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1 Dynamic Adsorption of CO₂ by CHA Zeolites –

2 Size Matters

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10

11 **ABSTRACT** The performance of K-CHA nanozeolite composed of discrete nanoparticles
12 prepared by an organic template-free direct synthesis is compared to that of conventional
13 micron-sized K-CHA with an order of magnitude difference in particle size and identical
14 chemical composition (Si/Al ratio and cations) for the separation of dilute CO₂ from N₂.
15 Breakthrough curve analysis of the zeolites meshed to identical sizes demonstrates the
16 superior performance of nanozeolites for gas separation due to the significantly faster
17 diffusion of CO₂ molecules through the bed composed of meshed nanozeolite particles
18 evidenced by the enhanced mass transfer, more rapid establishment of equilibrium, and faster
19 desorption of CO₂. Modelling of the CO₂ breakthrough curves indicates enhanced mass
20 transfer properties of the CHA nanozeolite due to the higher linear driving force parameter
21 values. Variation of the modelling parameters and back-calculation of the diffusion
22 coefficients indicates that axial diffusion contributes significantly to the mass transfer
23 behaviour yet also reveals significantly lower micropore diffusion resistance for the nano-
24 sized K-CHA. These results demonstrate for rapid kinetically controlled sorption-based

25 separations, that by reducing the size of the discrete crystallites of the meshed adsorbent
 26 particle by an order of magnitude, significant improvements in the utilization of the bed can
 27 be achieved due to the shortening of the mass-transfer zone, improving the separation
 28 performance.

29 **Keywords:** zeolites, crystal size, CO₂ adsorption, separation, breakthrough analysis

30 **Nomenclature**

c_{in}	concentration at column inlet, mol·m ⁻³
c_{out}	concentration at column outlet, mol·m ⁻³
$c_{g,i}$	component concentration in the gas phase, mol·kg ⁻¹
c_{pg}	specific heat capacity of gas at constant pressure, J·kg ⁻¹ ·K ⁻¹
c_{ps}	specific heat capacity of adsorbent at constant pressure, J·kg ⁻¹ ·K ⁻¹
c_{pw}	specific heat capacity of wall at constant pressure, J·kg ⁻¹ ·K ⁻¹
D_{ax}	axial mass dispersion coefficient, m ² ·s ⁻¹
D_c	micropore diffusivity, m ² ·s ⁻¹
D_p	macropore diffusivity, m ² ·s ⁻¹
d_i	internal diameter of column, m
K	dimensionless Henry's Law equilibrium constant
K_i	affinity constant
$K_{i,0}$	affinity constant at reference temperature
k_f	film mass transfer coefficient, s ⁻¹
k_i	overall mass transfer coefficient, s ⁻¹
k_{in}	heat transfer coefficient between the bed and wall, W·m ⁻² ·K ⁻¹
k_{out}	heat transfer coefficient between the wall and bath, W·m ⁻² ·K ⁻¹
k_{LDF}	effective mass transfer coefficient, s ⁻¹
$n_{adsorbed}$	amount of molecules adsorbed, mol
q_{eq}	adsorbed concentration in equilibrium with $c_{g,i}$, mol·kg ⁻¹
\bar{q}_i	component average concentration on the adsorbed phase, mol·kg ⁻¹
$q_{max,i}$	maximal loading, mol·kg ⁻¹
$q_{max0,i}$	maximal loading at reference temperature T_0 , mol·kg ⁻¹
R	ideal gas constant, J·mol ⁻¹ ·K ⁻¹
r_c	average crystal radius, m
r_p	average particle radius, m
T	bulk phase temperature, K
T_0	reference temperature for isotherm fitting
T_w	wall temperature, K
T_{env}	environmental temperature (reference temperature), K
t	Toth heterogeneity parameter
t_0	heterogeneity parameter at reference temperature T_0
u	interstitial velocity, m·s ⁻¹
V_{He}	volume of He, m ⁻³

V_{in}	volume at column inlet, m^{-3}
V_{out}	volume at column outlet, m^{-3}
WS	wall thickness, m
$y_{adsorptive,i}$	adsorptive volume fraction
ΔH_{ads}	isosteric enthalpy of adsorption, $J \cdot mol^{-1}$
ΔH_i	isosteric enthalpy of adsorption for component i , $J \cdot mol^{-1}$
α	parameter for the temperature dependency of the Toth exponent
ε	bed porosity
ε_p	particle porosity
λ	axial heat dispersion coefficient, $J \cdot s^{-1} \cdot m^{-1} \cdot K^{-1}$
ρ_p	average particle density, $kg \cdot m^{-3}$
ρ_b	average fixed bed density, $kg \cdot m^{-3}$
ρ_g	fluid density, $kg \cdot m^{-3}$
ρ_w	wall density, $kg \cdot m^{-3}$
χ_i	coefficient for the temperature dependency of the maximum capacity

31

32 Introduction

33 The bulk separation and purification of gases are essential industrial processes in which
34 zeolites play key roles in a range of applications including gas drying, S removal, O₂ and N₂
35 production, landfill gas separation (CO₂/CH₄), and H₂ production from methane reforming
36 and refinery off-gas.[1] In the last decade enormous efforts have been dedicated to
37 developing materials for carbon capture and storage (CCS) because of the rising atmospheric
38 concentration of CO₂ and its contribution to anthropogenic global climate change.[2-22]
39 However, due to the presence of H₂O in industrial streams, such as flue gas, the energy and
40 cost efficient separation of CO₂ is considerably challenging. The high cationic content of
41 industrial molecular sieves, such as 4A, 5A and 13X, and their strong interaction with H₂O
42 demands appropriate regeneration to maintain their longevity. Employment of activated
43 alumina upstream of the molecular sieve can be also increase their lifetime considerably, but
44 at additional capital cost.[23] While solvent-based absorption processes are currently the
45 most widely applied for post-combustion CO₂ capture, these can be associated with large
46 energy requirements for regeneration, degradation issues with temperature and the presence

47 of oxygen and toxicity.[24-26] With these points in mind, alternatives to the use of amines
48 solvents such as green solvents, membranes and adsorption-based separations are
49 investigated, with the latter of interest to the current study. Pressure swing adsorption (PSA)
50 and temperature swing adsorption (TSA) are the processes often used for gas separation.
51 Whilst PSA processes can be quite rapid (steps can occur in seconds), currently mature TSA
52 process cycles can be quite long (hours). Whilst TSA may be quite adapted to anthropogenic
53 CO₂ capture, shorter process sequences are required. A rapid TSA process is currently being
54 developed,[27] where the whole capture, regeneration and conditioning steps can take a
55 minute. In such cases however, kinetics of the gas/solid interactions are as important as the
56 thermodynamics and to control the gas diffusion at the particle level can prove critical to
57 separation properties.

58 The development of zeolite materials possessing high CO₂ separation performance has been a
59 focal point because of the established roles zeolites play in petrochemistry and air separation
60 processes thereby providing a rapidly deployable solution at an industrial scale.[23, 28]
61 However, conventional zeolites are composed of micrometre sized particles which means a
62 CO₂ molecule must diffuse a distance through the pores of a particle tens of thousands of
63 times longer than its size. This problem can be partly addressed by improving molecular
64 access to the zeolite micropores through introducing mesoporosity, or by reducing the
65 particle size.[29, 30] However, while creating mesoporosity can significantly improve the
66 diffusion and catalytic properties of zeolites, it typically involves either post-synthesis
67 treatments or the use of expensive organic templates and structure directing agents,
68 increasing the time, cost and waste of the material production.[31]

69 By preparing zeolites with nanoscale dimensions the distance guest molecules must diffuse
70 through the particle can be reduced by an order of magnitude. To benefit from this we have
71 developed pure inorganic one-pot syntheses of industrially important nanozeolites composed

