Supporting Information for the manuscript

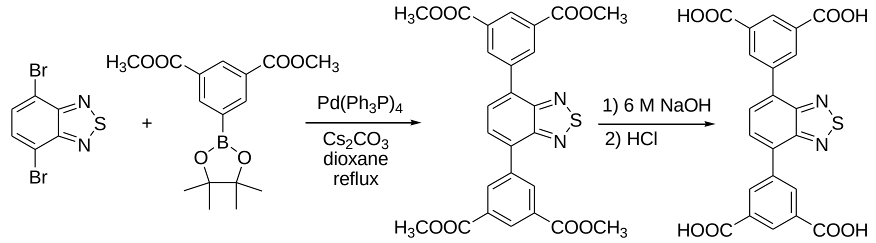
Enhanced CO_2 Sorption and Selectivity by Functionalization of a NbO-type Metal-Organic Framework with Polarized Benzothiadiazole Moieties

Chengling Song,[a] Yabing He,[a*] Bin Li,[b] Yajing Ling,[a] Hailong Wang,[b] Yunlong Feng,[a] Rajamani Krishna,[c] Banglin Chen[b*]
[a] College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn.
[b] Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: +1-210-458-7428
[c] Van't Hoff Institute for Molecular Sciences, University of Amsterdam Science Park 904, 1098 XH Amsterdam (The Netherlands)

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). ^1H 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

$$q = q^{excess} + \frac{pV_{pore}}{ZRT} \tag{1}$$

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

$$q = q_{sat}\frac{bp}{1+bp} \tag{2}$$

with T-dependent parameter b

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

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

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

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

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \tag{5}$$

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, $\varepsilon = 0.4$; 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**.

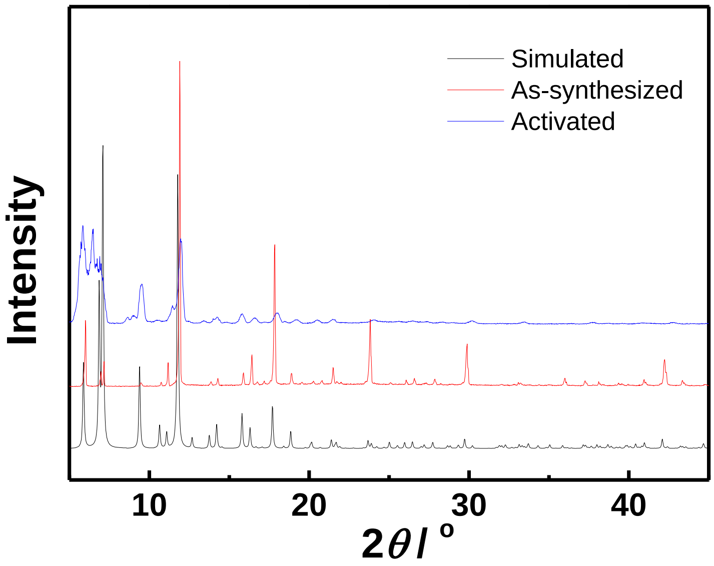


Fig. S1 PXRD patterns of the as-synthesized **ZJNU-40** (red) and the activated **ZJNU-40a** (blue), along with the one simulated from the cif file (black).

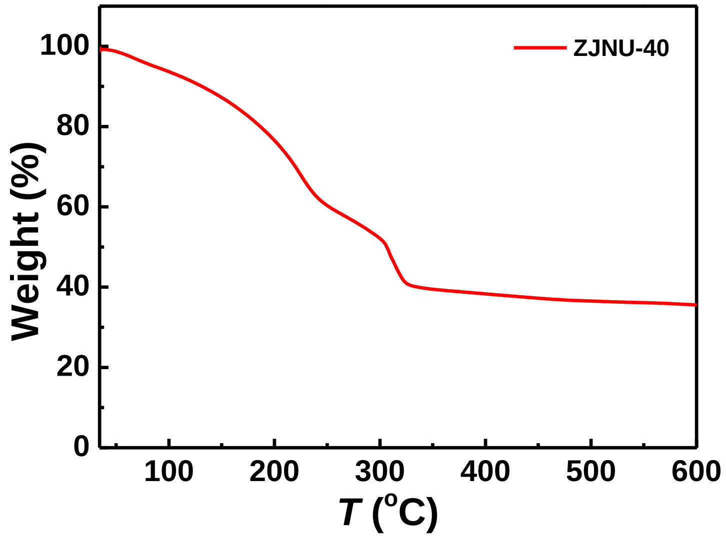


Fig. S2 TGA curve of the as-synthesized **ZJNU-40** under a nitrogen atmosphere.

