**Supporting Information**

**Adsorption and Diffusion of N\(_2\) and CO\(_2\) and their mixture on Silica Gel**

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Table S1: List of references in which adsorption and diffusion of N\(_2\) and CO\(_2\) on silica adsorbents is studied.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Adsorbent</th>
<th>Experimental method</th>
<th>Isotherm type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Song et al.(^1)</td>
<td>Unmodified and chemically modified silica adsorbents with base sites</td>
<td>Static volumetric method (Micromeritics Accusorb 2100E)</td>
<td>CO(_2) isotherms at 298.15,373.15 and 523.15 K</td>
<td></td>
</tr>
<tr>
<td>Drake et al.(^2)</td>
<td>Silica gel-70Å</td>
<td>Gravimetric method (Omnisorb 360)</td>
<td>N(_2) isotherm at 77.4 K</td>
<td>BET equation, Type-IV isotherm</td>
</tr>
<tr>
<td>Zhao et al.(^3)</td>
<td>Silica gel - 110Å</td>
<td>Thermal gravimetric (TGA) method</td>
<td>N(_2) and CO(_2) isotherms, CO(_2) isotherms at 298.15 K</td>
<td>Type-IV isotherm of N(_2)</td>
</tr>
<tr>
<td>Zhou et al.(^4)</td>
<td>Silica gel-70Å</td>
<td>Volumetric method</td>
<td>N(_2) isotherm (103.15K-298.15K)</td>
<td>Type-I isotherm at 298.15 K, Type-II isotherm below 138 K</td>
</tr>
<tr>
<td>Berlier and Frere(^5)</td>
<td>Silica gel-20Å</td>
<td>Volumetric method</td>
<td>CO(_2) isotherm (278 K-328 K) up to 33 bar pressure</td>
<td>Nearly constant adsorbed mass of CO(_2) up to 33 bar</td>
</tr>
<tr>
<td>Gonzalez and Holland(^6)</td>
<td>Silica gel</td>
<td>Volumetric method</td>
<td>CO(_2) isotherm (297-422 K) at 1-68.95 bar pressure</td>
<td>Two-layer kinetic model</td>
</tr>
<tr>
<td>Wurzbacher et al.(^7)</td>
<td>Diamine functionalized silica gel-94Å</td>
<td>TGA method</td>
<td>CO(_2) isotherm (298.15-383.15 K)</td>
<td>Freundlich isotherm model</td>
</tr>
<tr>
<td>Li et al.(^8)</td>
<td>Silica gel</td>
<td></td>
<td>Pure N(_2), CO(_2) isotherms (288.15-333.15 K) up to 3 bar</td>
<td>Extended Langmuir-Binary CO(_2)/N(_2) isotherm prediction but no results to support the validity of the extended Langmuir model. LDF model</td>
</tr>
<tr>
<td>Zhang et al.(^9)</td>
<td>Macroporous silica gel</td>
<td>Volumetric method</td>
<td>Pure N(_2), CO(_2) isotherms at 303.15 K up to 14 bar</td>
<td>Linear isotherm</td>
</tr>
<tr>
<td>Li and Tezel(^10)</td>
<td>Silicalite</td>
<td>Pure N(_2),CO(_2) isotherm-Constant volume method</td>
<td>Pure N(_2),CO(_2) isotherm (313.15-373.15 K) up to 5 bar</td>
<td>Pure N(_2), CO(_2) isotherm-Toth isotherm model</td>
</tr>
</tbody>
</table>

S1
The constant volume setup (shown in Figure S1) consists of a dose side and a test side. The dose side consists of the volume to the left of valve V2 and is used to give a known step change in pressure of adsorbate gas on the test side. The test side comprises of volume to the right of V2 and adsorbent is filled in the test cell. The dose pressure can be controlled quite precisely to above atmospheric pressure using a back-pressure regulator (GO BPR) and below atmospheric pressure down to 2 mbar using the vacuum pump equipped with automated pressure control (CVC 3000 controller). Low dose pressures are crucial to obtain the equilibrium data in the linear range of isotherm. The temperature of the test side is maintained...
constant using a water bath (JULABO). The adsorbent is regenerated in-situ using a silicone oil bath at 150°C while simultaneously pulling deep vacuum for up to 10-12 hours. The apparatus can be used to measure both adsorption & desorption isotherms.

