Electronic Supplementary Information

A supramolecular porous material comprising Fe(II) mesocates

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General

All reagents and solvents used were of reagent grade unless otherwise stated and did not require further purification and only distilled water was used. Chemicals were sourced from Sigma Aldrich and used as received. ¹H and ¹³C NMR measurements were carried out on an Agilent 400 NMR spectrometer operating at 400 MHz for ¹H and 101 MHz for ¹³C. Chemical shift values are given in parts per million (ppm). Infrared measurements were carried out using a Bruker ALPHA Platinum ATR FT-IR spectrometer measuring in the range 4000-450 cm⁻¹. The following abbreviations were used to describe the signals: s (strong), m (medium), w (weak), br (broad). Mass spectrometry experiments were carried out on a Bruker maXis 4G time of flight spectrometer operating in ESMS+ mode. For C, H, N analysis samples were sent to Campbell Micro-analytical Laboratories, Otago University, Dunedin. Samples were dried to constant weight under vacuum before analysis. Thermogravimetric analysis was carried out on an Alphatech SDT Q600 TGA/DSC apparatus. The sample holder was platinum crucible and it was heated at 1 degree/min under a nitrogen flow of 100 mL min⁻¹. Gas sorption isotherms were carried out on a Quantachrome Autosorb iQ2 instrument using ultrahigh-purity gases. After solvent exchange (vide *infra*), microcrystalline samples of **1** were transferred to a pre-weighed analysis tube and heated under high vacuum for 18 hours at 25 °C prior to sorption measurements being performed. Accurate sample masses were calculated by using degassed samples after the activated samples were backfilled with nitrogen. Powder X-Ray Diffraction data were collected using an Oxford-Agilent SuperNova instrument using Cu K α ($\lambda = 1.5418$ Å) radiation and an ATLAS CCD area detector at 120 K. Samples were prepared by grinding crystals of **1** and packing inside an open glass tube. A baseline correction was manually applied using the baseline feature within the CrysAlis^{Pro} analysis software.

Syntheses

Synthesis of L1

Dimethyl isophthalate

Dimethyl isophthalate was synthesized following a literature preparation.¹ Isophthalic acid (3.1 g, 27 mmol) was added to dry methanol (120 mL) and concentrated sulfuric acid (0.5 mL) and then heated at reflux overnight. The solvent was removed under reduced pressure and the organic residue

was extracted with dichloromethane (4 × 50 mL) and washed with brine (2 × 50 mL) and saturated NaHCO₃ (2 × 50 mL). The organic layer was dried over MgSO₄ and the solvent removed under reduced pressure to give a white solid. Yield: 3.1 g (59%); $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.68 (1H, s, H_a), 8.09-8.31 (2H, m, H_b), 7.53 (1H, t, *J* = 7.6 Hz, H_c), 3.94 (6H, s, H_d).

Isophthaloyl hydrazide

Isophthalate dihydrazide was synthesized following a slightly modified literature preparation.¹ Dimethyl isophthalate (1.0 g, 5.1 mmol) was dissolved in warm ethanol (5 mL) and hydrazine monohydrate (2 mL, 41 mmol) added slowly with stirring. The solution was heated at reflux

water $(2 \times 5 \text{ mL})$ then cold ethanol $(2 \times 5 \text{ mL})$ and air

for approximately 4 hours and then allowed to cool to room temperature. The resultant white solid was separated by filtration, washed with water (2 × 5 mL) then cold ethanol (2 × 5 mL) and air dried. Yield: 313 mg (32%); $\delta_{\rm H}$ (400 MHz, [D₆]-DMSO): 9.78 (2H, br. s, H_d), 8.23 (1H, s, H_a), 7.89 (2H, d, *J* = 8.0 Hz, H_b), 7.49 (1H, t, *J* = 8.00 Hz, H_c), 4.49 (4 H, s, H_e).