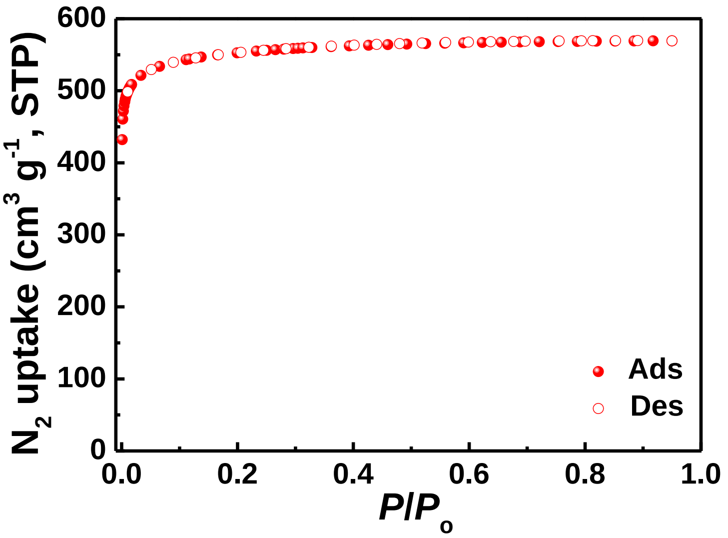


Fig. S3 N_2 sorption isotherm of **ZJNU-40a** at 77 K. The solid and open symbols represent adsorption and desorption, respectively.

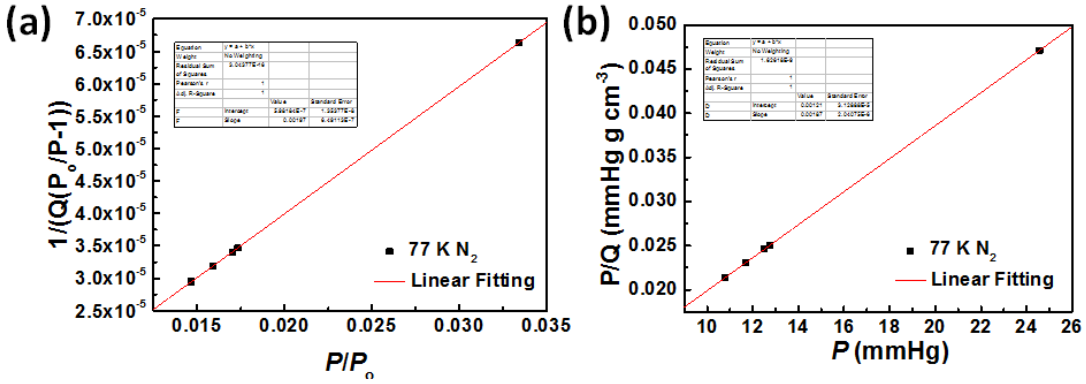


Fig. S4 BET and Langmuir analysis from N_2 adsorption isotherm at 77 K.

