CO_2 are provided in *Tables S3*, and *S4* for **ZJNU-40a** and **NOTT-101**.

Figure S6 provides a comparison of the experimental isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **ZJNU-40a** with the isotherm fits. *Figure S7* provides a comparison of the experimental isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **NOTT-101** with the isotherm fits. For all guest/host combinations, the isotherm fits are excellent.

Isosteric heat of adsorption

The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q \quad (4)$$

was determined using the Clausius-Clapeyron equation by fitting the adsorption isotherms taken at 273 and 296 K to a Langmuir expression. The values of Q_{st} for CO_2, CH_4, and N_2 in **ZJNU-40a**, and **NOTT-101** are shown in *Figure S17*.

IAST calculations of adsorption selectivities and uptake capacities

The selectivity of preferential adsorption of component *1* over component *2* in a mixture containing *1* and *2*, perhaps in the presence of other components too, can be formally defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (5)$$

In equation (5), q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[1]

Figures S8a and *S8b* present the values of the adsorption selectivity for (a) 50/50

CO_2/CH_4, and (b) 5/95 CO_2/CH_4 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**. We note that **ZJNU-40a** has higher selectivity towards CO_2 for both mixture compositions.

ZJNU-40a has a higher selectivity towards CO_2 for adsorption from 15/85 CO_2/N_2 gas mixtures; see *Figure S8c*.

Besides the adsorption selectivities, the separation performance is also dictated by uptake capacities. *Figures S9a, S9b,* and *S9c* present IAST calculations for uptake of CO_2 from (a) 50/50 CO_2/CH_4, (b) 5/95 CO_2/CH_4, and (c) 15/85 CO_2/N_2 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**. **ZJNU-40a** has higher uptake of CO_2 in all three cases.

The combination of higher selectivity and higher uptake of CO_2 is most desirable and leads to enhanced sepatations in fixed beds.

Transient breakthroughs in fixed bed adsorbers

The performance of industrial fixed bed adsorbers is dictated by a combination of *adsorption selectivity* and *uptake capacity*. For a proper comparison of various MOFs, we perform transient breakthrough simulations using the simulation methodology described in the literature.[2-6] For the breakthrough simulations, the following parameter values were used: length of packed bed, L = 0.3 m; voidage of packed bed, ε = 0.4; superficial gas velocity at inlet, u = 0.04 m s^{-1}; see schematic in *Figure S10*.

The transient breakthrough simulation results are presented in terms of a dimensionless time, τ, defined by dividing the actual time, t, by the characteristic time, $\frac{L\varepsilon}{u}$.

Figure S11 compares 50/50 CO_2/CH_4 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with **ZJNU-40a** and **NOTT-101**. For both materials the sequence of breakthroughs is CH_4, and CO_2 that is dictated by the adsorption strengths; the more strongly adsorbing CO_2 elutes last in the sequence. The breakthrough of CO_2 occurs at a later time with **ZJNU-40a** and this material has the better separation performance. The reason for the improved separation can be traced to two separate factors: (a) higher CO_2 uptake capacity of **ZJNU-40a**, and (b) higher CO_2/CH_4 adsorption selectivities.

In natural gas purification processes, the primary objective is to produce CH_4 with a specified purity level, which is typically 500 ppm CO_2, *i.e.* 0.05 mole % CO_2. Let us compare the productivities of pure CH_4 that fulfills the specified impurity level for CO_2. *Figure S12* presents a comparison of the % CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101**. During the time interval $\Delta\tau$, 99.95%+ pure CH_4 can be produced. These amounts can be determined from a material balance on the fixed bed adsober; the productivities are 2.84 mol *per* kg of **ZJNU-40a**, and 1.78 mol *per* kg of **NOTT-101**. This implies that **ZJNU-40a** has a 50% higher productivity than **NOTT-101**.

Let us consider separations of 5/95 CO_2/CH_4 mixtures. *Figure S13* compares 5/95 CO_2/CH_4 mixture breakthrough characteristics of **ZJNU-40a** and **NOTT-101**. *Figure*

S14 presents a comparison of the % CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101**. From a material balance on the fixed bed adsober; the productivities are 5.80 mol *per* kg of **ZJNU-40a**, and 3.62 mol *per* kg of **NOTT-101**. These productivity values are higher than the corresponding ones for 50/50 mixtures because of the lower amount of CO_2 that needs to be captured. For 5/95 CO_2/CH_4 mixtures, **ZJNU-40a** has a 60% higher productivity than **NOTT-101**.

Let us now compare separations of 15/85 CO_2/N_2 gas mixtures that is relevant for CO_2 capture from flue gases. *Figure S15* presents the 15/85 CO_2/N_2 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with **ZJNU-40a**, and **NOTT-101** at a total pressure of 100 kPa. N_2 with a purity of 99.95% can be produced during the time interval $\Delta\tau$, as indicated in *Figure S16*. The productivity can be determined to be 3.29 mol *per* kg of **ZJNU-40a**, and 2.08 mol *per* kg of **NOTT-101**.