N,N-3-bis(1-(pyrazin-2-yl)ethylidene)isophthalohydrazide, L

Isophthaloyl dihydrazide (0.5 g, 2.6 mmol) was suspended in ethanol (50 mL) and solid acetylpyrazine (0.673 g, 5.5 mmol) added and the suspension heated at reflux overnight. The white precipitate was allowed



to cool to room temperature and separated by filtration, washed with ethanol (3 × 10 mL) then diethyl ether (1 × 10 mL) to give a white powder. Yield: 0.85 g (81%); $\overline{\nu}_{max}/cm^{-1}$: 3160 (w, br), 2990 (w, br), 1673 (m), 1652 (s), 1615 (w), 15334 (s), 1518 (m), 1471 (m), 1425 (m), 1407 (w), 1368 (w), 1322 (m), 1308 (s), 1257 (s), 1171 (m), 1154 (s), 1118 (s), 1089 (s), 1050 (w), 1024 (w), 1014 (s), 1001 (w), 983 (m), 934 (m), 889 (w), 861 (m), 852 (m), 819 (m), 799 (w), 773 (w), 761 (w), 744 (m), 719 (s), 690 (m), 662 (m), 651 (s), 622 (m), 602 (m); *m*/*z* (HR-ESMS) 403.1634 [M + H⁺] calc. for [C₂₀H₁₈N₈O₂ + H]⁺ 403.1631. $\delta_{H/C}$ L insufficiently soluble.



Synthesis of 1

$[Fe_{2}L_{3}](BF_{4})_{4}$

A suspension of L (15 mg, 0.037 mmol) and Fe(BF₄)₂·6H₂O (8.4 mg, 0.024 mmol) were stirred in nitromethane (10 mL) overnight at room temperature. The resulting red solution was filtered and the filtrate subjected to vapour-diffusion with toluene as an anti-solvent. Red prism crystals, suitable for single crystal X-ray diffraction, formed after one week. Yield: 30 mg (75%); Microanalysis performed upon freshly isolated crystals; Found: C, 42.0; H, 4.3; N, 17.5% [Fe₂(C₂₀H₁₈N₈O₂)₃](BF₄)₄·C₇H₈·9H₂O requires: C, 41.9; H, 4.2; N, 17.5%; though equally these data can be fit by [Fe₂(C₂₀H₁₈N₈O₂)₃](BF₄)₄·C₇H₈·7.5H₂O·MeNO₂ requires: C, 41.8; H, 4.13; N, 17.8% or subtle variations to this solvent admixture; \vec{v}_{max}/cm^{-1} : 3591 (br, w), 3226 (br, w), 1677 (s), 1634 (w), 1602 (w), 1570 (m), 1527 (w), 1505 (s), 1462 (s), 1430 (m), 1408 (w), 1376 (m), 1344 (m), 1290 (w), 645 (m), 600 (w), 505 (m), 462 (m). Solution based analyses were thwarted by the insolubility of the crystals in common laboratory solvents.

Thermogravimetric Analysis on 1

The onset of mass loss from freshly isolated crystals of **1** was evident at RT from thermosgravimetric analysis and the contents of the voids were shown to account for *ca*. 12% by mass up to *ca*. 60 °C with an additional *ca*. 4% mass lost up to *ca*. 200 °C. Thereafter slow decomposition commenced and was essentially complete by *ca*. 550 °C. Elemental analysis (above) suggested a solvent composition accounting for *ca*. 13-15% molecular mass per mesocate unit, and matches well the volatile contents suggested by thermogravimetric analysis.



Fig. S1. Thermogravimetric data for 1.

Crystallographic Data

Single crystal X-ray diffraction for **1** was carried out on an Agilent Supernova with an Atlas CCD area detector using graphite-monochromatized Cu-K α ($\lambda = 1.54178$ Å) radiation. The structure was solved using direct methods with SHELXT² and refined in Olex2³ using all data by full matrix least-squares procedures with SHELXL-97.⁴ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimized were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma 2(F_o^2) + aP2 + bP]^{-1}$, where $P = [max(F_o)^2 + 2F_c^2]/3$.