Figure S1: Schematic of the constant volume apparatus [V1,2,3= manual gate valves; SV = solenoid valve; PT = pressure transmitter; PI = pressure gauge].

**S1.1 Blank volume measurement**

After ensuring that the set up was leak proof, blank volume of the total system, dose side and test side, were measured by a combination of two methods first before filling the adsorbent in the test cell. In the first method, Valve V1 and V2 were opened (Figure S1) and SV1 and V3 were closed. SV2 was then opened and after attaining a low vacuum level, SV2 was closed and pressure was allowed to stabilize. The pressure was recorded as \( P_0 \). V2 was then closed SV1 was opened to pressurize the system and then it was closed. The pressure was allowed to stabilize and recorded as \( P_1 \). After that, V2 was opened and the system was allowed to attain equilibrium. Pressure was noted as \( P_2 \). In the second method, valve V1 and V2 were opened and SV2 and V3 were closed. SV1 was opened and system was pressurized up to 2 atm pressure. After pressurizing, SV1 was closed and after stabilization, pressure was noted \( P_1 \). V3 was then opened and gas bubble in the bubble meter was allowed to rise across 10 cc volume
and V3 was then closed. The stabilized pressure was noted as $P_2$. Applying mass balance on dose and test side gives the following equations (S2.1 & S2.2) which were used to calculate the volume of the system:

\[ V_1(P_1 - P_o) = (V_1 + V_2)(P_2 - P_o) \]  
\[ (V_1 + V_2)(P_1 - P_2) = V \]

where; $V_1$: Dose side volume (cc); $V_2$: Test side volume (cc) and $V$: Volume flown out of bubble meter (cc).

**S1.2 Sample preparation**

The silica gel sample was regenerated for 10-12 hours in a furnace (Thermcraft) at 150°C with continuous Helium purge. The sample was then transferred to the test column inside a glove box in an inert environment to prevent any contamination with moisture. The dry weight of the sample was then recorded as 10.496 g. The test column was then again connected to the constant volume set up. The measured volumes of the different sections of the constant volume set up have been summarized in the Table S2.

Table S2: Volumes in constant volume set-up.

<table>
<thead>
<tr>
<th>Dose side volume $V_d$ (cc)</th>
<th>Volume $V_2$ (cc)</th>
<th>Volume of adsorbent $V_{ads}$ (cc)</th>
<th>Test side volume $V_t$ (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.6</td>
<td>26.9</td>
<td>8</td>
<td>18.9</td>
</tr>
</tbody>
</table>

**S1.3.1 Adsorption equilibrium measurement**

For adsorption equilibrium measurement, a constant temperature was maintained on the test side by immersing it in a water bath. Vacuum was then pulled to attain the lowest pressure and after stabilization, pressure was recorded as the initial pressure $P_o$. The test side was then isolated from the dose side by turning off the valve V2. A known amount of adsorbate gas was then added to the dose side. The pressure was allowed to stabilize and recorded as $P_i$. The test side valve V2 was then turned ON and left in that position to allow the pressures on the dose and test sides to be equalized and the system to reach a new equilibrium at a lower pressure. The equilibrium pressure was recorded as $P_{eqi}$. The steps were repeated to cover the complete range of the isotherm.
Applying mass balance on test side and dose side for the $i$th equilibrium step gives:

$$\frac{(P_i - P_{eq(i-1)})V_d}{R_gT_d} = \frac{(P_{eq(i)} - P_{eq(i-1)})V_d}{R_gT_d} = \Delta q_i V_{ads} + \frac{(P_{eq(i)} - P_{eq(i-1)})V_t}{R_gT_t}$$

(S2.3)

Rearranging equation (S2.3) gives equation (S2.4):

$$\Delta q_i = \frac{[\frac{(P_i - P_{eq(i-1)})V_d}{R_gT_d} - \frac{(P_{eq(i)} - P_{eq(i-1)})V_d}{R_gT_d} - \frac{(P_{eq(i)} - P_{eq(i-1)})V_t}{R_gT_t}]}{V_{ads}}$$

(S2.4)

$$q_i = \Delta q_i + q_{i-1}$$

(S2.5)

where, $V_d$, $V_t$ and $V_{ads}$ are dose side, test side and adsorbent volume respectively in (cc), $T_d$ and $T_t$ are the dose side and test side temperature respectively in (K), $i=1,2,..$ indicates run number, $R_g$ is universal gas constant (mbar cc/K/mol), $P_i$ is the dose pressure (mbar), $P_{eq(i)}$ is the equilibrium pressure (mbar), $\Delta q_i$ is the adsorbed concentration per unit adsorbent volume (mol/cc) in $i$th run and $q_i$ is total adsorbed concentration per unit adsorbent volume (mol/cc) up to the $i$th run.