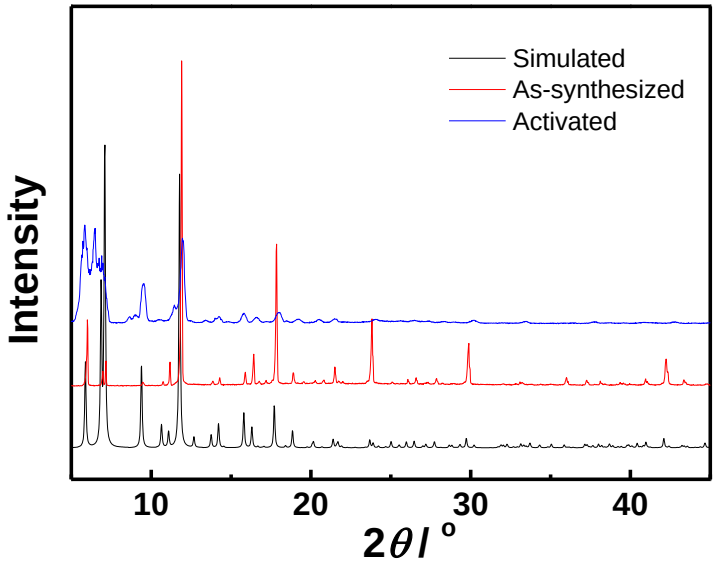


Fig. S1 PXRD patterns of the as-synthesized **ZJNU-40** (red) and the activated **ZJNU-40a** (blue), along with the one simulated from the cif file (black).

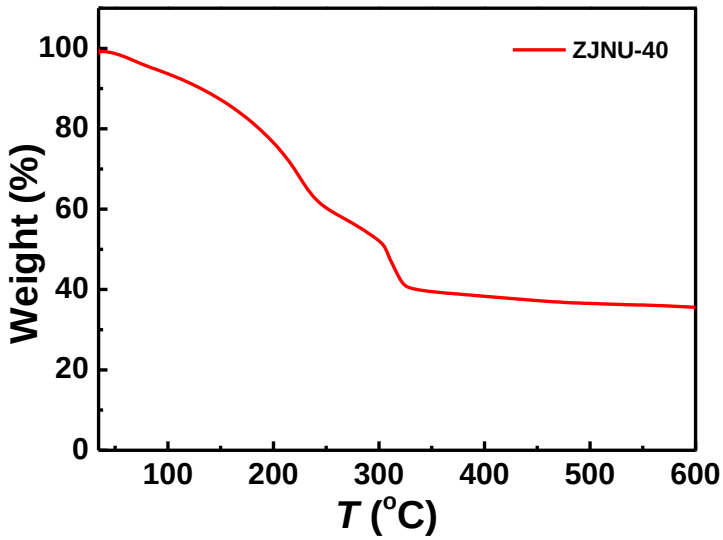


Fig. S2 TGA curve of the as-synthesized **ZJNU-40** under a nitrogen atmosphere.

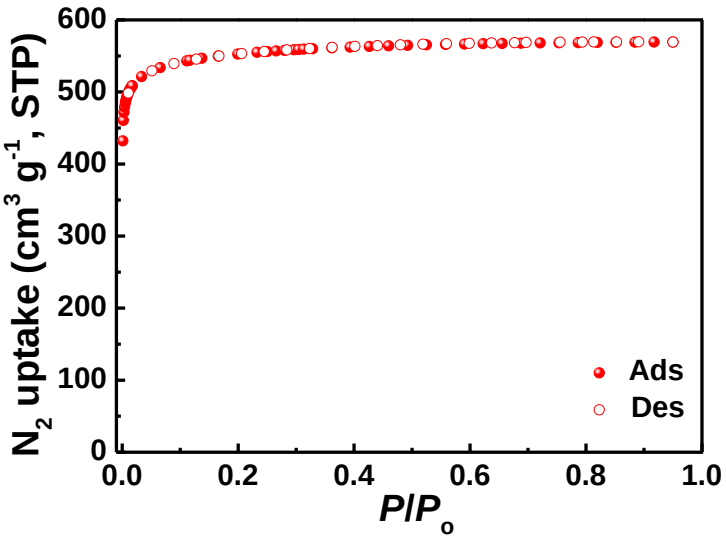


Fig. S3 N_2 sorption isotherm of **ZJNU-40a** at 77 K. The solid and open symbols represent adsorption and desorption, respectively.