$S_{BET} = 1/(0.00197 + 5.98184\times10^{-7})/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2209\ m^2\ g^{-1}$
$S_{Langmuir} = (1/0.00187)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2328\ m^2\ g^{-1}$

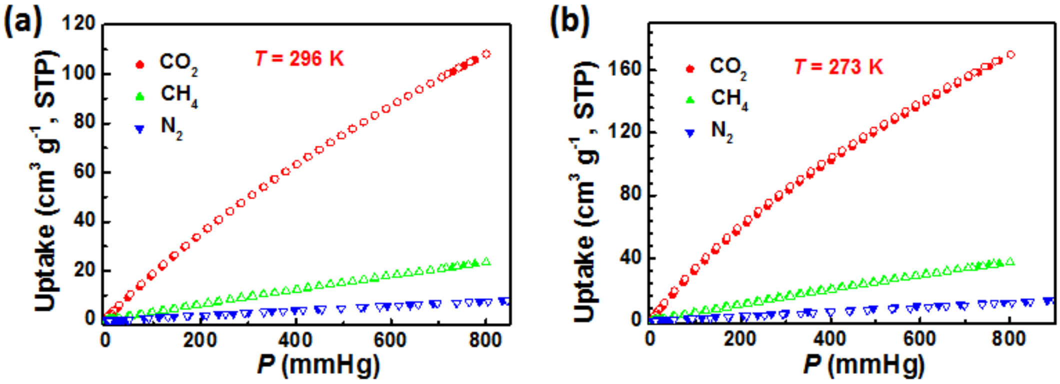


Fig. S5 CO_2, CH_4 and N_2 sorption isotherms of **ZJNU-40a** at 296 K (a), and 273 K (b). The solid and open symbols represent adsorption and desorption, respectively.

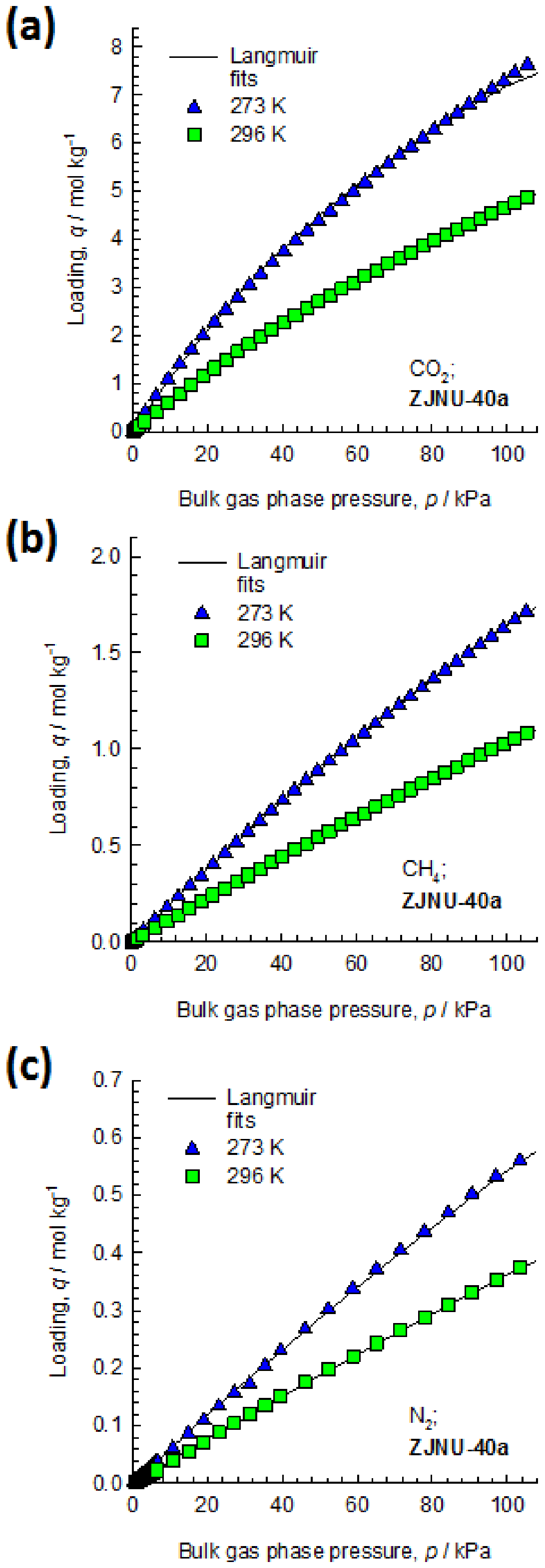


Fig. S6 Comparison of the pure-component isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **ZJNU-40a** with the fitted isotherms (shown by continuous solid lines) at 273 K, and 296 K.