S1.3.2 Desorption equilibrium measurement

For desorption isotherm measurement, the last (highest) equilibrium point reached during adsorption was noted as $P_{j eq}$ mbar and the equilibrium loading was $q_j$. The test side was isolated from dose side by closing the valve V2. The vacuum level was set to $P_{j-1}$ such that $P_{j-1} < P_{j eq}$ and it was allowed to stabilize. The test side valve V2 was then opened and left in that position to allow the system to attain a new equilibrium. The new equilibrium pressure was recorded as $P_{(j-1) eq}$ and steps were repeated i.e., valve V2 was closed and the vacuum level was set to $P_{j-2} < P_{(j-1) eq}$ and so on to cover the complete range of isotherm.

Applying mass balance on dose side and test side gives equations (S2.6) and (S2.7);

$$\frac{P_{j eq}V_t}{R_gT_t} + q_j V_{ads} + \frac{P_{j-1}V_d}{R_gT_d} = \frac{P_{(j-1) eq}V_t}{R_gT_t} + q_{(j-1)} V_{ads} + \frac{P_{(j-1) eq}V_d}{R_gT_d}$$

(S2.6)

$$q_{(j-1)} = q_j + \frac{\frac{(P_{j eq} - P_{(j-1) eq})V_{test}}{R_gT_{test}} + \frac{(P_{j-1} - P_{(j-1) eq})V_{dose}}{R_gT_{dose}}}{V_{ads}}$$

(S2.7)

where, $V_d$, $V_t$ and $V_{ads}$ are the dose side, test side and adsorbent volume respectively in (cc), $T_d$ and $T_t$ are the dose side and test side temperature respectively in (K), $j=1,2,3..$ indicates the run number, $R_g$ is the universal gas constant (mbar cc/K/mol), $P_{j-1}$ is the dose pressure
(mbar), $P_{(j-1)eq}$ is the equilibrium pressure (mbar), $q_{(j-1)}$ is the total adsorbed concentration per unit adsorbent volume (mol/cc) up to the $j$th run.

**S2 The multi-purpose rig**

The multi-purpose rig (shown in Figure S2) is used in the current study. The rig has the provision for three adsorbent columns which are jacketed for flowing fluid to maintain a desired constant wall temperature. There are provisions to measure the temperature of the adsorbent bed at three locations along the column length (Temperature sensor: WIKA TR10 series resistance temperature detectors and Transmitter: West P6100 1/16 Din Process controller). Pressure is measured through pressure transmitters (WIKA: Model A-10) and solenoid valves (ASCO 24DC) are used to automate the closing and opening of the valves. The working and data acquisition of the rig are controlled through a Labview software (National Instruments). There are separate mass flow controllers (MFC) (Brooks) for He, N$_2$ and CO$_2$ gas to control the flow of feed gases. Silicone oil is allowed to flow through the column jacket and the temperature can be controlled in the range 20 – 150 °C using a Lauda thermostat (RK8 KS). It is also possible to maintain deep vacuum in the columns down to 2 mbar using a vacuum pump (Vacubrand PC 3004 Vario). Therefore, it is possible to conduct experiments and in situ adsorbent regeneration at any fixed temperature in this range. During regeneration vacuum is also pulled simultaneously with heating. The exit composition and flowrate are monitored through a mass spectrometer (HIDEN QGA) and a Coriolis mass flow meter (Siemens Sitrans FC Flow sensor MASS 2100 DI 1.5), respectively.