72 of discrete nanoparticles.[32-38] While the yield of particular nanozeolite syntheses warrants
73 further optimisation, the elimination of expensive organic structure-directing agents (OSDAs)
74 and calcination treatments offers a reduction in energy consumption and emissions while also
75 avoiding undesirable changes to the zeolite structure and properties caused by H₂O vapour
76 during calcination. Here we report on the comparison of K-CHA zeolites for the separation of
77 CO₂ from a dilute stream at various temperatures, investigating the difference in performance
78 by varying only the size of the discrete zeolite particles forming the meshed particles by an
79 order of magnitude; the size of the meshed particles for both samples is identical. We provide
80 direct experimental evidence and validation of the enhanced diffusion properties of adsorbent
81 particles composed of discrete nano-sized zeolites applicable to industrially relevant
82 separations. The concentration of CO₂ employed (5 vol%) is comparable to that of the
83 exhaust of a natural gas combined-cycle plant.[39] The choice of examining high aluminium
84 (Si/Al < 3) K-CHA zeolite derives from their attractive properties for CO₂ separation
85 applications, *i.e.*, high CO₂ capacity, and selectivity towards CO₂ over N₂ (4 mmol/g, 27 with
86 Si/Al = 2.4 and 2.1 mmol/g, 80 with Si/Al = 1.2).[6, 40, 41]

87 **Experimental**

88 **Materials**

89 All reagents were used as received unless otherwise specified. Potassium hydroxide (90
90 wt%), LUDOX AS-40, sodium aluminate (NaAlO₂, 40–45% Na₂O, 50–56% Al₂O₃) and
91 sodium hydroxide pellets (98 wt%) were purchased from Sigma-Aldrich. An aqueous
92 solution of caesium hydroxide (CsOH, 50 wt% Cs) was prepared by dissolving caesium
93 hydroxide (Alfa Aesar 20% H₂O, 98%) in ultrapure (Type 1) water. Zeolite Y (H-form,
94 CBV400), was purchased from Zeolyst. Ultrapure water was prepared by a Milli-Q Direct 8
95 system and used for all syntheses. Quartz fine granular washed and calcined (900 °C, 0.2–0.8

96 mm, Merck) was used for blank breakthrough curve measurements. Helium (helium 4.5, \geq
97 99.995%), carbon dioxide (dioxyde de carbone 4.5, \geq 99.995%) and nitrogen (azote 5.0, \geq
98 99.999%) were purchased from Linde.

99 **Synthesis**

100 Micron-sized K-CHA was prepared according to the procedure employed by Shang *et al.*[40]
101 Zeolite Y powder (CBV400, 25 g) was added to de-ionised water (198 mL) and 9.5 M KOH
102 solution (27 mL) in a sealed 250 mL polypropylene bottle. The mixture was shaken for 30 s
103 and then placed in an oven preheated at 95 °C for 15 days. The sample was then cooled to
104 room temperature and washed with de-ionised water by centrifugation at 20,000 rpm until the
105 supernatant had a pH value between 7 and 8. The washed sample was then oven-dried at 60
106 °C overnight. The yield of the micron-sized K-CHA based on the initial mass of CBV400
107 was 37%.

108 Nano-sized K-CHA was prepared according to a procedure described previously.[42] 10.8 g
109 of NaAlO₂ was mixed with 84.0 g of water with rapid stirring. Afterwards, 34.3 g of NaOH,
110 16.5 g of KOH, and 8.8 g of CsOH (50 wt% Cs in water) were added and stirred for 2 h to
111 obtain a clear solution. 200 g of LUDOX AS-40 was added dropwise under vigorous stirring
112 to make a final composition of 0.284 Cs₂O: 2.27 K₂O: 8.56 Na₂O: 22.9 SiO₂: 1.00 Al₂O₃: 198
113 H₂O. The alkali colloidal gel was then aged under vigorous stirring at room temperature for
114 17 days followed by hydrothermal treatment in a static oven at 90 °C for 7 h. The CHA
115 nanocrystals were recovered by centrifugation and washed with hot water (90 °C) until a
116 neutral pH (7–8) of the decanted solution was achieved. The recovered CHA nanocrystals
117 were dried in an oven at 60 °C overnight. The final as-prepared CHA nanocrystals were ion
118 exchanged with a 1 M KCl solution with a liquid/solid ratio (ml/g) of 40 for 2 hours.
119 Afterwards, the CHA nanocrystals were recovered by centrifugation and washed with

120 deionised water three times. This procedure was repeated three times, and the recovered
121 nano-sized K-CHA was dried in an oven at 60 °C overnight. The yield of the nano-sized K-
122 CHA based on the initial combined mass of SiO₂ and Al₂O₃ was 21%.

123 **Characterisation**

124 Powder X-ray diffraction (PXRD) patterns were collected with a PANalytical X'Pert Pro
125 diffractometer using Cu-Kα₁ radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV, 40 mA). The patterns were
126 collected between 5 and 60° 2 θ with a step size of $\sim 0.0167^\circ$ and time per step of 1000 s.
127 Elemental analysis was performed by inductively-coupled plasma mass spectrometry (ICP-
128 MS) using a 7900 ICP-MS from Agilent Technologies. Samples (50 mg) were digested at
129 110 °C for 1 h with hydrofluoric acid and aqua regia (6:1 vol. ratio) followed by
130 neutralisation with boric acid (2 g) and de-ionised water (10 mL) and stirred overnight. The
131 samples were then diluted up to 100 mL; a 10 mL aliquot was filtered before analysis.
132 Thermogravimetric analysis (TG/DTG) was performed using a Setsys Evolution
133 (SETARAM). Analysis under air was performed by heating from 30 to 800 °C (heating rate
134 of 10 °C min⁻¹) and held at 800 °C for 10 minutes. Scanning electron microscopy (SEM) of
135 samples was performed using a Tescan Mira I LMH operating at 30 kV, samples were coated
136 in metal before analysis. Particle size analysis was performed using ImageJ. Energy-
137 dispersive X-ray spectroscopy (EDS) analysis of samples was performed using two Bruker
138 XFLASH 6/30 detectors; the composition was determined from the average of several
139 different measured points. Low temperature N₂ adsorption/desorption isotherms were
140 measured at -196 °C using a Micromeritics 3Flex Surface Characterization unit. Samples
141 were degassed at 350 °C (heating rate of 1 °C min⁻¹) under vacuum for 8 h prior to analysis.
142 High temperature (20, 40 and 60 °C) N₂ and CO₂ adsorption isotherms were measured on a
143 Micromeritics ASAP 2020 instrument, samples were degassed at 350 °C (heating rate of 1 °C
144 min⁻¹) under vacuum for 8 h. CO₂ and N₂ isosteric enthalpies of adsorption (ΔH_{ads}) were

145 calculated directly from the experimental data points of the isotherms recorded at 20, 40 and
146 60 °C using the Clausius Clapeyron equation in the VersaWin software. Mercury porosimetry
147 was performed using a Micromeritics AutoPore V. *In situ* FTIR spectroscopic analysis was
148 performed using a self-supported pellet (~20 mg, 16 mm diameter) of zeolite sample; the
149 transmission spectra were recorded with a ThermoScientific Nicolet iS50 FTIR spectrometer
150 equipped with an MCT detector, at a spectral resolution of 4 cm⁻¹. An IR-cell equipped with
151 a heating device was used to activate the samples at 350 °C prior to the measurements. The
152 cell was connected to a high vacuum line of 10⁻⁶ Torr. The sample was activated by heating
153 with a ramp rate of 3 °C min⁻¹ followed by heating at 350 °C for 4 h under high vacuum. All
154 spectra were recorded at room temperature and normalised to the area and mass of the pellet;
155 determination of the physisorption and chemisorption isotherms was performed as described
156 previously.[43]

157 **Breakthrough Curve Analysis**

158 Breakthrough curve experiments were performed using a 3P Instruments mixSorb SHP eco
159 and Cirrus-3 Quadrupole Mass Spectrometer. Powder samples of zeolite adsorbent were
160 initially pelletised by loading the powder between two core dice in a 20 mm die sleeve, with a
161 base plate and plunger, and increasing the applied pressure to ~1.5 tonnes. The pellets were
162 gently crushed with an agate pestle and meshed from 60 to 35 (250–500 µm) before being
163 loaded into the column, weighed, and covered with a thin layer of glass wool. After each
164 instance of loading the meshed sample into the column, the column was tapped 100 times to
165 remove inter-particle voids. The inner diameter of the column was 6 mm and the height of the
166 adsorbent bed was 6 cm. The ratio of the column inner diameter to the meshed particle
167 diameter was 12–24. The samples were pre-treated under He flow (20 mL/min) with heating
168 from room temperature to 300 °C at 10 °C/min (measured by an internal temperature probe)
169 and held at 300 °C for 6 h using a heating mantle. TG analysis of the zeolite samples was

170 performed to determine the weight-loss of water during the pre-treatment step. The final
171 amounts of nano-sized and micron-sized K-CHA loaded in the column after activation were
172 0.601 and 0.676 g respectively. After pre-treatment the samples were kept under a flow of
173 He (20 mL) at room temperature before commencing the breakthrough curve experiments.