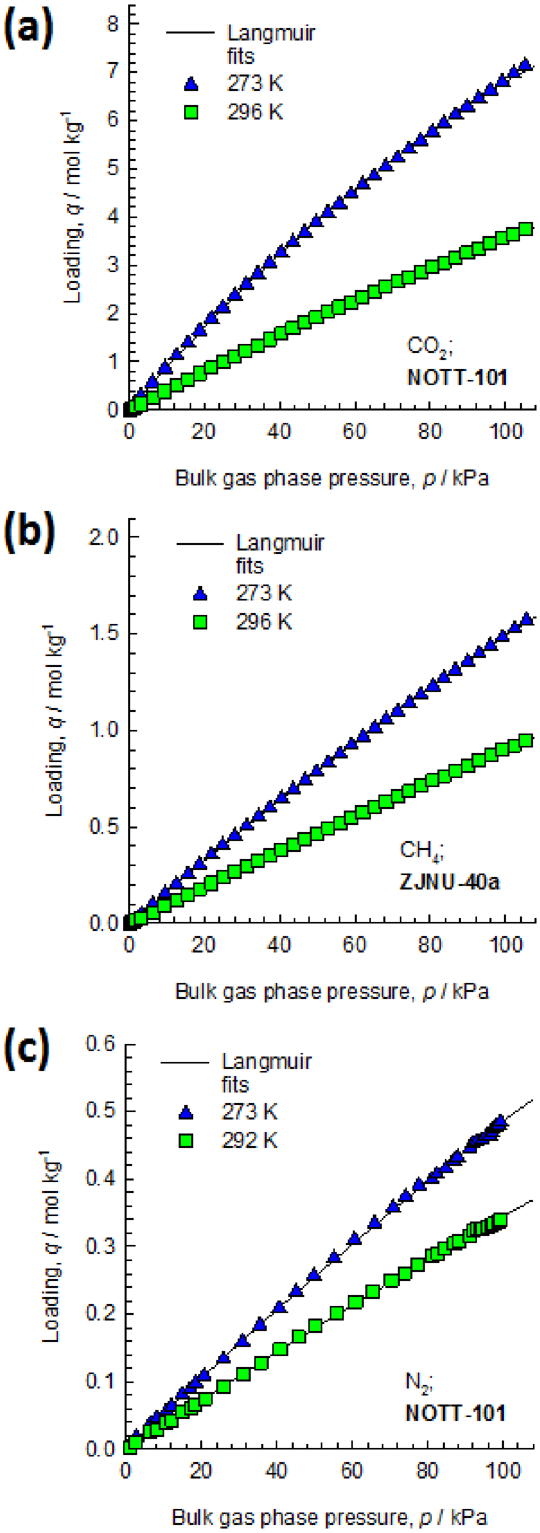


Fig. S7 Comparison of the pure-component isotherm data for (a) CO_2, (b) CH_4, and (c) N_2 in **NOTT-101** with the fitted isotherms (shown by continuous solid lines).

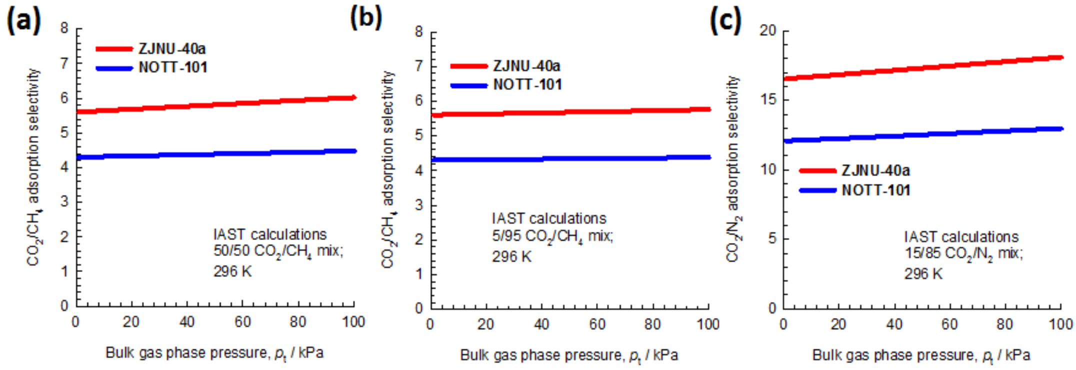


Fig. S8 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz[1] for adsorption selectivitites for (a) 50/50 CO_2/CH_4, (b) 5/95 CO_2/CH_4, and (c) 15/85 CO_2/N_2 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**.