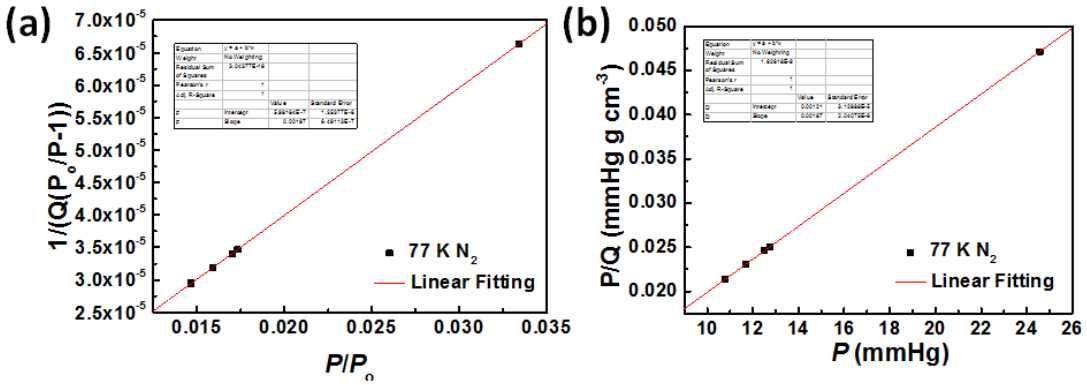


Fig. S4 BET and Langmuir analysis from N_2 adsorption isotherm at 77 K.

S_{BET} = 1/(0.00197 + 5.98184×10^{-7})/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2209 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00187)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 2328 m^2 g^{-1}

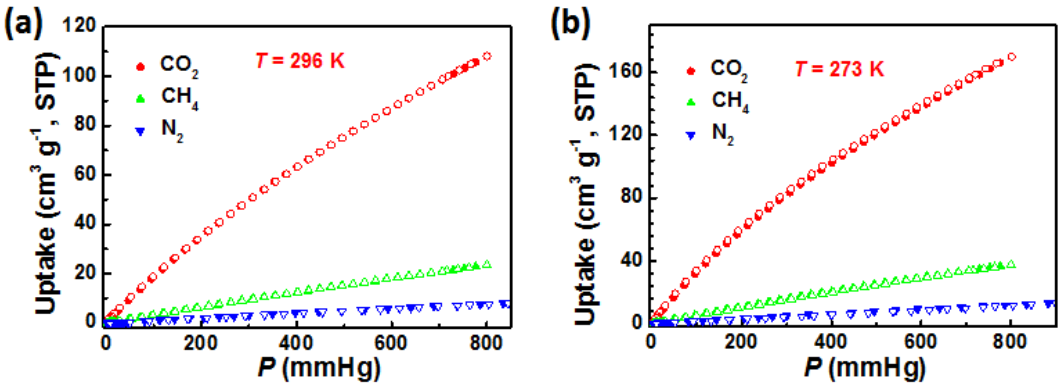


Fig. S5 CO_2, CH_4 and N_2 sorption isotherms of **ZJNU-40a** at 296 K (a), and 273 K (b). The solid and open symbols represent adsorption and desorption, respectively.

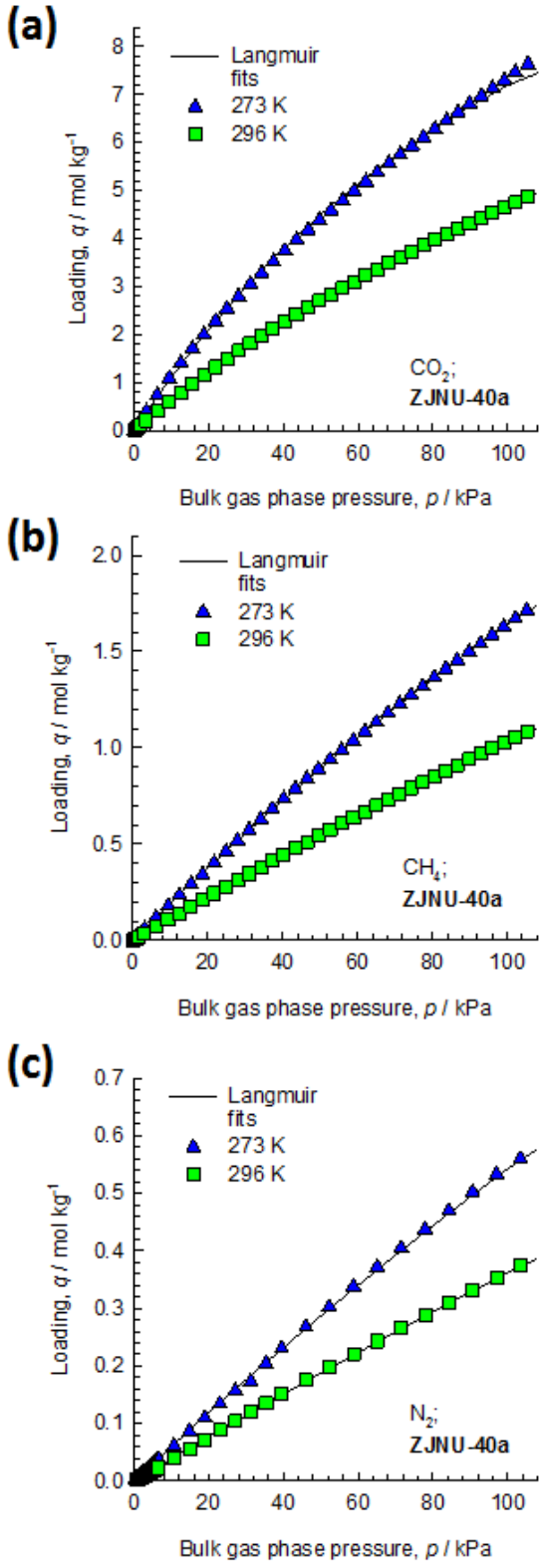


Fig. S6 Comparison of the pure-component isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **ZJNU-40a** with the fitted isotherms (shown by continuous solid lines) at 273 K, and 296 K.