174 Breakthrough curve experiments were conducted using a ternary mixture of CO₂, N₂
175 (analytical components) and He (carrier gas) at 1 bar with a flowrate of 2, 10 and 28 mL/min
176 respectively (total 40 mL/min), representing 5, 25 and 70 vol% of the feed composition for
177 the adsorption step. Prior to the breakthrough curve experiments the mass spectrometer was
178 calibrated by passing the ternary feed mixture through a bypass line to the mass spectrometer.
179 Before contacting the ternary feed mixture with the adsorbent column the sample was
180 maintained under He flow. The adsorption feed mixture was flowed through the adsorbent
181 column after the temperature and spectrometer signals were stable, as determined using a
182 bypass line. After a specified amount of time whereby the bed had reached equilibrium,
183 desorption was conducted immediately by switching the feed to 100% He (40 mL/min). Both
184 the adsorption and desorption steps for each experiment were conducted at the same
185 temperature; experiments were conducted at 20, 40 and 60 °C by immersing the column in a
186 water bath isothermally maintained by a chiller. The time for each step of the analysis was 60
187 min at 20 °C and 30 min at 40 and 60 °C to allow sufficient time for the bed to reach
188 equilibrium after breakthrough. The pressure drop across the column loaded with sample was
189 determined by a pressure sensor located immediately before the column and the pressure
190 controller located immediately after the column. For all experiments conducted the pressure
191 drop was < 0.07 bar or 6% of the column pressure.

192 All breakthrough curve data was processed using the mixSorb Manager software. The
193 differential loading of the adsorbates (CO₂ and N₂) was calculated from the integrated areas
194 exemplified in Figures S1 and S2.

195
$$n_{\text{adsorbed}} = \int V_{\text{in}}(t)c_{\text{in}}(t)dt - \int V_{\text{out}}(t)c_{\text{out}}(t)dt \quad (1)$$

196 The advanced computed flowrate changes was employed to account for changes in the flow
 197 rate using the He carrier gas as an internal standard.

198
$$V_{\text{out}}(t) = \frac{V_{\text{He}}(t)}{1 - \sum_{i=1}^n y_{\text{adsorptive},i}(t)} \quad (2)$$

199 Blank experiments under identical feed composition, temperature, flowrate and pressure
 200 conditions were performed using granular quartz to determine the loading of molecules in the
 201 free space between the adsorbent particles and were directly subtracted from the loading
 202 values of the zeolite samples (Fig. S3). He is considered as a non-adsorbing gas. The dead-
 203 time of the system was estimated at ≈ 2 s based on the time of the activation of the mass-flow
 204 controllers and the recording of the flow composition by the mass spectrometer through the
 205 by-pass line. The void fraction or bed porosity was calculated using the dry mass of the
 206 meshed K-CHA zeolite, the bulk particle density, and the internal column volume.

207 **Breakthrough Curve Modelling**

208 All isotherm and CO₂ breakthrough curve modelling was performed using the 3P-Sim
 209 software package. The experimental CO₂ adsorption isotherms were fitted with a temperature
 210 dependent model. Sips, Dual-Site Langmuir and Toth models were employed; Toth afforded
 211 the best goodness of fit of the data and was employed for the CO₂ breakthrough curve
 212 modelling. The parameters obtained from the modelling of the CO₂ adsorption isotherms with
 213 the Toth equation (3) which were used in the CO₂ breakthrough curve modelling are
 214 presented in Table S4.

215
$$q_{eq} = q_{max,i} \cdot \frac{K_i \cdot c_{g,i}}{(1 + (K_i \cdot c_{g,i})^t)^{\frac{1}{t}}} \quad (3)$$

216 The temperature dependency of the isotherm parameters including the affinity constant, K_i ,
217 maximum loading, q_{max} , and heterogeneity parameter, t , are accounted for with the following
218 equations:

$$219 \quad K_i = K_0 \cdot \exp\left(\frac{\Delta H_{ads}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (4)$$

$$220 \quad q_{max,i} = q_{max,0} \cdot \exp\left(\chi_i \left(1 - \frac{T}{T_0}\right)\right) \quad (5)$$

$$221 \quad t = t_0 + \alpha \left(1 - \frac{T}{T_0}\right) \quad (6)$$

222 Global parameters for the CO₂ breakthrough curve modelling are presented in Table 1.
223 Breakthrough curves were calculated with the following assumptions commonly employed in
224 the literature:[44, 45]

- 225 1. Ideal gas behaviour of the adsorptive through the column.
- 226 2. No mass, heat or velocity gradients in the radial direction; instantaneous thermal
227 equilibrium between the adsorbent and gas.
- 228 3. Dispersed plug flow model.
- 229 4. Negligible effects due to external mass transfer (film mass transfer and macropore
230 diffusion).
- 231 5. Description of the mass transfer through the particle by the linear driving force (LDF)
232 model.[46-48]
- 233 6. Heat capacity of the carrier gas dominates.
- 234 7. Heat capacity of the adsorbed phase neglected.
- 235 8. Constant internal (bed-wall) and external (wall-bath) heat transfer, and axial heat
236 dispersion.
- 237 9. Constant and uniform adsorbent/bed porosity.

238 10. No pressure drop, constant pressure.

239 The model consists of dispersive plug flow with non-isothermal behaviour and variable gas
240 velocity described by a mass and energy balance for the fixed bed and an energy balance for
241 the column wall. The mass balance is expressed as:

$$242 \quad \frac{\partial c_{g,i}}{\partial t} = D_{ax} \frac{\partial^2 c_{g,i}}{\partial z^2} - u \frac{\partial c_{g,i}}{\partial z} - c_{g,i} \frac{\partial u}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \rho_p \frac{\partial \bar{q}_i}{\partial t} \quad (7)$$

243 With respect to the assumptions employed for the calculations, the two energy balance
244 equations are expressed as:

$$245 \quad \Delta H_i \rho_b (1 - \varepsilon) \frac{\partial \bar{q}_i}{\partial t} - (c_{ps} \cdot \rho_b (1 - \varepsilon) + c_{pg} \cdot \varepsilon \cdot \rho_g) \frac{\partial T}{\partial t} - u \varepsilon \rho_g c_{pg} \frac{\partial T}{\partial z} - T \varepsilon \rho_g c_{pg} \frac{\partial u}{\partial z} +$$
$$246 \quad \lambda \varepsilon \frac{\partial^2 T}{\partial z^2} - k_{in} \frac{4}{d_i} (T - T_w) = 0 \quad (8)$$

$$247 \quad k_{in} \cdot d_i (T - T_w) - (d_i \cdot WS + WS^2) c_{pw} \cdot \rho_w \frac{\partial T_w}{\partial t} - k_{out} (d_i + 2 \cdot WS) (T_w - T_{env}) = 0 \quad (9)$$

248 The heat transfer parameters, k_{in} (bed-wall) and k_{out} (wall-bath), and the axial heat dispersion
249 (λ) were estimated according to the according to the shape of the breakthrough curve. The
250 axial dispersion coefficient was calculated using the correlation according to Kast in the 3P-
251 Sim software package [47]:

$$252 \quad D_{ax} = u \cdot \frac{3 \cdot 10^{-3}}{2} \text{ for } 2r_p < 3 \text{ mm} \quad (10)$$

253 Neglecting the external mass transfer resistance and using the LDF approach, the mass
254 transfer is expressed as[49]:

$$255 \quad \frac{\partial \bar{q}_i}{\partial t} = k_{LDF} (q_{eq} - \bar{q}_i) \quad (11)$$

256 The LDF parameter was assumed to be constant for a given operation and fitted to each
257 breakthrough curve. Calculations were performed using the Crank-Nicolson solver (trapezoid

258 scheme). The bed porosity was calculated from the dry mass of zeolite and the bulk particle
 259 density.

260

261

262 **Table 1.** Column, adsorbent and carrier gas parameters used for modelling the CO₂
 263 breakthrough curves of the nano- and micron-sized K-CHA.