There is one crystallographically unique tetrafluoroborate anion in the asymmetric unit, which has an occupancy of 2/3. Positional disorder over two positions has been assigned to some atoms in a ratio of 1:1. Six symmetry equivalents of the anion exist, totalling four anions per mesocate complex. The high symmetry of the space group and the disordered nature of the solvent molecules meant the residual electron density within the hexagonal channels could not be accurately assigned. As such the contribution of this electron density was subtracted from the reflection data by the SQUEEZE⁵ method as implemented in the program PLATON⁵. This equates to a solvent accessible void volume of 1164 Å³ and the removal of 369 electrons from the unit cell (185 per mesocate complex). TGA and microanalytical data (above) suggest the identity of the solvent mix is comprised from a combination of water (7-9 molecules), toluene (1 molecule) and/or nitromethane (1 molecule) which sum to *ca*. 140-160 electrons. These data match that suggested by SQUEEZE quite well when consideration is given to the potential for partial desolvation of the crystals during handling.

Complex	1
Empirical formula	$C_{60}H_{54}B_4F_{16}Fe_2N_{24}O_6$
Formula weight	1666.21*
Temperature/K	120.00(10)
Crystal system	hexagonal
Space group	$P6_{3}/m$
a/Å	14.3872(3)
<i>b</i> /Å	14.3872(3)
c/Å	24.9442(4)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	90
$\gamma/^{\circ}$	120
Volume/Å ³	4471.49(18)
Ζ	2
$ ho_{ m calc} g/cm^3$	1.238
μ/mm^{-1}	3.379
<i>F</i> (000)	1692.0
Crystal size/mm ³	$0.288 \times 0.106 \times 0.083$
Radiation	$CuK\alpha (\lambda = 1.54184)$
2Θ range for data collection/°	7.088 to 140.12
Index ranges	$-17 \le h \le 12, -17 \le k \le 16, -27 \le l \le 30$
Reflections collected	15316
Independent reflections	2906 [<i>R</i> _{int} = 0.0256, <i>R</i> _{sigma} = 0.0167]
Data/restraints/parameters	2906/69/224
Goodness-of-fit on F^2	1.141
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0780, wR_2 = 0.2296$
Final <i>R</i> indexes [all data]	$R_1 = 0.0785, wR_2 = 0.2300$
Largest diff. peak/hole / e Å ⁻³	1.18/-0.53

 Table S1. Crystallographic data for 1

*Does not include the disordered solvent molecules within the solvent accessible voids.



Fig. S2. Asymmetric unit of **1** with atom labelling scheme. Tetrafluoroborate anions and disordered solvent molecules omitted for clarity.



Fig. S3. (Top). Single mesocate structure, showing intramolecular H-bonding between N11-H11...O13. H-bonds shown by cyan dashed lines. Viewed down the crystallographic *b*-axis.

(Bottom). View of mesocate with intramolecular H-bonding viewed down the 6-fold crystallographic *c*-axis. Tetrafluoroborate anions and disordered solvent molecules omitted for clarity.



Fig. S4. View of the crystal structure of 1 highlighting selected intra- and inter- molecular interactions between two neighbouring molecules including H-bonding (cyan dashed lines); offset face-to-face π-π interaction of the pyrazine rings (dashed green lines, CentPyz , 3.687 Å); edge-to-face C-H…π interaction of the phenyl rings (dashed green lines, C15-H15…CentC₆H₄, 2.903 Å). By virtue of the crystal symmetry, all of these interactions reciprocate at each end of each ligand strand. Therefore, a given mesocate participates in 36 H-bonding interactions [3 × 2 (as donor *and* acceptor) × 6 (each pyrazine)] and 6 offset face-to-face π-π interactions between pyrazine rings. Tetrafluoroborate anions and disordered solvent molecules omitted for clarity.



Fig. S5. Crystal packing viewed down the 6-fold crystallographic *c*-axis of **1** shown in space filling representation. Tetrafluoroborate anions and disordered solvent molecules omitted for clarity.