![Figure S2: A multi-purpose rig for wet flue gas dynamic column breakthrough and vacuum swing adsorption studies (Red: Silica gel column (Drying unit), Blue: Z-13X columns (CCC unit)).](image)
S3 Model formulation for simulating the breakthrough response

For an n component gas mixture, there are (n-1) component mass balance, total mass balance, total energy balance and n mass transfer rate equations:

Component mass balance:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z} \left[ CD_i \frac{\partial y_i}{\partial z} + C_i v \right] - \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t}$$  \hspace{1cm} (S3.1)

Applying ideal gas law: \( C_i = \frac{P y_i}{R_g T} \), the equation takes the following form:

$$\frac{\partial y_i}{\partial t} + \frac{y_i \partial P}{P \partial t} - \frac{y_i \partial T}{T \partial t} = \frac{T}{P} D_i \frac{\partial}{\partial z} \left( \frac{P}{T} \frac{\partial y_i}{\partial z} \right) - \frac{T}{P} \frac{\partial}{\partial z} \left( \frac{y_i P}{T} v \right) - \frac{R_g T}{P} \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t}$$  \hspace{1cm} (S3.2)

Overall Mass Balance:

$$\frac{1}{P} \frac{\partial P}{\partial t} - \frac{1}{T} \frac{\partial T}{\partial t} = \frac{T}{P} \frac{\partial}{\partial z} \left( \frac{P}{T} v \right) - \frac{1-\varepsilon}{\varepsilon} \frac{R_g T}{P} \sum_{i=1}^{n_{comp}} \frac{\partial q_i}{\partial t}$$  \hspace{1cm} (S3.3)

Adsorbate transfer rate into adsorbent:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i)$$  \hspace{1cm} (S3.4)

where \( q_i^* \) is calculated from the isotherm model and \( k_i \) is the mass transfer coefficient. In general, it can be represented as a function of fluid phase concentration and temperature:

$$q_i^* = f(C_i, T)$$  \hspace{1cm} (S3.5)

Column Energy Balance:

$$\left[ \frac{1-\varepsilon}{\varepsilon} \left( \rho_s C_{p,s} + C_{p,a} \sum_{i=1}^{n} q_i \right) \right] \frac{\partial T}{\partial t} = \frac{K_s}{\varepsilon} \frac{\partial^2 T}{\partial z^2} - \frac{C_{p,a}}{R_g} \frac{\partial}{\partial z} \left( v P \right) - \frac{C_{p,a}}{R_g} \frac{\partial P}{\partial t} - \frac{1-\varepsilon}{\varepsilon} C_{p,a} T \sum_{i=1}^{n} \left( \frac{\partial q_i}{\partial t} \right) - \frac{1-\varepsilon}{\varepsilon} \sum_{i=1}^{n} \left( -\Delta H_i \right) \frac{\partial q_i}{\partial t} - \frac{2h_{in}}{\varepsilon r_{in}} (T - T_w)$$  \hspace{1cm} (S3.6)

Wall Energy Balance:

$$\rho_w C_{p,w} \frac{\partial T_w}{\partial t} = K_w \frac{\partial^2 T_w}{\partial z^2} + \frac{2r_{in} h_{in}}{r_{out}^2 - r_{in}^2} (T - T_w) - \frac{2r_{out} h_{out}}{r_{out}^2 - r_{in}^2} (T_w - T_a)$$  \hspace{1cm} (S3.7)

Pressure Drop (Darcy’s Equation):

$$- \frac{\partial P}{\partial z} = \frac{150}{4} \frac{1}{r_P^3} \left( \frac{1-\varepsilon}{\varepsilon} \right)^2 \mu v$$  \hspace{1cm} (S3.8)
Equation (S3.8) on rearrangement gives the expression for local velocity:

\[ v = \frac{4}{150} \left( \frac{\varepsilon}{1-\varepsilon} \right)^2 \frac{r^2}{\mu} \left( -\frac{\partial P}{\partial z} \right) \]  

(S3.9)

The axial dispersion is calculated by using Edwards and Richardson\textsuperscript{18} correlation:

\[ D_L = \gamma D_m + \frac{Pe_\infty^{-1}(v_0 d_p)}{1 + \left( \frac{\rho u D_m}{v_0 d_p} \right)^2} \]  