Parameter	Value	Source	
Column			
Bed height (cm)	6	Measured	
Column inner diameter (cm)	0.6	Manufacturer	
Gas flow (mL·min ⁻¹)	40	Measured	
Column temperature (°C)	20, 40, 60	Measured	
Pressure (bar)	1.1	Measured	
Axial dispersion coefficient (m ² ·s ⁻¹)	nano	micron	W. Kast estimation
	8.98×10 ⁻⁵	6.97×10 ⁻⁵	
	9.46×10 ⁻⁵	7.40×10 ⁻⁵	
	9.89×10 ⁻⁵	7.92×10 ⁻⁵	
Wall thickness (mm)	3	Manufacturer	
Wall density (g·cm ⁻³)	7.9	Assumed, stainless steel	
Heat transfer bed-wall (internal), [W/(m ² ·K)]	50	Estimated	
Heat transfer wall-bath (external), [W/(m ² ·K)]	500	Estimated	
Heat capacity wall [J/(K·g)]	0.477	Assumed, stainless steel	
Axial heat dispersion [J/(K·min·cm)]	5	Estimated	
Adsorbent			
Mass (g)	0.601 (nano), 0.676 (micron)	Measured	
Particle diameter (mm)	0.25	Assumed	
Bed porosity	0.39 (nano), 0.49 (micron)	Measured	
Particle porosity	0.54 (nano), 0.49 (micron)	Measured	
Heat capacity [J/(K·g)]	1.27	Reference[50]	
Carrier Gas			
Molecular weight (g·mol ⁻¹)	4.0	NIST	
Heat capacity [J/(K·g)]	5.19	NIST	

264

265 Calculation of the MTZ was performed using equation (12):

266

$$267 \quad 1 - \left(\frac{\text{time to breakthrough} \left(\frac{C}{C_0} > 1 \times 10^{-4} \right), \text{min}}{\text{time of bed saturation} \left(\frac{C}{C_0} = 0.95 \right), \text{min}} \right) \times \text{bed length, cm} \quad (12)$$

268

269 Calculation of the CO₂/N₂ selectivity for the competitive dynamic adsorption experiments
270 was performed using equation (13):

$$271 \quad CO_2/N_2 \text{ Selectivity} = \left(\frac{q_{CO_2}}{n_{CO_2}} \right) / \left(\frac{q_{N_2}}{n_{N_2}} \right) \quad (13)$$

272 Where q is the differential loading of the adsorbate and n is the molar amount of adsorbate in
273 the feed.

274

275 **Results and Discussion**

276 **Synthesis and Characterisation of K-CHA**

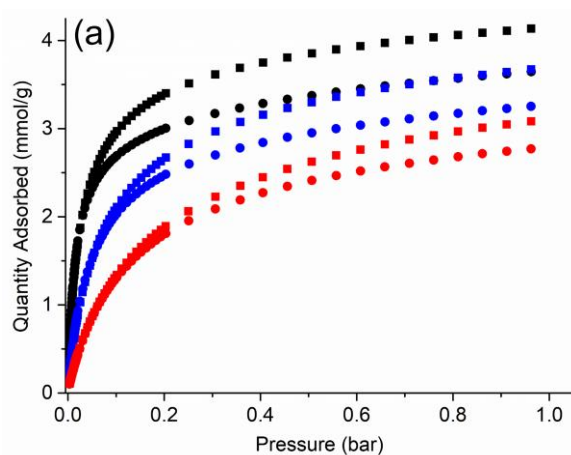
277 A conventional well-studied micron-sized K-CHA was prepared according to the patent
278 literature of Bourgogne *et al.*[40, 51, 52] The nano-sized K-CHA was prepared following an
279 up-scaled procedure derived from our previous work by Ghosravand *et al.* using an identical
280 precursor composition, ageing time, and hydrothermal treatment.[42, 43] The synthesis of
281 nano-sized chabazite has been methodically optimised to obtain discrete zeolite nano-
282 crystallites of sizes below 100 nm with a specific Si/Al ratio. Both samples are highly
283 crystalline (Fig. S4) with near-identical chemical compositions (Table S1); the XRD patterns
284 of both samples are consistent with those previously reported for hydrated K-CHA.[53] The
285 broad Bragg reflections of the nano-sized K-CHA are indicative of the presence of nano-
286 sized crystalline domains.[42] The size of the crystalline domains was determined by
287 Scherrer analysis as 80 nm for the nano-sized K-CHA and 200 nm for the micron-sized K-
288 CHA. Thermogravimetric analysis of the nano- and micron-sized K-CHA samples reveals
289 they possess a similar content of water of 17 and 19 wt% respectively (Fig. S5). Scanning
290 electron microscopy (SEM) results confirms the order of magnitude difference in the particle
291 size between the samples. Analysis of the nano-sized K-CHA shows the sample is composed
292 of discrete nano-crystallites with primary particle sizes ranging predominantly between 50–
293 80 nm (Figs S6a).[42] In comparison, the morphology of the micron-sized K-CHA is that of

294 irregular flake-like particles approximately 100–300 nm thick and 400–1000 nm at maximum
295 width; the particles are composed of intergrown crystallite aggregates approximately 40–80
296 nm in size (Figs S6b).[52]

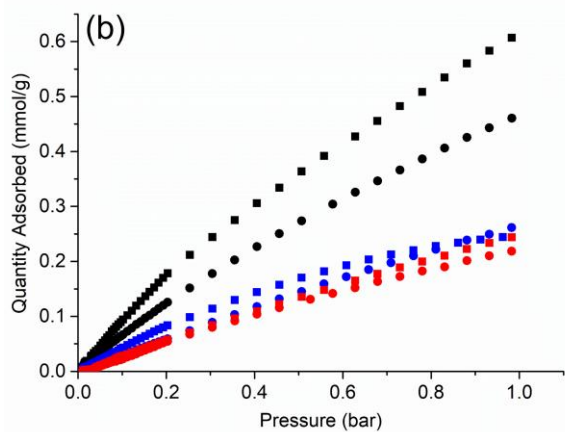
297 The difference in the textural properties of both samples is also evidenced by N₂ sorption
298 analysis performed at –196 °C; both samples exhibit low micropore adsorption due to
299 trapdoor behaviour which restricts access of N₂ to the micropores, however, the nano-sized
300 K-CHA possesses significant inter-particle mesoporosity at high relative pressure due to its
301 nanoparticle morphology (Fig. S7).[40] Both samples were subjected to single component
302 CO₂ and N₂ sorption analysis at 20, 40 and 60 °C up to 1 bar (Figs 1 (a) and (b), Tables S2
303 and S3). The CO₂ and N₂ adsorption capacity decreases with increasing temperature (Fig. 1);
304 for both samples, the adsorbed amount of N₂ is low and increases linearly with increasing
305 pressure while CO₂ exhibits a Type I isotherm due to strong adsorbent-adsorbate interactions.
306 The slightly lower CO₂ adsorption capacity of the nano-sized K-CHA is due to the presence
307 of a phillipsite impurity. The isosteric enthalpy of adsorption (ΔH_{ads}) as a function of loading
308 were determined from the raw single-component isotherms (Fig. 1(c)). Both samples exhibit
309 near-homogeneous adsorption sites for CO₂; the ΔH_{ads} of the nano-sized K-CHA decreases
310 above a coverage of 2 mmol/g due to the saturation of the dual-cation adsorption sites and
311 limited inter-molecular interactions.[35, 43, 54, 55] Both samples also exhibit similar trends
312 for the N₂ ΔH_{ads} with a minor decrease as the loading increases, however, the decrease is
313 more significant for the nano-sized K-CHA. The lower N₂ ΔH_{ads} of the nano-sized K-CHA is
314 ascribed to the higher external surface of the particles providing lower energy adsorption
315 sites. Temperature-dependent modelling of the CO₂ adsorption isotherms was performed
316 using the Sips, Dual-Site Langmuir and Toth equations. The Toth model afforded the best
317 goodness of fit of the data (Fig. S8) and the parameters obtained were used for the modelling
318 of the CO₂ breakthrough curves (Table S4). Satisfactory temperature-dependent models of

319 the N₂ adsorption isotherms could not be obtained ($R^2 < 0.990$) and so the IAST selectivity
320 was not determined.