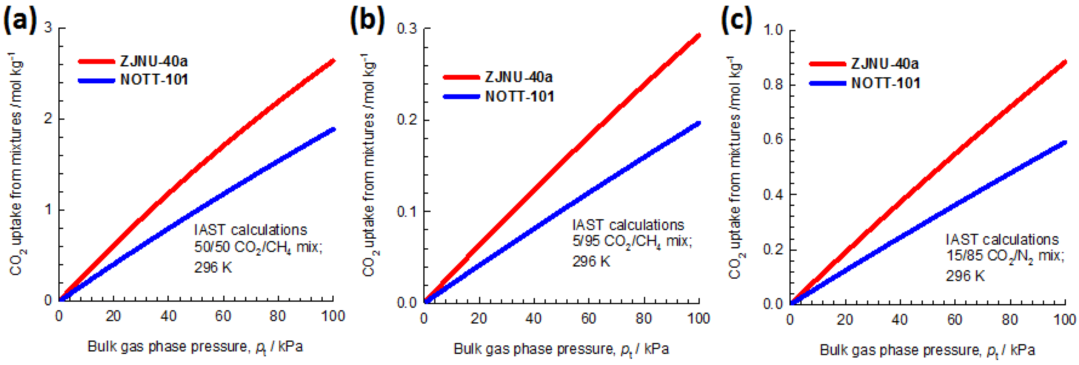


Fig. S9 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz[1] for uptake of CO_2 from (a) 50/50 CO_2/CH_4, (b) 5/95 CO_2/CH_4, and (c) 15/85 CO_2/N_2 gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-40a**, and **NOTT-101**.

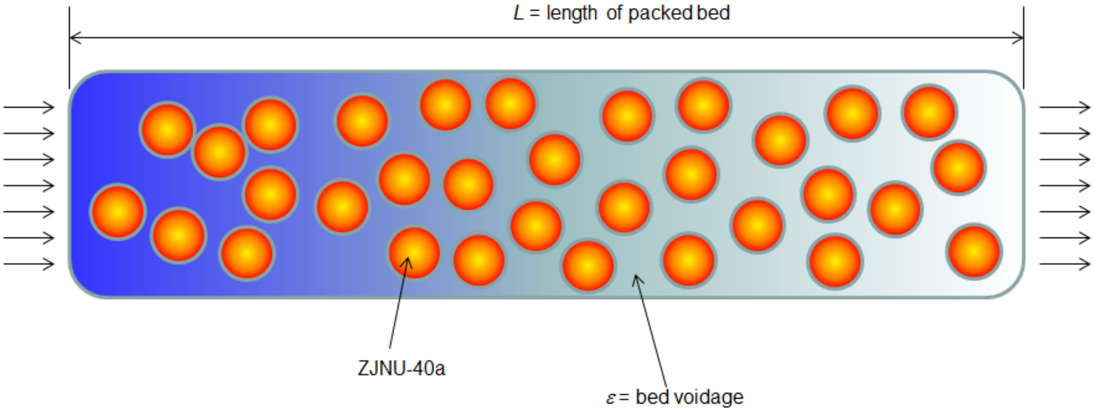


Fig. S10 Schematic of the breakthrough apparatus. The tube length L = 0.3 m. The apparatus is operated at 296 K, and at a total gas pressure of 200 kPa or 100 kPa. The bed porosity, ε = 0.4. The interstitial gas velocity, v = 0.04 m s^{-1}.