Fig. S6. Crystal packing of **1** viewed down the 6-fold crystallographic *c*-axis. Space filling representation of BF₄⁻ anions within the one-dimensional channels shown. Disordered solvent molecules omitted for clarity.



Fig. S7. Crystal packing viewed down the crystallographic *b*-axis of **1.** Tetrafluoroborate anions and disordered solvent molecules omitted for clarity.

Table S2. Structural information on hydrogen bonding interactions for 1.

D-H···A	<i>d</i> (D-H) Å	$d(\mathbf{D}-\mathbf{H}\cdots\mathbf{A})$ Å	$d(\mathbf{D}\cdots\mathbf{A})$ Å	<(D-H··· A) °	Symmetry Code
N11-H11N6	0.88	2.248	3.009(8)	144.23	1+y, 1-x+y ,1-z
N11-H11013	0.88	2.355	2.956(7)	125.88	1-y, x-y, z
C5-H5…O13	0.95	2.555	3.17(1)	122.91	2-x, 1-y, 1-z
C16-H16…N6	0.95	2.602	3.516(8)	160.86	1+y, 1-x+y, 1-z

Table S3. Structural information on $\pi \cdots \pi$ interactions for **1**.

Interaction	Dist. Å	d(D-H··· centroidC6H4) Å	< °
centroid _{pyz} centroid _{pyz}	3.687	-	Parallel face-to-face $\pi \cdots \pi$
C15-H15····centroid _{C6H4}	3.754	2.903	149.6 (D-H···A)

Activation of crystals of 1: The activation of 1 was achieved by washing isolated crystalline samples with toluene, then allowing them to soak in dichloromethane for 72 hours, exchanging the solvent once every 24 hours, then acetone for 48 hours. The dichloromethane and acetone solvents were regularly refreshed during the soaking time. The acetone was then removed by placing the sample under high vacuum for 18 hours. Removal of the solvent was confirmed by IR spectroscopy and elemental analysis. Powder X-ray Diffraction (PXRD) post-activation verified retention of sample crystallinity and integrity.



Fig. S8. PXRD for 1. The calculated powder pattern was obtained from the single crystal data of1. The 'as-synthesised' pattern was obtained from a polycrystalline powder of freshly isolated single crystals of 1. The 'activated' powder pattern was obtained as described above.

Single Component Gas Adsorption Isotherms



Fig. S9. H₂ sorption isotherm performed at 77 K.



Fig. S10. Sorption isotherms for O₂, N₂, CO₂, CH₄, C₂H₆ and C₂H₄ at 273 K. Filled symbols indicate adsorption, empty symbols indicate desorption.

Isosteric Heat of Adsorption (Q_{st}) Calculations

Adsorption data at 273 and 294.5 K for **1** was fit to a virial function and the isosteric enthalpy of adsorption (Q_{st}) was calculated using the Clausius–Clapeyron equation.⁶



Fig. S11. Plots of isosteric heats of adsorption (Q_{st}) vs. uptake for gases CO₂, N₂, CH₄, C₂H₄, C₂H₆ and O₂ within **1**.



Fig. S12. CO₂ adsorption isotherms of **1** at 273 and 294.5 K, fitted using the virial equation (Table S4).

Model	Virial		
Equation	$y = \ln(x) + 1/T^*(a0 + a1^*x + a2^*x^2 + a3^*x^3 + a4^*x^4 + a5^*x^5) + (b0 + b1^*x + b2^*x^2 + b3^*x^3)$		
Reduced Chi-Sqr	4.36E-07		
Adj. R-Square	1		
		Value	Standard Error
	Т	273	0
	a0	-4334.76	5.22959
	a1	828.9611	27.08479
	a2	-1075.83	37.13463
	a3	370.6392	17.61651
	a4	60.74544	4.67733
	a5	-18.6771	0.87389
	b0	24.05483	0.01788
	b1	-2.09316	0.09066
	b2	3.83154	0.11803
	b3	-1.36633	0.04393
	Т	294.5	0
	a0	-4334.76	5.22959
	a1	828.9611	27.08479
	a2	-1075.83	37.13463
	a3	370.6392	17.61651
	a4	60.74544	4.67733
	a5	-18.6771	0.87389
	b0	24.05483	0.01788
	b1	-2.09316	0.09066
	b2	3.83154	0.11803
	b3	-1.36633	0.04393

Table S4. Parameters used to fit virial equation for CO_2 in 1 (Fig. S12)



Fig. S13. CO₂ isosteric heats of adsorption (Q_{st}) of 1 using the fitted data measured at 273 and 294.5 K.