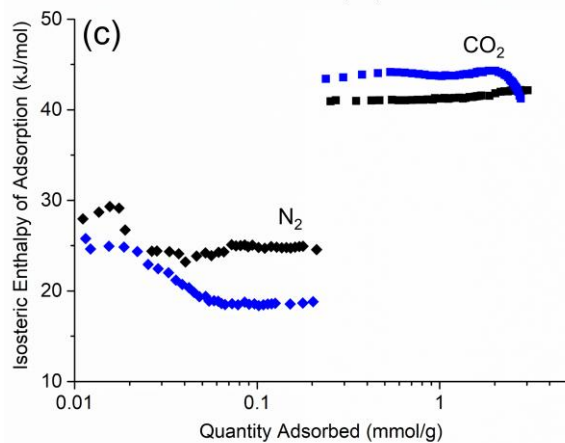
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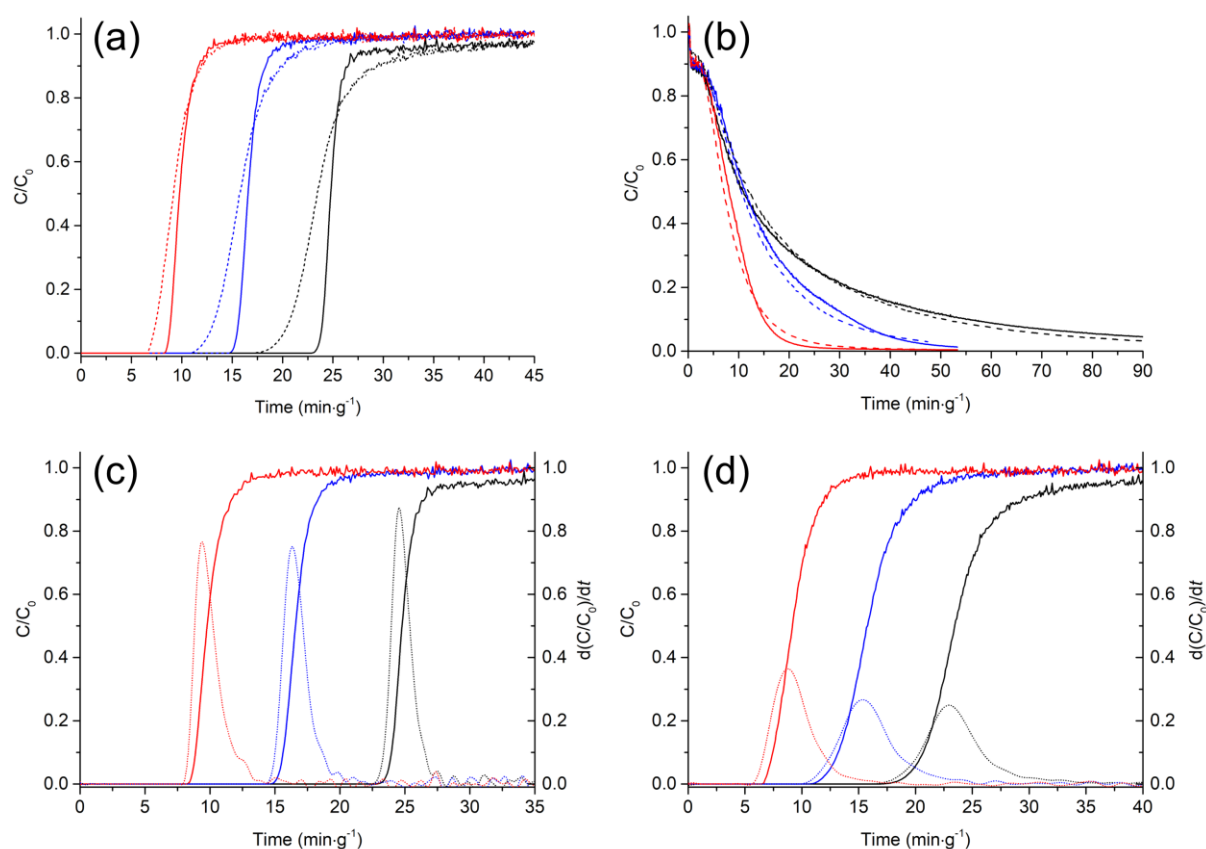


324 **Figure 1.** (a) CO₂ and (b) N₂ adsorption isotherms recorded at 20 (black), 40 (blue) and 60
325 °C (red) on nano-sized (circles) and micron-sized (squares) K-CHA. (c) CO₂ (squares) and
326 N₂ (diamonds) isosteric enthalpies of adsorption for nano-sized (blue) and micron-sized
327 (black) K-CHA.
328

329 **Dynamic Adsorption of CO₂/N₂ on K-CHA and Breakthrough Curve Modelling**

330 Breakthrough curve analysis of the K-CHA samples was conducted using a ternary mixture
331 of He/N₂/CO₂ (70/25/5 vol%) at 1 bar and 20, 40 and 60 °C (Fig. 2); plots of the entire
332 adsorption step show the breakthrough of N₂ on the K-CHA samples is instantaneous and
333 exhibits a roll-up feature due to the displacement of N₂ by CO₂ from within the bed (Fig. S9).
334 Due to the difference of the mass between the adsorbent, column and water bath the
335 temperature profile of the column did not change significantly during the breakthrough
336 experiment (Figure S10, Table S5). A minor temperature excursion of 0.30 and 0.25 °C was
337 observed for the micron- and nano-sized K-CHA for the breakthrough curve analyses at 20
338 °C; smaller deviations were observed at 40 °C, and no discernible temperature excursion was
339 observed at 60 °C. The CO₂ breakthrough profiles of the K-CHA samples clearly exhibit
340 significantly steeper curves for the nano-sized K-CHA across the measured temperatures
341 compared to the micron-sized sample (Fig. 2a), indicative of more uniform diffusion of CO₂
342 through the bed and a reduction in the length of the MTZ, *i.e.* enhanced overall kinetics.
343 While both K-CHA samples were prepared with the same mesh, the discrete nano-crystallites
344 of the nano-sized K-CHA facilitate significantly more rapid intraparticle diffusion. This is
345 also visualised by the plots of $d(C/C_0)/dt$ illustrating the higher rate of change of the slope of
346 the breakthrough curve for the nano-sized K-CHA compared to the micron-sized K-CHA
347 (Figs 2c and d). A slight decrease in the slope of the breakthrough curve for nano-sized K-
348 CHA occurs when the temperature increases from 20 to 40 °C, while the micron-sized K-
349 CHA exhibits a slight increase in the breakthrough curve slope above 40 °C. The time
350 necessary to achieve the desorption under pure He flow (Fig 2b) of CO₂ ($C/C_0 < 0.05$)
351 dramatically decreased with increasing temperature for both samples; at 60 °C the nano- and
352 micron-sized K-CHA required 11 and 14 minutes respectively. The difference in the
353 desorption behaviour between the samples is not as dramatic as the initial breakthrough

354 because of the endothermic nature of the desorption step. Increasing the bed temperature
 355 from 20 to 60 °C resulted in a linear decrease of the differential loading of CO₂ at saturation
 356 for both K-CHA samples (Table 2). The differential loadings of CO₂ calculated from the
 357 competitive breakthrough curves compare well with the isotherm values. In comparison, the
 358 integration of the N₂ loading from the breakthrough curves affords values five times higher
 359 compared to the equilibrium isotherms. Alternatively, integration under the N₂ desorption
 360 curves was performed to calculate the N₂ loading, affording realistic values comparable to
 361 earlier work by Du *et al.*[56] Overall, both samples exhibit similar selectivity towards CO₂
 362 over N₂; the nano-sized K-CHA exhibits slightly higher CO₂ loading under dynamic
 363 adsorption conditions.



364
 365 **Figure 2.** CO₂ breakthrough and desorption curves, and first derivatives of CO₂ breakthrough
 366 curves at 20 °C (black), 40 °C (blue) and 60 °C (red) obtained from competitive dynamic
 367 adsorption experiments, He/N₂/CO₂, 70/25/5. (a) CO₂ breakthrough curves and (b) CO₂
 368 desorption curves of the nano-sized (solid) and micron-sized (dashed) K-CHA zeolites. CO₂
 369 breakthrough curves (solid) and first derivative (dashed) of the (c) nano-sized and (d)
 370 micron-sized K-CHA zeolites.

371 **Table 2.** Differential loading of CO₂ calculated from breakthrough curves at saturation, N₂
 372 differential loading calculated from desorption curves, and CO₂/N₂ selectivity calculated
 373 from equation 13. Data from breakthrough curve analysis (He/N₂/CO₂, 70/25/5) at 20, 40 and
 374 60 °C.