(S3.10)

where \( D_m \) is the molecular diffusivity for gas mixture \( v_o \) is the interstitial velocity and \( d_p \) is the particle diameter. In Eq. (S3.10), \( Pe_\infty \) is the limiting value of the Peclet number, which is a function of the adsorbent particle size. Based on the literature data, Langer et al.\textsuperscript{19} have proposed the Eq. (S3.10a) to calculate \( Pe_\infty \) with \( d_p \) in units of cm and the same equation used to approximate the particle size transition region. Wicke\textsuperscript{20} has proposed Eq. (S3.10b) to estimate \( \gamma \).

\[ Pe_\infty = 2, \quad d_p > 0.3 \text{ cm} \]

\[ Pe_\infty = 6.7d_p, \quad d_p \leq 0.25 \text{ cm} \]  

(S3.10a)

\[ \gamma = 0.45 + 0.55\varepsilon \]  

(S3.10b)

After estimating \( Pe_\infty \) and \( \gamma \), Eq. (S3.10c) proposed by Bischoff\textsuperscript{21} can give an estimate for \( \beta \).

\[ \frac{1}{Pe_\infty} = \frac{\beta}{\alpha} \]  

(S3.10c)

Here \( \alpha \) accounts for velocity distribution and is a function of particle diameter. \( \alpha \) values reported by Langer et al.\textsuperscript{19} at four different particle diameters from 0.056 to 0.225 cm are well correlated by Eq. (S3.10d) with a \( R^2 \) value of 0.9881.

\[ \alpha = 8.1352\ln(d_p) + 24.807 \]  

(S3.10d)

In the above equation, \( d_p \) is in cm. In the present study, \( d_p = 0.2 \text{ cm} \) and \( \varepsilon = 0.34 \). For these values, \( Pe_\infty = 1.34, \gamma = 0.637, \alpha = 11.714 \text{ and } \beta = 8.74 \). The latter value is near to the theoretical value of 8 for a highly turbulent random walk model.\textsuperscript{19} Edwards and Richardson\textsuperscript{18} conducted experiments in packed beds by varying particle size in the range of 0.0377 – 0.607 cm keeping column to particle diameter ratio constant at 10 and used a constant value of \( \beta = 13 \) to fit the experimentally measured axial dispersion coefficient. We used
\( \beta = 8.74 \) for a conservative estimate of the axial dispersion coefficient for different breakthrough runs. In the wide range of literature experimental data from several studies analysed by Langer et al.\(^1\), any systematic effect of column to particle diameter ratio was not obvious, but it should be noted that in the minimum column to particle diameter ratio used in these studies was 10.

The adsorption equilibrium is described by Langmuir isotherm equation:

\[
q_i = q_{si} \frac{b_i C_i}{1 + b_i C_i} \tag{S3.11}
\]

LDF model equation:

\[
k_i = \left( \frac{C_i 15 \varepsilon_p D_e}{q_i^* r_p^2} \right) \tag{S3.12}
\]

\( r_p \) is the particle diameter; \( C_i \) is gas phase concentration of \( i \); \( q_i^* \) is mixture equilibrium loading of \( i \) corresponding to \( C_i \) and \( \varepsilon_p \) is macroparticle porosity; \( D_e \) is the effective diffusivity given by:

\[
\frac{1}{D_e} = \tau \left( \frac{1}{D_m} + \frac{1}{D_{K+s}} \right); \text{where } D_{K+s} = D_K + \left( \frac{1-\varepsilon_p}{\varepsilon_p} \right) \left( \frac{q_i^*}{C_i} \right) D_s \tag{S3.13}
\]

\( D_K \) (cm\(^2\)/s) is the Knudsen diffusivity and \( \varepsilon_p \) (dimensionless) is porosity of the adsorbent particle.

Knudsen’s original representation of diffusion in a porous media, given by Eq. (3.13a), was written by drawing analogy to the bulk gas diffusion equation from kinetic theory of gases by simply replacing mean free path with number-averaged pore diameter.\(^2\)

\[
D_K = \frac{d_\mu}{3} \bar{u} \tag{S3.13a}
\]

where \( d_\mu (= < l_\mu >) \) is number-averaged (mean) pore diameter and \( \bar{u} \) is the mean molecular velocity of gas. Using Maxwell’s velocity distribution of gas molecules to replace \( \bar{u} \), Eq. (3.13a) becomes:

\[
D_K = \frac{d_\mu}{3} \left( \frac{8 R_g T}{\pi M} \right) \tag{S3.13b}
\]