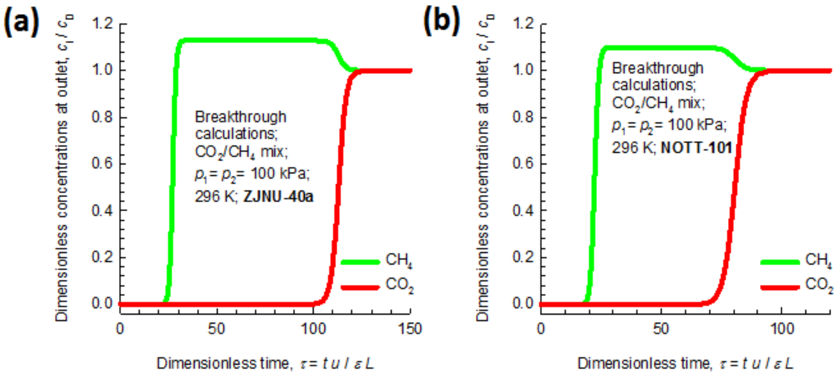


Fig. S11 50/50 CO_2/CH_4 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 200 kPa.

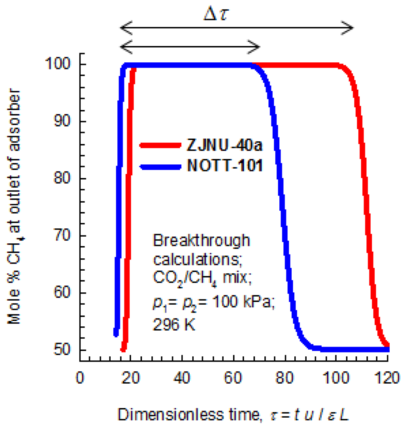


Fig. S12 Comparison of the %CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 50/50 CO_2/CH_4 gas mixtures at 200 kPa total pressure and 296 K.

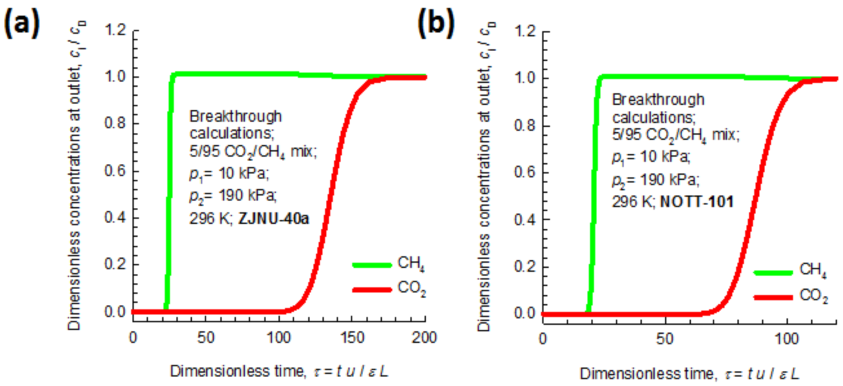


Fig. S13 5/95 CO_2/CH_4 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 200 kPa.

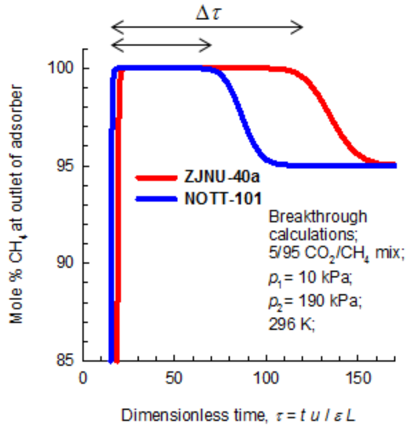


Fig. S14 Comparison of the %CH_4 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 5/95 CO_2/CH_4 gas mixtures at 200 kPa total pressure and 296 K.