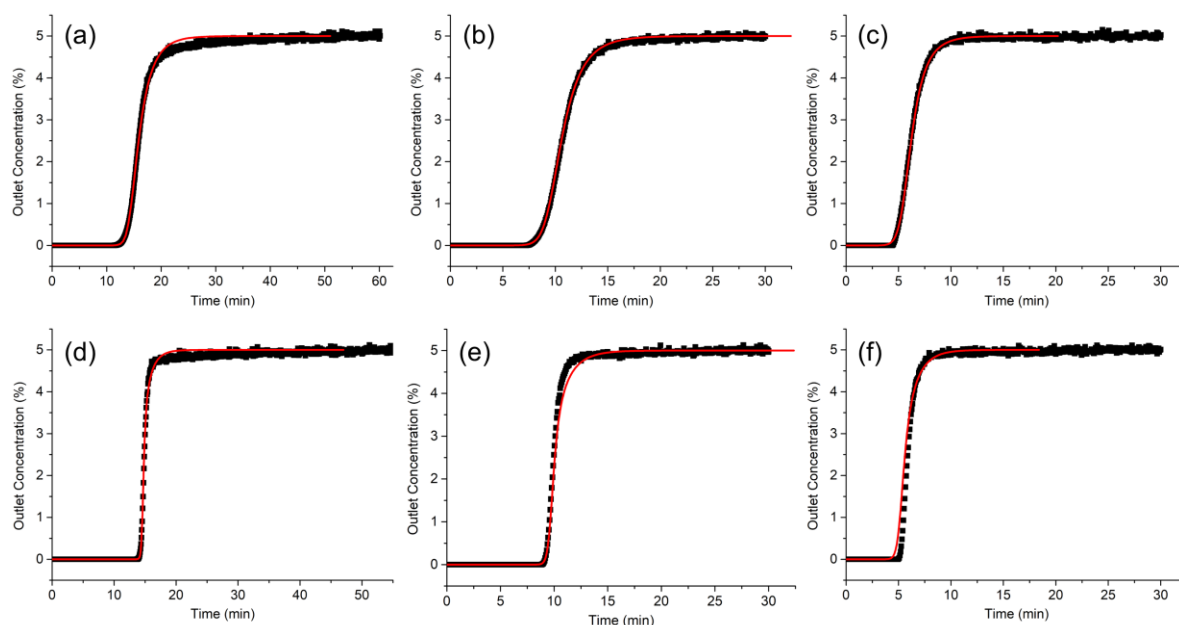
Temperature (°C)	Nano-sized K-CHA			Micron-sized K-CHA		
	Differential loading, q (mmol/g)		CO ₂ /N ₂ selectivity	Differential loading, q (mmol/g)		CO ₂ /N ₂ selectivity
	CO ₂	N ₂		CO ₂	N ₂	
20	2.33	0.085	137	2.22	0.092	121
40	1.49	0.041	182	1.43	0.070	102
60	0.87	0.007	618	0.82	0.006	685

375

376 Comparison of the CO₂ breakthrough curves of the nano- and micron-sized K-CHA at 60 °C,
 377 akin to flue gas conditions, further highlights the difference in the performance of the solid
 378 adsorbents with different particle sizes (Fig. S11). By defining the MTZ between the first
 379 point of breakthrough, $C/C_0 > 1 \times 10^{-4}$ (*i.e.* the end of pure production of the weakly adsorbing
 380 component), and saturation of the bed, $C/C_0 = 0.95$, it is clear that the micron-sized K-CHA
 381 not only exhibits a shallower breakthrough curve but also takes a longer time to reach
 382 equilibrium. Due to the similar CO₂ uptakes of 0.87 mmol/g for both K-CHA samples at 0.05
 383 bar (*i.e.* the partial pressure of CO₂ in the feed) at 60 °C, the longer time to reach equilibrium
 384 for the micron-sized K-CHA is ascribed to the larger particle size and thus longer diffusion
 385 path length. Expressed as a percentage of the total bed length, the length of the MTZ is
 386 significantly shorter (35% vs 52%) for the nano- compared to the micron-sized K-CHA
 387 (Table S6).

388 In addition, simple modelling of the CO₂ breakthrough curves was performed to extract the
 389 effective mass transfer coefficient, or linear driving force parameter (k_{LDF}), to describe the
 390 mass transfer kinetics of CO₂ through the adsorbent bed (Fig. 3).[44] Thus a global
 391 characteristic of the diffusion can be compared between the two samples. Employing the
 392 parameters derived from the Toth models of the CO₂ adsorption isotherms at different
 393 temperatures, the fitted model of the CO₂ breakthrough on the nano-sized K-CHA was found

394 to have 1–2 orders of magnitude higher k_{LDF} compared to that of the micron-sized K-CHA
 395 (Table 3), consistent with the sharper experimental breakthrough curves. The calculated CO₂
 396 equilibrium loadings from the breakthrough curve modelling agree well with the
 397 experimental values, within 10% error. The k_{LDF} for CO₂ of the micron-sized K-CHA are of a
 398 similar magnitude to those of other commercial zeolite adsorbents such as NaX, CaA and
 399 4A.[44, 57, 58] Modelling of the CO₂ breakthrough curves for the micron-sized K-CHA
 400 using the maximal loading term extracted from the isotherm modelling resulted in slight
 401 offsets between the experimental and modelled curves. This is may be due to the CO₂
 402 equilibrium adsorption curves of the micron-sized K-CHA having not completely levelled off
 403 leading to an overestimation of the $q_{max,i}$.[59] To fit the model to the experimental data the
 404 maximal loading terms were reduced by 10%, 7% and 4% for the curves at 20 °C, 40 °C and
 405 60 °C respectively. The adjustments to the maximal loading did not affect the k_{LDF} values of
 406 the fitted curves (Fig. S12).[60]

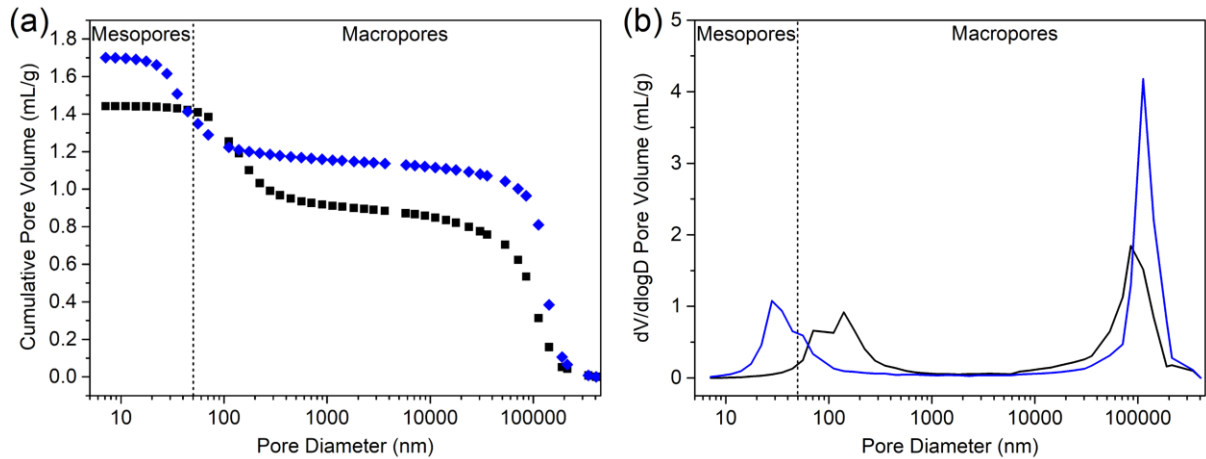


407
 408 **Figure 3.** Experimental CO₂ breakthrough curves (black squares) and the fitted model of CO₂
 409 breakthrough curves (red lines) using the parameters from Tables 1 and S4 for the micron-
 410 sized K-CHA at (a) 20 °C, (b) 40 °C and (c) 60 °C, and for the nano-sized K-CHA at (d) 20
 411 °C, (e) 40 °C and (f) 60 °C.

412 **Table 3.** Calculated linear driving force parameters and CO₂ equilibrium loadings obtained
 413 from the modelling of the CO₂ breakthrough curves for the nano- and micron-sized K-CHA
 414 at 20, 40 and 60 °C.