Fig. S14. C_2H_4 adsorption isotherms of 1 at 273 and 294.5 K, fitted using the virial equation (Table S5).

Model	Virial			
Equation	$y = \ln(x) + 1/T^{*}(a0 + a1^{*}x + a2^{*}x^{2} + a3^{*}x^{3} + a4^{*}x^{4} + a5^{*}x^{5}) + (b0 + b1^{*}x + b2^{*}x^{2} + b3^{*}x^{3})$			
Reduced Chi-Sqr	3.69793E-5			
Adj. R-Square	0.99997			
		Value	Standard Error	
	Т	273	0	
	a0	-4272.52161	38.03823	
	a1	649.87483	119.86119	
	a2	-373.04813	90.84459	
	a3	-61.37017	6.41249	
	a4	0	0	
	a5	0	0	
	b0	23.69546	0.13087	
	b1	-1.20333	0.40255	
	b2	2.35543	0.28574	
	b3	0	0	
	Т	294.5	0	
	a0	-4272.52161	38.03823	
	a1	649.87483	119.86119	
	a2	-373.04813	90.84459	
	a3	-61.37017	6.41249	
	a4	0	0	
	a5	0	0	
	b0	23.69546	0.13087	
	b1	-1.20333	0.40255	
	b2	2.35543	0.28574	
	b3	0	0	

Table S5. Parameters used to fit virial equation for C_2H_4 in **1** (Fig. S14).



Fig. S15. C_2H_4 isosteric heats of adsorption (Q_{st}) of 1 using the fitted data measured at 273 and 294.5 K.



Fig. S16. C_2H_6 adsorption isotherms of 1 at 273 and 294.5 K, fitted using the virial equation (Table S6).

Model	Virial		
Equation	y = ln(x)+1/T*(a0 + a1*	x + a2*x ² + a3*x ³ + a4*x ⁴ + a5*x ⁵)	+ (b0 + b1*x + b2*x ² + b3*x ³)
Reduced Chi-Sqr	1.68E-04		
Adj. R-Square	0.99989		
		Value	Standard Error
	Т	273	0
	aO	-3842.52	47.27743
	a1	461.3459	55.70895
	a2	0	0
	a3	0	0
	a4	0	0
	a5	0	0
	b0	21.97075	0.16504
	b1	-0.07827	0.21353
	b2	1.11712	0.12306
	b3	-0.19408	0.05895
	Т	294.5	0
	aO	-3842.52	47.27743
	a1	461.3459	55.70895
	a2	0	0
	a3	0	0
	a4	0	0
	a5	0	0
	b0	21.97075	0.16504
	b1	-0.07827	0.21353
	b2	1.11712	0.12306
	b3	-0.19408	0.05895

Table S6. Parameters used to fit virial equation for C_2H_6 in 1 (Fig S16).



Fig. S17. C_2H_6 isosteric heats of adsorption (Q_{st}) of **1** using the fitted data measured at 273 and 294.5 K.



Fig. S18. CH₄ adsorption isotherms of **1** at 273 and 294.5 K, fitted using the virial equation (Table S7).