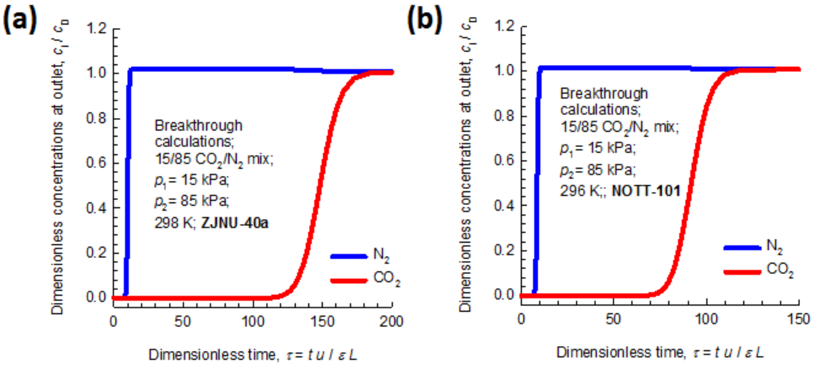


Fig. S15 15/85 CO_2/N_2 mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with (a) **ZJNU-40a**, and (b) **NOTT-101** and maintained at isothermal conditions at 296 K. In these calculations, the total pressure is maintained at 100 kPa.

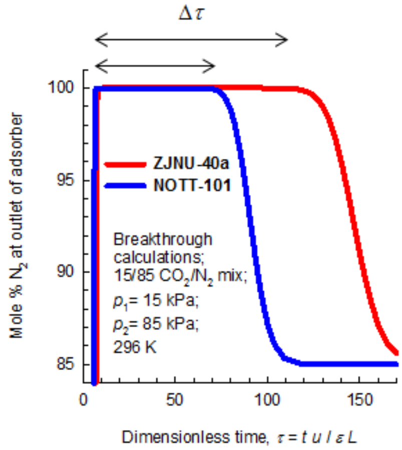


Fig. S16 Comparison of the % N_2 exiting the adsorber packed with **ZJNU-40a**, and **NOTT-101** fed with 15/85 CO_2/N_2 gas mixtures at 100 kPa total pressure and 296 K.

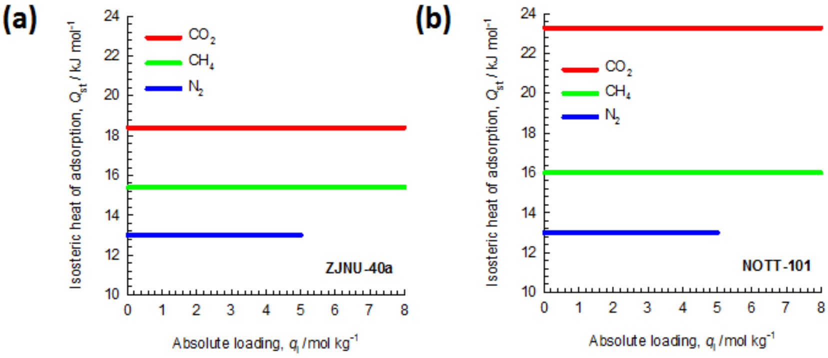


Fig. S17 Isosteric heats of adsorption of CO_2, CH_4, and N_2 in **ZJNU-40a** (a) and **NOTT-101** (b).