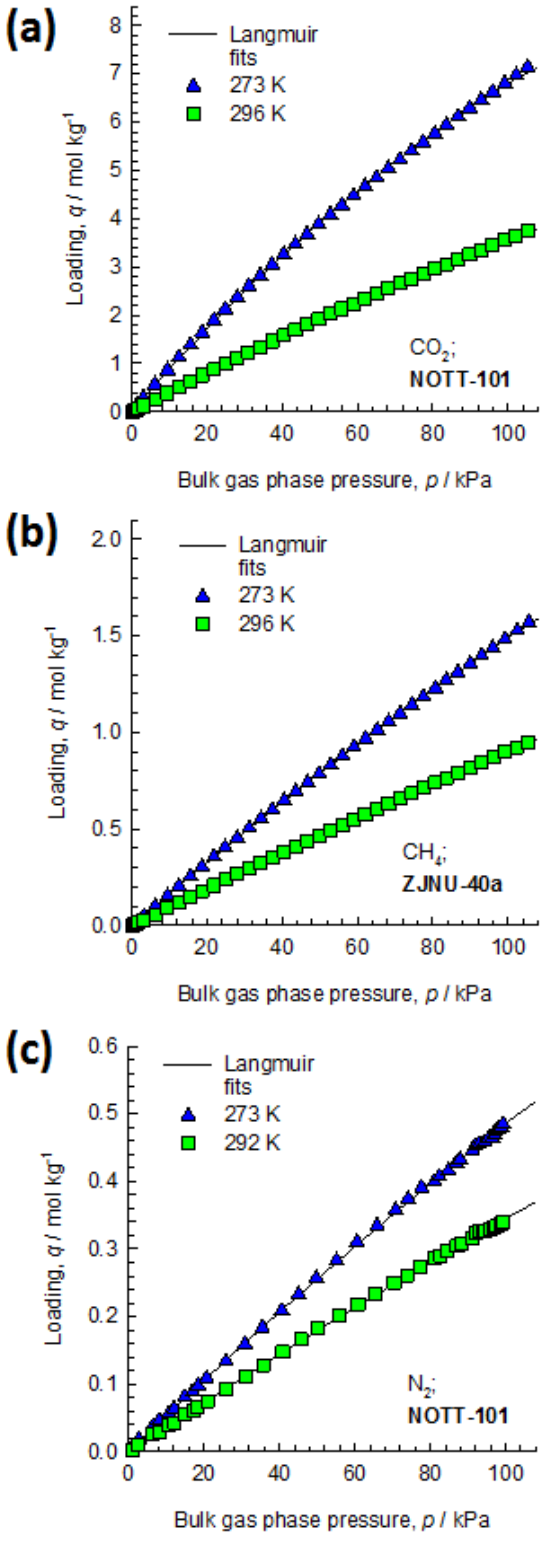


Fig. S7 Comparison of the pure-component isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **NOTT-101** with the fitted isotherms (shown by continuous solid lines).

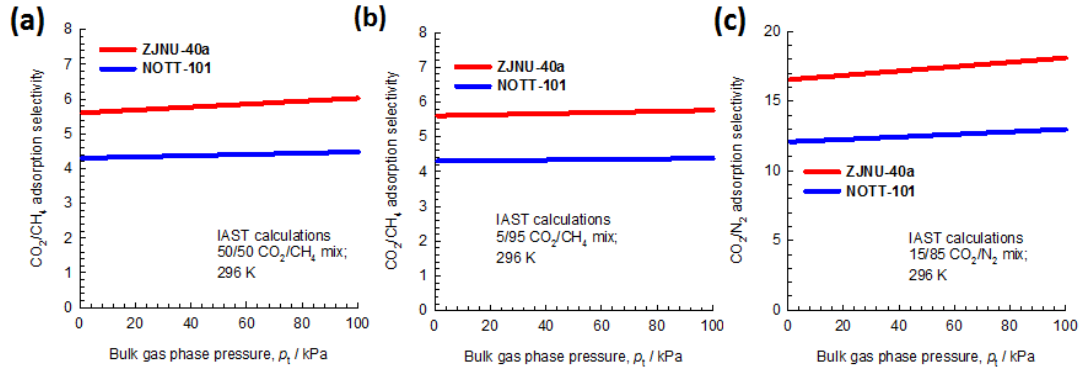


Fig. S8 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz[1] for adsorption selectivitites for (a) 50/50 CO_2/CH_4, (b) 5/95 CO_2/CH_4, and (c) 15/85 CO_2/N_2 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**.