Model	Virial		
Equation	$y = \ln(x) + 1/T^*(a0 + a1^*x + a2^*x^2 + a3^*x^3 + a4^*x^4 + a5^*x^5) + (b0 + b1^*x + b2^*x^2 + b3^*x^3)$		
Reduced Ch	Chi-Sqr 4.45E-04		
Adj. R-Squa	are 0.99967		
		Value	Standard Error
	Т	273	0
	a0	-2385.04	44.02511
	a1	178.635	169.9816
	a2	0	0
	a3	0	0
	a4	0	0
	a5	0	0
	b0	20.39388	0.15489
	b1	0.26137	0.60924
	b2	0	0
	b3	0	0
	Т	294.5	0
	aO	-2385.04	44.02511
	a1	178.635	169.9816
	a2	0	0
	a3	0	0
	a4	0	0
	a5	0	0
	b0	20.39388	0.15489
	b1	0.26137	0.60924
	b2	0	0
	b3	0	0

Table S7. Parameters used to fit virial equation for CH4 in 1 (Fig. S18).



Fig. S19. CH₄ isosteric heats of adsorption (Q_{st}) of 1 using the fitted data measured at 273 and 294.5 K.



Fig. S20. N₂ adsorption isotherms of **1** at 273 and 294.5 K, fitted using the virial equation (Table S8).

Model	Virial			
Equation	$y = \ln(x) + 1/T^*(a0 + a1^*x + a2^*x^2 + a3^*x^3 + a4^*x^4 + a5^*x^5) + (b0 + b1^*x + b2^*x^2 + b3^*x^3)$			
Reduced Ch	Chi-Sqr 1.23E-02			
Adj. R-Squa	re 0.99093			
		Value	Standard Error	
	Т	273	0	
	aO	-2278.59	215.3335	
	a1	2935.682	3036.2	
	a2	0	0	
	a3	0	0	
	a4	0	0	
	a5	0	0	
	b0	21.58713	0.75925	
	b1	-10.4347	10.92339	
	b2	0	0	
	b3	0	0	
	Т	294.5	0	
	aO	-2278.59	215.3335	
	a1	2935.682	3036.2	
	a2	0	0	
	a3	0	0	
	a4	0	0	
	a5	0	0	
	b0	21.58713	0.75925	
	b1	-10.4347	10.92339	
	b2	0	0	
	b3	0	0	

Table S8. Parameters used to fit virial equation for N_2 in 1 (Fig. S20).



Fig. S21. N₂ isosteric heats of adsorption (Q_{st}) of 1 using the fitted data measured at 273 and 294.5 K.



Fig. S22. O₂ adsorption isotherms of **1** at 273 and 294.5 K, fitted using the virial equation (Table S9).

Model	Virial			
Equation	$y = \ln(x) + 1/T^*(a0 + a1^*x + a2^*x^2 + a3^*x^3 + a4^*x^4 + a5^*x^5) + (b0 + b1^*x + b2^*x^2 + b3^*x^3)$			
Reduced Ch	Chi-Sqr 1.17E-02			
Adj. R-Squa	are 0.99132			
		Value	Standard Error	
	Т	273	0	
	a0	-2128.84	210.2693	
	a1	3994.136	3279.626	
	a2	0	0	
	a3	0	0	
	a4	0	0	
	a5	0	0	
	b0	21.19067	0.74111	
	b1	-14.3842	11.7789	
	b2	0	0	
	b3	0	0	
	Т	294.5	0	
	а	-2128.84	210.2693	
	a1	3994.136	3279.626	
	a2	0	0	
	a3	0	0	
	a4	0	0	
	a5	0	0	
	b0	21.19067	0.74111	
	b1	-14.3842	11.7789	
	b2	0	0	
	b3	0	0	

Table S9. Parameters used to fit virial equation for O_2 in **1** (Fig. S22).



Fig. S23. O₂ isosteric heats of adsorption (Q_{st}) of **1** using the fitted data measured at 273 and 294.5 K.

IAST and Breakthrough Calculations

IAST selectivity calculations for binary gas mixtures

Mixed gas adsorption isotherms and gas selectivities for equimolar mixtures of CO_2/CH_4 and CO_2/N_2 were calculated at 294.5 K based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz.⁷ In order to predict the adsorption performance of **1** toward the separation of binary mixed gases, the parameters were fitted from the single-component CO_2 , N_2 and CH_4 adsorption isotherms based on dual site Langmuir model as below:

$$y = \frac{Q_1 a_1 P}{1 + b_1 P} + \frac{Q_2 a_2 P}{1 + b_2 P}$$

Where y is the uptake of a gas, P is the equilibrium pressure and Q_1 , a_1 , b_1 , Q_2 and b_2 are constants.