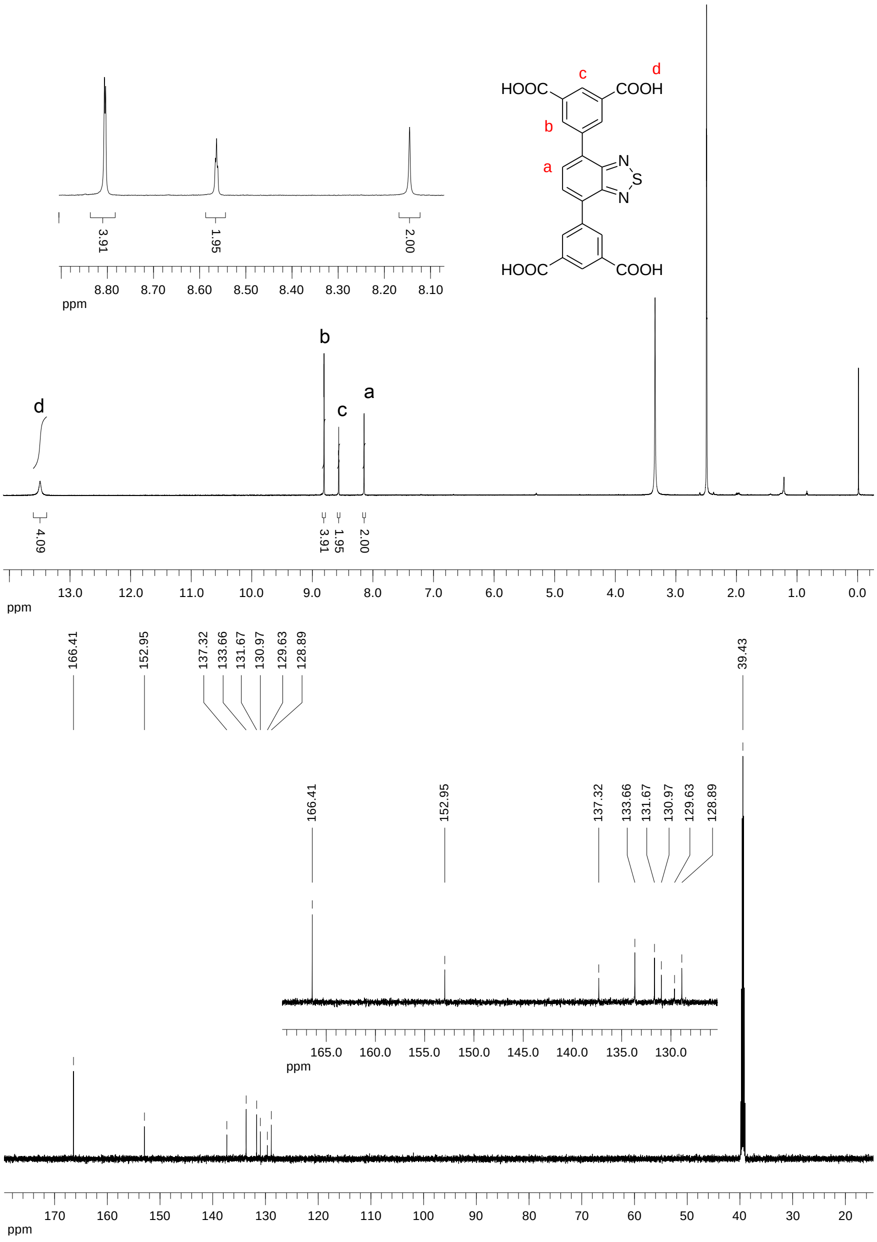


Fig. S18 ^1H NMR (DMSO-d_6, 600.1 MHz) and ^{13}C NMR (DMSO-d_6, 150.9 MHz) spectra of the organic linker H_4L.

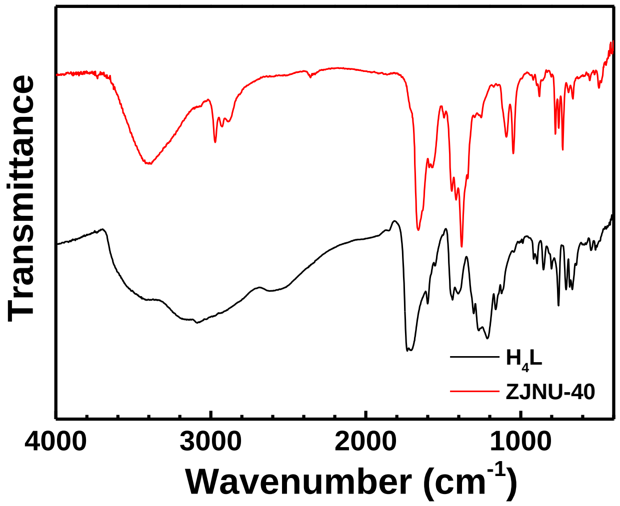


Fig. S19 FTIR spectra of the organic linker H_4L (black) and as-synthesized **ZJNU-40** (red).

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	$-24 \leq h \leq 24$ $-24 \leq k \leq 24$ $-50 \leq l \leq 50$
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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