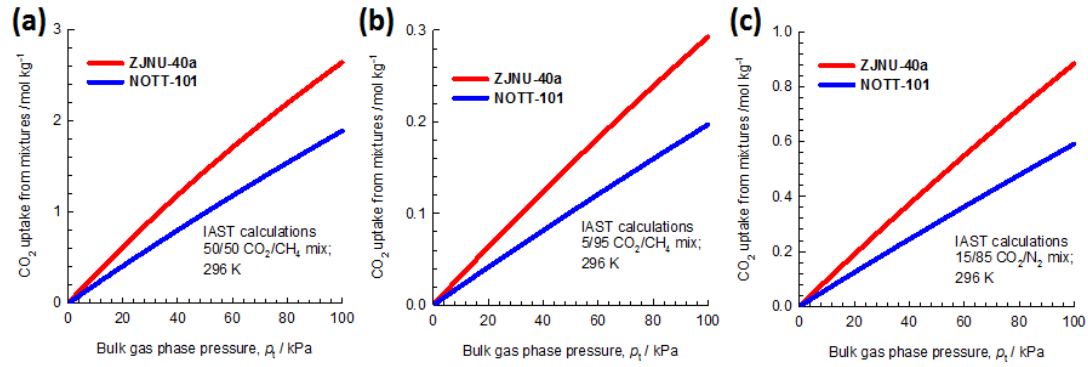


Fig. S9 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz[1] for uptake of CO_2 from (a) 50/50 CO_2/CH_4, (b) 5/95 CO_2/CH_4, and (c) 15/85 CO_2/N_2 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**.

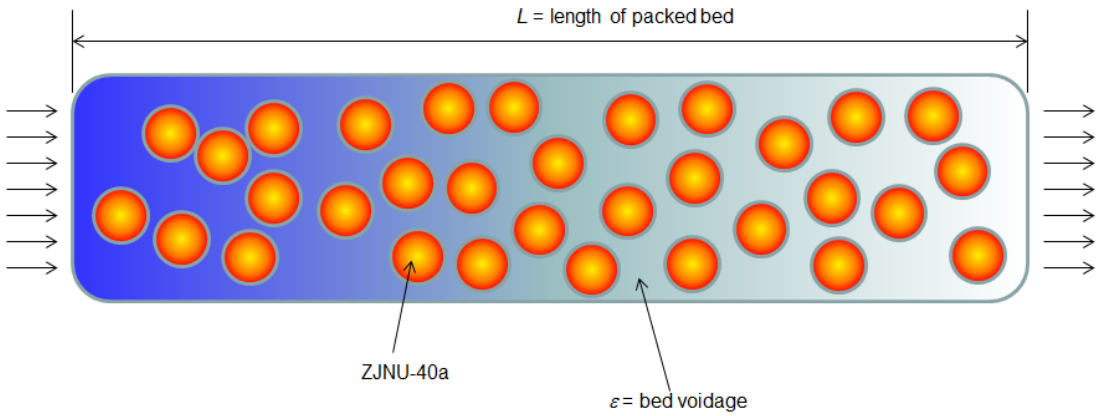


Fig. S10 Schematic of the breakthrough apparatus. The tube length L = 0.3 m. The apparatus is operated at 296 K, and at a total gas pressure of 200 kPa or 100 kPa. The bed porosity, ε = 0.4. The interstitial gas velocity, v = 0.04 m s^{-1}.

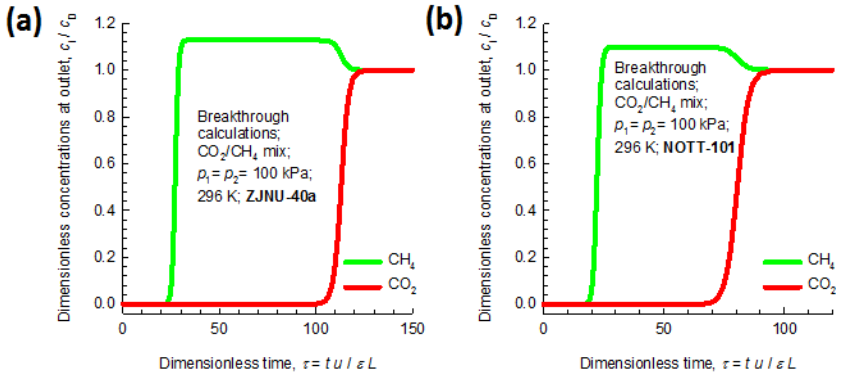


Fig. S11 50/50 CO_2/CH_4 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 200 kPa.

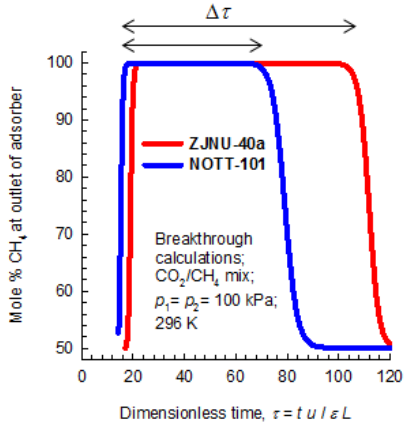


Fig. S12 Comparison of the %CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 50/50 CO_2/CH_4 gas mixtures at 200 kPa total pressure and 296 K.