Derjaguin\(^2\) and Levitz\(^2\) extended Knudsen’s equation to include statistics of length scale distribution and redirecting collisions\(^2\),\(^2\).
\[ D_K = \frac{d_\mu}{3} \left( \sqrt{\frac{8Rg}{\pi M}} \left[ \frac{<l_\mu^2>}{2<l_\mu^2>} - \beta_{Tr} \right] \right) \]  

(S3.13c)

In Eq. (S3.13c), \( \frac{<l_\mu^2>}{2<l_\mu^2>} \) corrects for non-exponential path distribution and \( \beta_{Tr} \) corrects for the nature of wall reflection.

\[ \beta_{Tr} = -\sum_{m=1}^{\infty} <\cos \gamma_m> \]  

(S3.13d)

\( <\cos \gamma_m> \) is the average cosine of the angles between trajectory segments separated by \( m \) wall collisions. Zalc et al.\(^2\) have shown that \( \frac{<l_\mu^2>}{2<l_\mu^2>} \) only varies between 0.982 and 1.003 for void fractions between 0.05 and 0.42. Consequently, this term may be approximated as 1.

Derjaguin determined a theoretical value of \( <\cos \gamma_m> = \left( \frac{4}{9} \right)^m \) and \( \beta_{Tr} = \frac{4}{13} \). Including these corrections, Eq (S3.13b) takes the following form:

\[ D_K = \frac{d_\mu}{3} \sqrt{\frac{8Rg}{\pi M}} \left[ 1 - \frac{4}{13} \right] = 67.15 r_\mu \sqrt{\frac{T}{M}} \]  

(S3.13e)

Eq. (S3.13e) gives \( D_K \) in m\(^2\)/s when the mean pore radius, \( r_\mu \), is in m. Eq (S3.13f) should be used when \( r_\mu \) is in cm and \( D_K \) obtained is in cm\(^2\)/s.

\[ D_K = 671.5 r_\mu \sqrt{\frac{T}{M}} \]  

(S3.13f)

**Boundary conditions:**

The initial conditions for each step are the conditions at the end of the preceding steps. The equations require two boundary conditions. For the component mass balance, Danckwert’s boundary conditions for a dispersed plug flow system are used.

\[ D_L \frac{\partial y_i}{\partial z} \bigg|_{z=0} = -v_i \bigg|_{z=0} (y_{i, feed} - y_i \bigg|_{z=0}) \]  

(S3.14)

In Equation S3.14, \( y_{i, feed} \) is the mole fraction of component \( i \) in the feed.

\[ \frac{\partial y_i}{\partial z} \bigg|_{z=1} = 0 \]  

(S3.15)

Boundary conditions for column heat balance equation (similar to component balance equation) are written by drawing analogy between heat and mass transfer:

\[ K_z \frac{\partial T}{\partial z} \bigg|_{z=0} = -v \bigg|_{z=0} (T_{feed} - T_i \bigg|_{z=0}) \]  

(S3.16)
\[ \frac{\partial T}{\partial z} \bigg|_{z=1} = 0 \quad (S3.17) \]

The boundary conditions for wall energy balance are as follows:

\[ T_w|_{z=0} = T_w|_{z=1} = T_a \quad (S3.18) \]

For the overall mass balance equation, when the velocity is replaced using Darcy’s law, the equation becomes second order in pressure and hence requires two boundary conditions.

\[ P|_{z=1} = P_H \quad (S3.19) \]

The inlet velocity acts as the second boundary condition,

\[ v|_{z=0} = v_{feed} \quad (S3.20) \]

The dimensionless equations and boundary conditions are provided below.