Mixed gas isotherms derived from IAST calculations were fitted by a single-site Langmuir model to be further used for breakthrough simulations:

$$y = \frac{QaP}{1+bP}$$



Fig. S24. CO₂ (black) and N₂ (red) mixed gas isotherm of **1** calculated using IAST for an equimolar mixture of CO₂/N₂ at 294.5 K fitted with a Langmuir model.



Fig. S25. CO₂ (black) and CH₄ (red) mixed gas isotherm of 1 calculated using IAST for an equimolar mixture of CO₂/CH₄ at 294.5 K fitted with a Langmuir model.



Fig. S26. IAST selectivity for equimolar mixture of CO₂/CH₄ (red) and CO₂/N₂ (black) at 294.5 K.

Mathematical modelling and breakthrough curves simulation

Considering a fixed bed adsorption column of length L filled with $\mathbf{1}$, the following assumptions were made to develop a mathematical model.⁸ This mathematical model was solved later to calculate the concentration of gasses at different times along the bed.



Fig. S27. Schematic diagram of a fixed adsorption bed

- The dynamic behaviour of the fluid obeys plug flow model in the bed.
- The gradient of the concentration along the radial and angular direction is neglected.
- The flow velocity is varied along the bed and it is calculated from total mass balance equation.
- The gas property is described by Peng-Robinson equation of state.
- Diffusion and adsorption into the particles is assumed as a lump transfer model.
- The mass transfer resistance was neglected and instant adsorption was assumed to be occurred in the bed (equilibrium model).
- The pressure drop is considered along the bed using Ergun equation.
- The adsorption columns operate under isothermal condition.
- Mixed gas isotherms calculated by IAST method were fitted by single site Langmuir model and fitting parameters were used for breakthrough curve simulations.

Based on the preceding assumptions, the component and overall mass balances in the bulk phase of the adsorption column are written as follow:

$$\varepsilon \frac{\partial C_i}{\partial t} = -\frac{\partial (uC_i)}{\partial z} - (1 - \varepsilon)\rho_s \frac{\partial q_i}{\partial t}$$
$$\varepsilon \frac{\partial C}{\partial t} = -\frac{\partial (uC)}{\partial z} - (1 - \varepsilon)\rho_s \sum_{1}^{n_c} (\frac{\partial q_i}{\partial t})$$

Where C_i and q_i are, respectively, concentration of components in the gas phase and in the adsorbed phase, z is axial coordinate in the bed, u is the superficial gas velocity, ρ_s is the adsorbent density, n_c is the number of the adsorbed components in the mixture and ε is the bed voidage.

The pressure drop is defined by the Ergun's equation as⁹:

$$\frac{\partial P}{\partial z} = -\left(\frac{37.5 (1-\varepsilon)^2 \mu u}{\left(r_p\right)^2 \varepsilon^3} + 0.875 \rho \,\frac{(1-\varepsilon)u^2}{r_p \varepsilon^3}\right)$$

Where *P* is the local pressure, μ is the gas viscosity and ρ is the gas density. The key metric used in the simulations are tabulated in Table S10.

Table S10. Adsorption column parameters and feed characterizations used in the simulations.

Adsorption bed	Feed
Length: 110 mm	Flow rate: 6 ml _N /min of
Diameter: 6.4 mm	equimolar mixture of gasses
Amount of adsorbent in the bed: 1 g	Temperature: 294.5 K
Bed voidage: 0.5	Pressure: 1 bar



Fig. S28. Simulated breakthrough curves for equimolar mixture of CO₂/N₂ (black) or CO₂/CH₄ (red) at 294.5 K and 1 bar in an adsorption column filled with 1 g of 1. C/C₀ is the fractional concentration; each component has an initial concentration of unity.

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