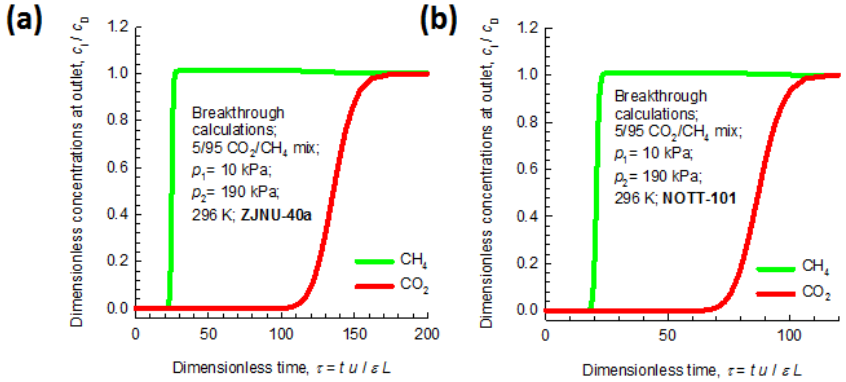


Fig. S13 5/95 CO_2/CH_4 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 200 kPa.

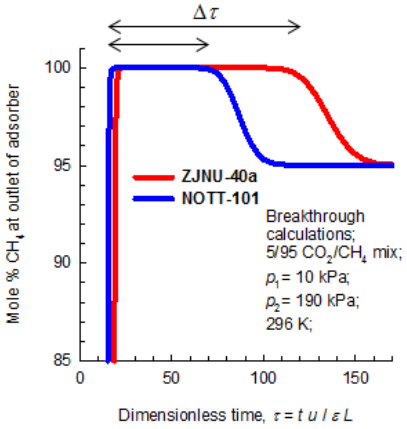


Fig. S14 Comparison of the %CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 5/95 CO_2/CH_4 gas mixtures at 200 kPa total pressure and 296 K.

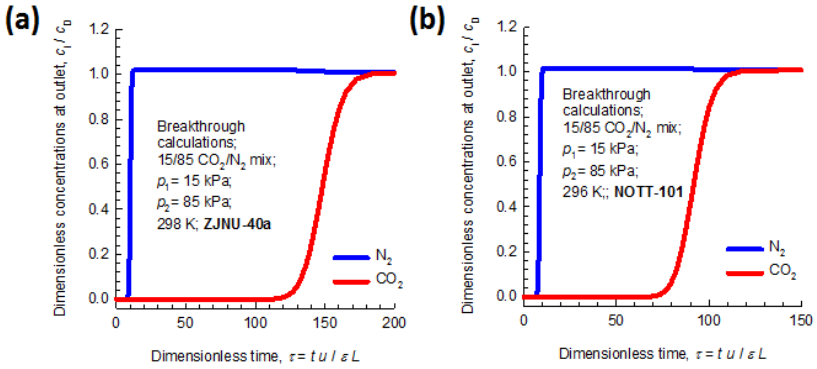


Fig. S15 15/85 CO_2/N_2 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 100 kPa.

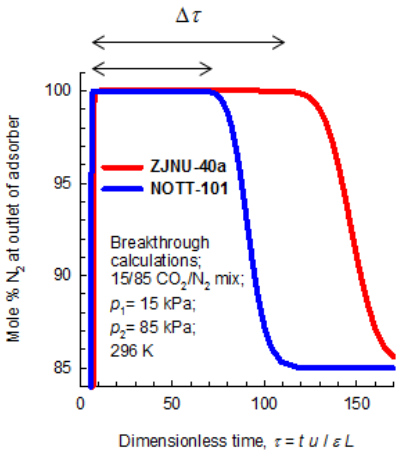


Fig. S16 Comparison of the % N_2 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 15/85 CO_2/N_2 gas mixtures at 100 kPa total pressure and 296 K.

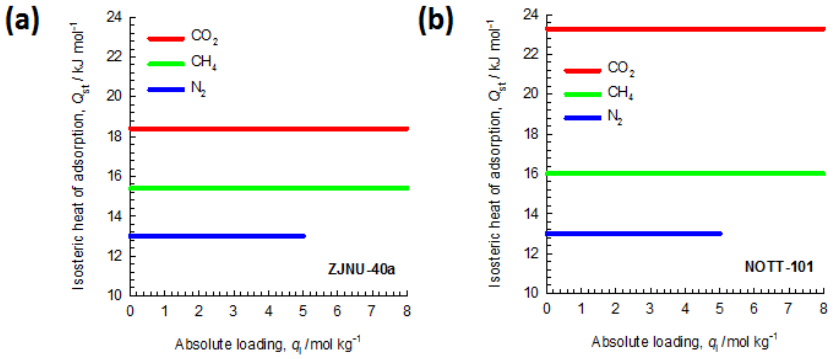


Fig. S17 Isosteric heats of adsorption of CO_2, CH_4, and N_2 in **ZJNU-40a** (a) and **NOTT-101** (b).