**S3.1 Non-dimensional variables**

\[ \bar{P} = \frac{P}{P_0}; \quad \bar{T} = \frac{T}{T_0}; \quad \bar{T}_w = \frac{T_w}{T_0}; \quad \bar{T}_a = \frac{T_a}{T_0}; \quad \xi_i = \frac{q_i}{q_{s,o}} \quad (S3.21) \]

\[ v = \frac{p}{v_0}; \quad Z = \frac{z}{L}; \quad \tau = \frac{v_0}{L}; \quad \alpha_i = \frac{k_iL}{v_0} \quad (S3.22) \]

\[ Pe = \frac{v_0L}{D_L}; \quad Pe_h = \frac{\varepsilon v_0L}{\rho g C_{p,g}} \quad (S3.23) \]

\[ \psi = \frac{R_g T_o q_{s,o} (1-\varepsilon)}{\rho \varepsilon} \quad (S3.24) \]

\[ \Omega_1 = \frac{K_z}{v_0L} \bar{X}_i \left( \sum_{n=1}^{\infty} \frac{x_i}{\alpha_n} \right); \quad \Omega_2 = \frac{C_{p,a} P_o}{R_g T_o} \left( \sum_{n=1}^{\infty} \frac{x_i}{\alpha_n} \right) \quad (S3.25) \]

\[ \Omega_3 = \frac{C_{p,a} q_{s,o}}{(\rho_s C_{ps} + q_{s,o} C_{pa} \varepsilon \sum_{n=1}^{\infty} \frac{x_i}{\alpha_n})}; \quad \Omega_4 = \frac{2h_{in} L}{r_{in} v_0} \left( \sum_{n=1}^{\infty} \frac{x_i}{\alpha_n} \right) \quad (S3.26) \]

\[ \sigma_i = \frac{q_{s,o}(\Delta H_i)}{(\rho_s C_{ps} + q_{s,o} C_{pa} \varepsilon \sum_{n=1}^{\infty} x_i)} \quad (S3.27) \]

\[ \Pi_1 = \frac{K_w}{\rho w C_{pw} v_0}; \quad \Pi_2 = \frac{2r_{in} h_{in}}{r_{out}^2 - r_{in}^2} \frac{L}{\rho w C_{pw} v_0}; \quad \Pi_3 = \frac{2r_{out} h_{out}}{r_{out}^2 - r_{in}^2} \frac{L}{\rho w C_{pw} v_0} \quad (S3.28) \]
S3.2 Non-dimensional equations

Equations (S3.1 - S3.20) were non-dimensionalized using the non-dimensional variables listed in section S3.1 and non-dimensional form of the discretized model equations are provided as below:

Component balance
\[
\frac{\partial y_{ij}}{\partial \tau} = \frac{1}{Pe} \frac{\partial}{\partial z} \left( \frac{y_{ij+1} - y_{ij}}{\Delta z} - \frac{P}{T} \left| y_{ij-1} - y_{ij} \right| \right) - \frac{1}{Pe} \frac{\partial}{\partial z} \left( y_i \frac{P}{T} \left| y_{ij+1} - y_{ij} \right| \right) - \frac{1}{Pe} \frac{\partial}{\partial z} \left( y_i \frac{P}{T} \left| y_{ij-1} - y_{ij} \right| \right)
\]

Total mass balance
\[
\frac{\partial P_j}{\partial \tau} = - \frac{\partial}{\partial z} \left( \frac{P}{T} \left| y_{ij+1} - y_{ij} \right| \right) - \psi \sum_{i=1}^{n_{comp}} \frac{\partial x_{ij}}{\partial \tau} + \frac{\partial}{\partial \tau} \left( \frac{\partial y_{ij}}{\partial \tau} \right) (S3.29)
\]

Solid phase balance
\[
\frac{\partial x_{ij}}{\partial \tau} = \alpha_i (x_{ij}^* - x_{ij}) \tag{S3.31}
\]

Column energy balance
\[
\frac{\partial T_j}{\partial \tau} = \Omega_{1,j} \frac{1}{\Delta z} \left( \frac{T_{j+1} - T_j}{\Delta z} - \frac{T_{j-1} - T_j}{\Delta z} \right) - \Omega_{2,j} \frac{1}{\Delta z} \left( \nu \left| y_{ij+1} - y_{ij} \right| - \nu \left| y_{ij-1} - y_{ij} \right| \right) - \Omega_{3,j} \frac{1}{\Delta z} \left( \frac{\partial x_{ij}}{\partial \tau} \right) + \sum_{i=1}^{n_{comp}} \left( \sigma_{ij} \frac{\partial x_{ij}}{\partial \tau} \right) - \Omega_{4,j} (T_j - T_{w,j}) - \Omega_{5,j} \frac{\partial P_j}{\partial \tau} \tag{S3.32}
\]