Temperature (°C)	k_{LDF} (s ⁻¹)		CO ₂ equilibrium loading (mmol/g)	
	Nano-sized K- CHA	Micron-sized K-CHA	Nano-sized K- CHA	Micron-sized K-CHA
20	2.37	0.0221	2.35	2.26
40	2.93	0.0442	1.61	1.51
60	3.27	0.125	0.92	0.90

415 To better understand the effect of particle size on the performance and diffusion properties of
 416 the K-CHA samples, mercury porosimetry analysis of the meshed K-CHA samples was
 417 performed, and diffusion resistances were considered using established correlations in the
 418 literature.[46, 61] Plots of the pore diameter against the cumulative pore volume (Fig. 4a) and
 419 pore size distribution (Fig. 4b) of the meshed K-CHA samples reveal two intrusion events
 420 corresponding to the initial filling of the macropores (interparticle porosity) and the filling of
 421 the remaining macropores and mesopores. Both samples exhibit similar intrusion of the
 422 interparticle porosity, however, the distribution of the macropores is different. The majority
 423 (80%) of the macropore volume of the meshed nano-sized K-CHA occurs for pores $\geq 6 \mu\text{m}$
 424 while for the meshed micron-sized K-CHA this corresponds to 61% (Table S7). This may be
 425 ascribed to the more uniform morphology of the nano-sized K-CHA compared to the flake-
 426 like morphology of the micron-sized K-CHA. The filling of the mesopores (7–50 nm) shows
 427 that the meshed nano-sized K-CHA exhibits ≈ 14 times higher mesopore volume compared to
 428 the meshed micron-sized K-CHA. This is a clear result of the meshed particle being
 429 composed of smaller discrete nanocrystals. For the nano-sized K-CHA the mesopores
 430 account for approximately 17% of the total pore volume determined by Hg porosimetry,
 431 while for the micron-sized K-CHA this value is 1.3%.



432
 433 **Figure 4.** Plot of the pore diameter (nm) vs the (a) cumulative pore volume, and (b) pore size
 434 distribution for the meshed nano-sized (blue) and micron-sized (black) K-CHA zeolite.
 435

436 Considering that each of the eight-membered ring pore apertures of K-CHA are occupied by
 437 extra-framework K^+ cations and are comparable in size to CO_2 , like for 4A zeolite, it may be
 438 expected that the diffusion behaviour of K-CHA to be micropore controlled.[62] However,
 439 considering that the meshed particle sizes are 0.25–0.5 mm, axial dispersion may be expected
 440 to contribute significantly to the mass transfer behaviour.[63] Recent breakthrough curve
 441 analysis of N_2/O_2 on lithium exchanged low silica X (LiLSX) zeolite demonstrated that axial
 442 dispersion effects must be considered for small particles and at low Reynolds number which
 443 is the case in this work.[64] The contributions from the different diffusion resistances to the
 444 overall mass transfer coefficient k_i were calculated using equation (14), which is a
 445 generalisation of the Glueckauf approximation[46]:

446

$$\frac{1}{k_i} = \frac{Kr_p}{3k_f} + \frac{Kr_p^2}{15\varepsilon_p D_p} + \frac{r_c^2}{15D_c} \quad (14)$$

447 where the first, second and third terms on the right-hand side of equation 14 represent the
 448 film mass transfer, macropore, and micropore resistances, and K is the equilibrium Henry's
 449 law constant. Calculation of the values for the axial dispersion, film and macropore
 450 contributions were performed using established correlations and experimental data.[46, 61]

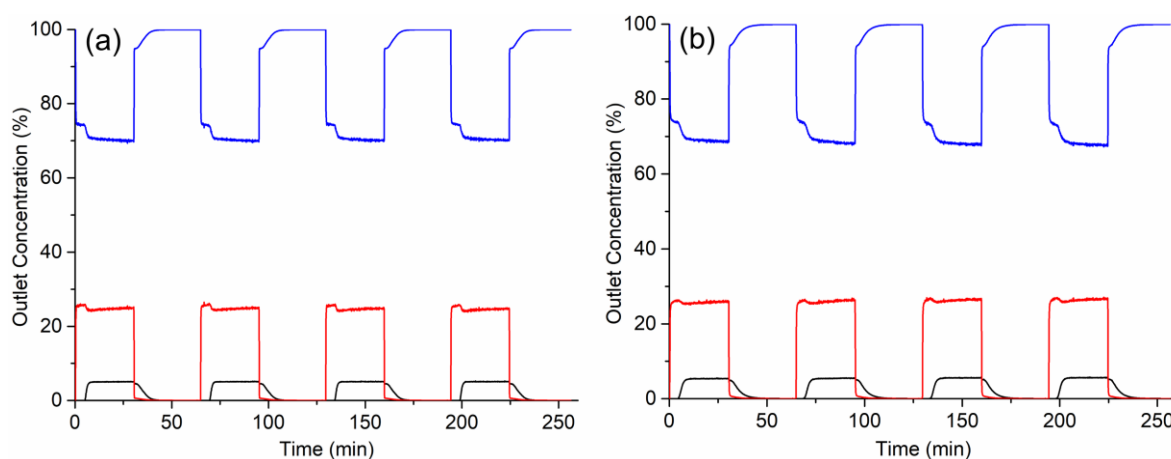
451 However, due to the unavailability of experimental intracrystalline diffusivity values for CO₂
452 in high-aluminium cation-containing chabazite zeolites, the micropore contribution was
453 estimated by subtracting the film and macropore contributions from the effective mass
454 transfer coefficients extracted from the breakthrough curve modelling. The calculated
455 intracrystalline diffusivity values of CO₂ for the K-CHA zeolites are 3–4 orders of magnitude
456 greater than for 4A.[65] Details describing the calculation of each contribution are provided
457 in the supporting information; the values and percentages of k_i are presented in Tables S12–
458 14. The calculations reveal that between the film, macropore and micropore resistances, the
459 micropore contribution is the most significant, being several orders of magnitude greater and
460 accounting for >99.5% of the mass transfer coefficient for the micron-sized K-CHA across all
461 measured temperatures. For the nano-sized K-CHA the micropore resistance is much less
462 significant than for the micron-sized K-CHA, but still accounts for 83, 87 and 92% of the
463 mass transfer coefficient at 20, 40 and 60 °C respectively. Both samples exhibit similar
464 absolute values of film and macropore resistance; their relative contribution is more
465 significant for the nano-sized K-CHA. Both K-CHA samples exhibit similar absolute values
466 for the contribution of axial dispersion, which are similar or greater in value to the
467 contribution of the micropore resistance. For the micron-sized K-CHA, the ratio of the axial
468 dispersion to micropore resistance increases from 0.8 at 20 °C to 1.1 at 40 °C and 2.1 at 60
469 °C due to the greater decrease in the micropore resistance. For the nano-sized K-CHA, the
470 ratio of the axial dispersion to the micropore resistance is significantly higher (54–91). This
471 indicates that the mass transfer behaviour of the meshed nano-sized K-CHA is primarily
472 affected by axial dispersion; the ratio of the axial dispersion to the micropore resistance
473 decreases with increasing temperature.

474 For comparison, the contributions from the lumped resistances and axial dispersion were also
475 explored by varying either the k_{LDF} parameter or axial dispersion values for the modelling of

476 the breakthrough curves.[58] Consistent with the trend of the calculated values presented in
477 Table S12 the shape of the modelled CO₂ breakthrough curves for the nano-sized K-CHA are
478 susceptible to variations in the axial dispersion, while varying the k_{LDF} parameter results in
479 little change (Fig S13). In comparison, the micron-sized K-CHA is much more susceptible to
480 changes of the k_{LDF} parameter, and similarly susceptible to changes of the axial dispersion
481 (Fig. S14). While increased axial dispersion increases spreading of the MTZ, the
482 experimental results presented here indicate that for adsorbent particles of identical size and
483 composition, reducing the size of the discrete crystals within the meshed particle may reduce
484 the size of the MTZ. Analysis of the results indicate this is primarily attributed to the
485 reduction of the micropore resistance, which may be a consequence of the shorter
486 intracrystalline diffusion pathway of CO₂ within the nano-sized K-CHA. While the
487 introduction of mesoporosity has shown to improve the CO₂ adsorption kinetics for LTA
488 zeolite, in the present case where the nano-sized K-CHA exhibits an order of magnitude
489 greater mesopore volume than the micron-sized K-CHA, the contribution from the macropore
490 diffusion resistance is negligible.[66]