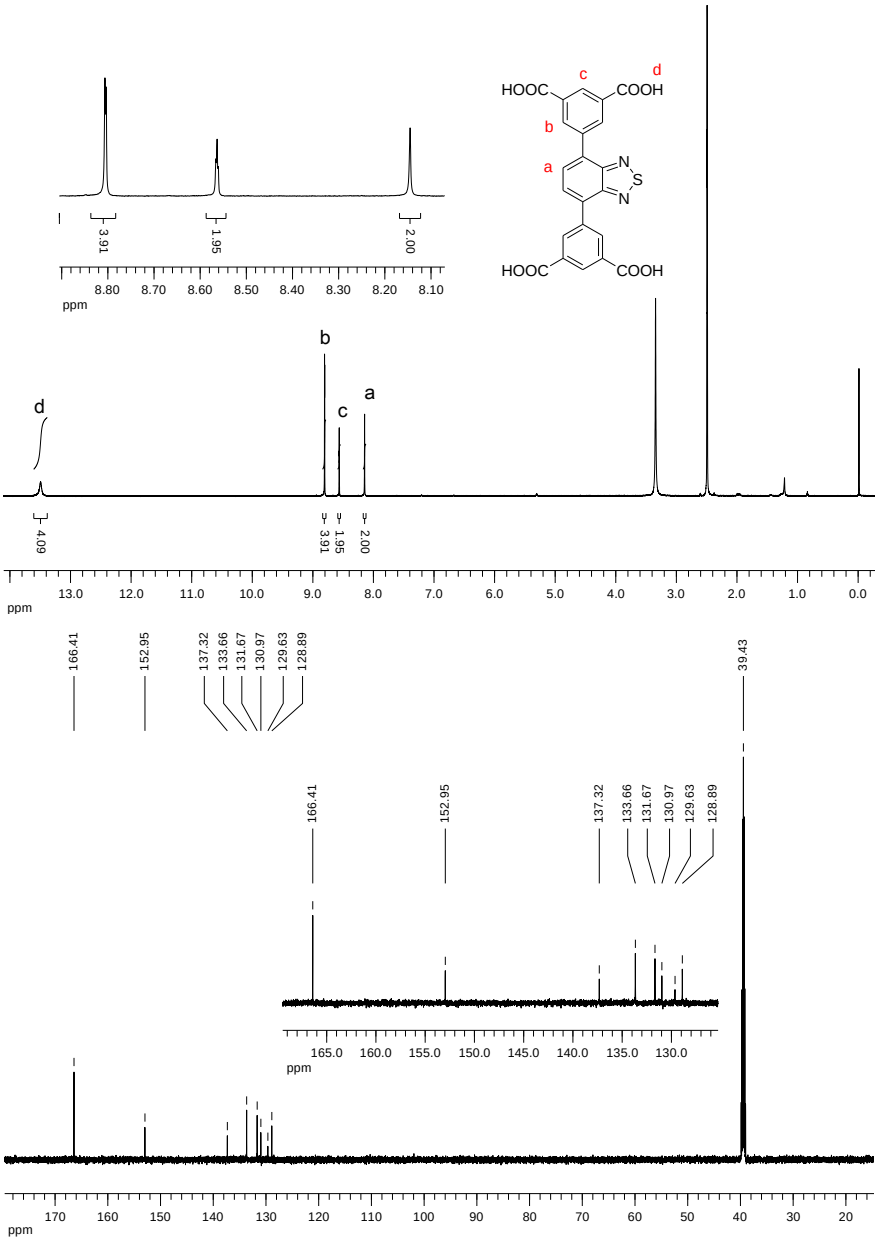


Fig. S18 ^{1}H NMR (DMSO-d_6, 600.1 MHz) and ^{13}C NMR (DMSO-d_6, 150.9 MHz) spectra of the organic linker H_4L.

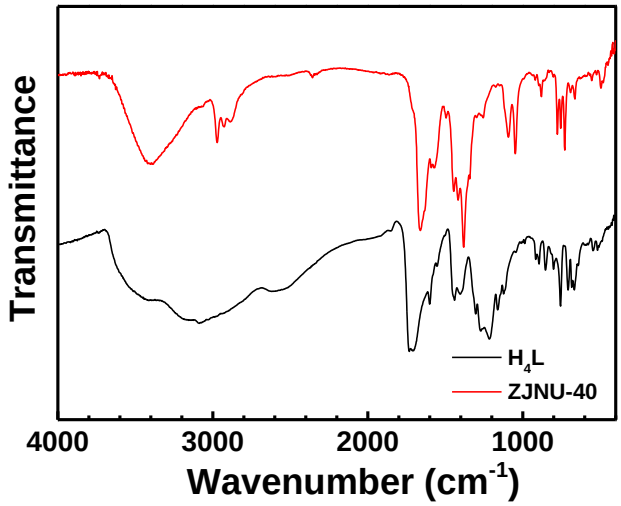


Fig. S19 FTIR spectra of the organic linker H_4L (black) and as-synthesized **ZJNU-40** (red).