491 Multiple cycles of CO₂ breakthrough, and desorption under pure He at 60 °C also
492 demonstrates the improved performance of the nano-sized K-CHA (Fig. 5) which exhibits a
493 29% higher CO₂ differential loading for the first cycle (Table 4). The CO₂ loading was
494 calculated up to the first point of breakthrough. Upon subsequent cycles of CO₂ adsorption,
495 and desorption under pure He, the CO₂ capacities of both samples decreases due to the
496 formation of chemisorbed carbonate species and the incomplete removal of adsorbed CO₂ by
497 He during the desorption step.[43] This is supported by integration of the CO₂ desorption
498 curves for the nano and micron-sized K-CHA at 60 °C which afforded 0.76 and 0.73 mmol/g,
499 or 87 and 88% of the differential loadings at saturation (Table 2). Over the next three cycles,
500 on average, the nano-sized K-CHA exhibits better performance up to the end of pure

501 production of the weakly adsorbing component, losing only 14% of its initial CO₂ capacity
 502 while the micron-sized K-CHA loses approximately 29% (Table 4). This may be due to
 503 compositional inhomogeneity of the micron-sized K-CHA particles due to their preparation
 504 by interzeolite conversion and the different solubilities of Si and Al species, as well as the
 505 possibility of internal structural rearrangements due to the long hydrothermal treatment time
 506 (15 days).[67] This rationale is supported by comparing the relative amounts of CO₂
 507 chemisorbed species. *In situ* FTIR spectroscopic analysis of the micron-sized K-CHA in the
 508 presence of CO₂ (17.9 kPa) revealed ~3 times greater the amount of CO₂ chemisorbed
 509 species compared to nano-sized K-CHA, *i.e.* 5% vs 1.7% of the total physisorbed and
 510 chemisorbed CO₂ (Fig. S15).[43]



511
 512 **Figure 5.** Four consecutive cycles of the adsorption step (He/N₂/CO₂, 70/25/5) and
 513 desorption step (He, 100) for breakthrough curve analysis on the (a) nano-sized K-CHA and
 514 (b) micron-sized K-CHA at 60 °C. Colour legend: He (blue), N₂ (red), and CO₂ (black).

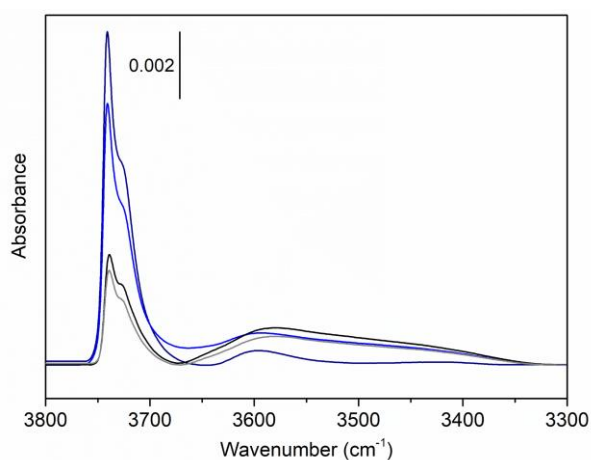
515 **Table 4.** Differential loading of CO₂ calculated from CO₂ breakthrough curves at $C/C_0 >$
 516 1×10^{-4} on nano- and micron-sized K-CHA subjected to multiple cycles of breakthrough
 517 (He/N₂/CO₂, 70/25/5) and desorption (He, 100) at 60 °C.

Cycle	CO ₂ differential loading, q (mmol/g)	
	Nano-sized K- CHA	Micron-sized K-CHA
1	0.66	0.51
2	0.56	0.35
3	0.56	0.36
4	0.57	0.36

519 ***In situ* FTIR Analysis of the Silanol Environments**

520 To consider the role defects may play in the separation performance of the K-CHA samples,
521 *in situ* FTIR spectroscopic analysis was also employed to examine the distributions of silanol
522 environments on both K-CHA samples (Fig. 6). Analysis before and after breakthrough curve
523 experiments reveals two peaks at 3740 cm^{-1} and 3727 cm^{-1} attributed to isolated silanol sites
524 corresponding to the external surfaces of the different K-CHA samples.[68] These peaks are
525 significantly more intense for the nano-sized K-CHA due to its larger external surface area.
526 Both micron and nano-sized K-CHA samples show a broad complex band in the range of
527 3333 and 3668 cm^{-1} . These peaks can be attributed to the internal silanol sites exhibiting
528 strong hydrogen bonding between them.[68] The micron-sized K-CHA exhibits a greater
529 initial population (black trace) of strong internal hydrogen bonding sites which may reflect
530 internal framework T-atom vacancies or missing T–O–T bonds due to the intergrown nature
531 of the crystallites. After multiple pre-treatment and breakthrough cycles this band decreases
532 slightly (grey trace). Conversely, the nano-sized K-CHA exhibits fewer sites initially (navy
533 trace) and an increased population of these sites after multiple pre-treatment and
534 breakthrough cycles (blue trace). This suggests that despite an increase in the population of
535 strong hydrogen-bonding silanol sites on the nano-sized K-CHA the diffusion performance is
536 dominated by the effect of the particle size difference. Deconvolution and exact peak
537 assignment in this region is not possible using exclusively FTIR spectroscopy and requires
538 additional characterization techniques (*i.e.* ^1H MAS NMR) beyond the scope of this work.
539 Table 5 presents the concentration of the silanol sites obtained by integration of the silanol
540 region for both the nano- and micron-sized K-CHA samples before and after the
541 breakthrough measurements. For both the nano- and micron-sized K-CHA samples a
542 reduction of $\sim 27\%$ of the silanol sites are observed after the breakthrough measurements

543 (Table 5). This can be partly attributed to the residual chemisorbed species chemically
544 bonded to the silanol sites and in agreement with our previous work.[43]



545
546 **Figure 6.** *In situ* FTIR spectra at 25 °C highlighting the silanol region of the nano-sized
547 (navy, blue) and micron-sized (black, grey) K-CHA samples zeolite (before, after
548 breakthrough curve analysis). Samples were pre-treated at 300 °C under high vacuum (10^{-6}
549 kPa) prior to measurement.

550
551
552 **Table 5.** The concentration of silanol sites of micron and nano-sized K-CHA samples before
553 (fresh) and after (used) breakthrough measurements obtained using *in situ* FTIR
554 spectroscopy.

Sample		Silanol site concentration ($\text{cm}^{-1}\cdot\text{g}^{-1}$)
Nano-sized K-CHA	Fresh	403
	Used	288
Micron-sized K-CHA	Fresh	306
	Used	224

555

556 Conclusions

557 As we move towards the need to control process rate, by improving the diffusion properties
558 of zeolites through the organic-template free direct synthesis of discrete zeolite nanoparticles,
559 instead of employing post-synthetic treatments, significant enhancements in the separation
560 performance can be achieved. By comparing meshed micron-sized and nano-sized K-CHA
561 with identical Si/Al ratios and cation compositions for CO₂ separation from N₂, the diffusion
562 of CO₂ through the bed of meshed nano-sized K-CHA is more rapid and uniform.

563 Breakthrough curve analysis shows steeper breakthrough curves and more rapid achievement
564 of equilibrium for the meshed nano-sized K-CHA due to the smaller discrete particle size.
565 While textural analysis by Hg porosimetry reveals improved mesoporosity for the nano-sized
566 K-CHA, back-calculation of the diffusion coefficients reveals significantly lower micropore
567 diffusion resistance as responsible for the improved mass transfer behaviour. This translates
568 to a greater k_{LDF} of the modelled and fitted CO₂ breakthrough curves and a reduction in the
569 size of the MTZ by 17% despite the significant contribution from axial dispersion to the mass
570 transfer behaviour. Furthermore, we also observe that the nano-sized K-CHA has
571 approximately three times less CO₂ chemisorbed species than micron-sized K-CHA. When
572 scouting for improved adsorbents, most academic researchers often concentrate on capacity
573 and selectivity and pay less attention to the kinetics of the process. The combination of these
574 three features will determine the productivity, often referred to in catalysis as STY (space
575 time yield, units: moles of a desired product.time⁻¹·reactor volume⁻¹). STY is a key parameter
576 to design the size of a unit, *i.e.*, this investment cost (CAPEX). While these results support
577 the potential of nanozeolites in realising greater performance improvements, further
578 investigation of the diffusion behaviour of nanozeolites in larger columns and their
579 comparison to micron-sized counterparts will yield greater insights due to the variety of pore
580 sizes, framework topologies, elemental compositions and shaping factors of zeolites which
581 influence the diffusion properties.

582 **Declaration of Competing Interests**

583 The authors declare no competing financial or professional interests.

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590

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592

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