Table S1. Crystal data and structure refinement for **ZJNU-40**.

Empirical formula	$C_{66}H_{24}Cu_6N_6O_{32}S_3$
Formula weight	1890.42
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	Trigonal, *R*-3m
Unit cell dimensions	a = 18.819(4) Å b = 18.819(4) Å c = 38.603(15) Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$
Volume (Å^3)	11840(6)
Z, Calculated density (g cm^{-3})	3, 0.795
Absorption coefficient (mm^{-1})	0.877
F(000)	2820
Crystal size (mm)	0.2 × 0.18 × 0.12
θ range for data collection (^{o})	3.27 to 27.56
Limiting indices	$-24 \le h \le 24$ $-24 \le k \le 24$ $-50 \le l \le 50$
Reflections collected / unique	42313 / 3293 (R_{int} = 0.0339)
Completeness to θ = 27.56	99.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.900 and 0.839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3293 / 1 / 124
Goodness-of-fit on F^2	1.132
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0544, wR_2 = 0.1823
R indices (all data)	R_1 = 0.0612, wR_2 = 0.1910
Largest diff. peak and hole (e.Å^{-3})	1.137 and -0.335
CCDC	1014276

Table S2. BET surface area, pore volume and CO_2 adsorption of the reported Cu-based NbO-type MOFs.

MOFs	BET[a] ($m^2\ g^{-1}$)	V_p[b] ($cm^3\ g^{-1}$)	CO_2 uptake under 1 atm at RT ($cm^3\ g^{-1}$)	Q_{st}[c] (kJ mol^{-1})	Selectivity[d] CO_2/CH_4	Selectivity[d] CO_2/N_2	*Ref.*
ZJNU-40	**2209**	**0.8806**	**108**	**18.4**	**6.6**	**22.9**	**This work**
HNUST-1	1400	0.571	93	31.2			[7]
MOF-505	1547		73				[8]
UTSA-40	1630	0.65	73	24.0	5.6		[9]
Cu_2dbip	1773	0.81	122	28.1		21.1	[10]
Cu_2ebtc	1852	1.008					[11]
ZJU-25	2124	1.183	83		5.5		[12]
SNU-50	2300	1.08	80	25.8			[13]
HNUST-2	2366	0.97		23.5	4.9	22.9	[14]
NJU-Bai14	2384		100	24.5			[15]
HNUST-3	2421	0.99	84.5	24.8	7.9	26.1	[16]
NOTT-125a	2447	1.1	93		4.8	16	[17]
NU-135	2530	1.02	79	25.5	4	14.5	[18]
NOTT-101	2805	1.080	83	23.3	4.6		[3]
ZJU-5	2823	1.074	85				[19]
Cu_2abtc	(2850)[e]	1.00					[20]
NJU-Bai12	3038	1.135		23.5	5.0	24.6	[21]
NOTT-102	3342	1.268	72[f]		4.84		[3]

[a] BET surface area; [b] pore volume; [c] the initial heat of CO_2 adsorption; [d] Henry's Law selectivity at room temperature, [e] Langmuir surface area, [f] the data measured at this work.

Table S3 Langmuir parameters for adsorption of CO_2, CH_4, and N_2 in **ZJNU-40a**.

	q_{sat} (mol kg^{-1})	b_0 (Pa^{-1})	E (kJ mol^{-1})
CO_2	17.8	2.05×10^{-9}	18.4
CH_4	10.3	2.14×10^{-9}	15.4
N_2	5	3.96×10^{-9}	13

Table S4. Langmuir parameters for adsorption of CO_2, CH_4, and N_2 in **NOTT-101**. The pure-component isotherm data for CO_2, CH_4, are from data measured in this work at temperatures of 273 K and 296 K. The pure-component isotherm data for N_2 are from Perry et al;[22] their data are reported at 273 K and 292 K.

	q_{sat} (mol kg^{-1})	b_0 (Pa^{-1})	E (kJ mol^{-1})
CO_2	26	1.24×10^{-10}	23.3
CH_4	14	1.04×10^{-9}	16
N_2	5	3.51×10^{-9}	13

Notation

b	Langmuir constant for species i at adsorption site A, Pa^{-1}
c_i	molar concentration of species i in gas mixture, mol m^{-3}
c_{i0}	molar concentration of species i in gas mixture at inlet to adsorber, mol m^{-3}
E	energy parameter, J mol^{-1}
L	length of packed bed adsorber, m
p_i	partial pressure of species i in mixture, Pa
p_t	total system pressure, Pa
q_i	component molar loading of species i, mol kg^{-1}
Q_{st}	isosteric heat of adsorption, J mol^{-1}
t	time, s
T	absolute temperature, K
u	superficial gas velocity in packed bed, m s^{-1}

Greek letters

ε	voidage of packed bed, dimensionless
τ	time, dimensionless

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