Wall energy balance
\[
\frac{\partial T_{w,j}}{\partial \tau} = \Pi_1 \frac{1}{\Delta z} \left( \frac{T_{w,j+1} - T_{w,j}}{\Delta z} - \frac{T_{w,j-1} - T_{w,j}}{\Delta z} \right) - \Pi_2 (T_j - T_{w,j}) - \Pi_3 (T_{w,j} - T_{a,j}) \tag{S3.33}
\]

Local velocities at finite volume edge
\[
\bar{v}_{j+0.5} = \frac{4}{150} \left( \frac{\epsilon}{1 - \epsilon} \right)^2 r^2 p \frac{1}{\mu \nu_0 L} \left( \frac{\bar{P}_{j+1} - \bar{P}_j}{\Delta z} \right) \tag{S3.34}
\]

Velocity at the column entrance and exit are calculated using half-cell approximations:
\[
\bar{v}_{0.5} = \bar{v}_{|z=0} = \frac{4}{150} \left( \frac{\epsilon}{1 - \epsilon} \right)^2 r^2 p \frac{1}{\mu \nu_0 L} \left( \frac{\bar{P}_{1} - \bar{P}_{0.5}}{\Delta z} \right) \tag{S3.35}
\]
\[
\bar{v}_{N+0.5} = \bar{v}_{|z=1} = \frac{4}{150} \left( \frac{\epsilon}{1 - \epsilon} \right)^2 r^2 p \frac{1}{\mu \nu_0 L} \left( \frac{\bar{P}_{N+0.5} - \bar{P}_{N}}{\Delta z} \right) \tag{S3.36}
\]

Dimensionless Boundary condition are as follows:
\[
\frac{\partial y_i}{\partial z} \bigg|_{z=0} = -\bar{v}_{|z=0} Pe \left( y_{i,feed} - y_i \bigg|_{z=0} \right) ; \quad \frac{\partial y_i}{\partial z} \bigg|_{z=1} = 0 \tag{S3.37}
\]
\[
\frac{\partial \text{T}}{\partial z} \bigg|_{z=0} = -\bar{v} \bigg|_{z=0} Pe_h \left( \bar{T}_{\text{feed}} - \bar{T} \bigg|_{z=0} \right); \frac{\partial \text{T}}{\partial z} \bigg|_{z=1} = 0 \quad (S3.38)
\]

\[
\bar{T}_w \bigg|_{z=0} = \bar{T}_w \bigg|_{z=1} = \bar{T}_a \quad (S3.39)
\]

\[
P \bigg|_{z=1} = 1 \quad ; \quad \bar{v} \bigg|_{z=0} = 1 \quad (S3.40)
\]

The list of adsorbent and adsorption column parameters used in simulation are reported in Table S3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column 1 dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>Column Length, ( L ) (m)</td>
<td>0.3</td>
</tr>
<tr>
<td>Inner column radius, ( r_{in} ) (m)</td>
<td>0.016</td>
</tr>
<tr>
<td>Outer column radius, ( r_{out} ) (m)</td>
<td>0.019</td>
</tr>
<tr>
<td>Column void fraction, ( \varepsilon )</td>
<td>0.34</td>
</tr>
<tr>
<td><strong>Column 2 dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>Column Length, ( L ) (m)</td>
<td>0.15</td>
</tr>
<tr>
<td>Inner column radius, ( r_{in} ) (m)</td>
<td>0.010</td>
</tr>
<tr>
<td>Outer column radius, ( r_{out} ) (m)</td>
<td>0.013</td>
</tr>
<tr>
<td>Column void fraction, ( \varepsilon )</td>
<td>0.41</td>
</tr>
<tr>
<td><strong>Adsorbent properties</strong></td>
<td></td>
</tr>
<tr>
<td>Particle voidage, ( \varepsilon_p )</td>
<td>0.33</td>
</tr>
<tr>
<td>Particle radius, ( r_p ) (m)</td>
<td>1×10^{-3}</td>
</tr>
<tr>
<td>Tortuosity, ( \tau )</td>
<td>3</td>
</tr>
<tr>
<td>Radius of pore, ( r_\mu ) (cm)</td>
<td>1×10^{-7}</td>
</tr>
<tr>
<td><strong>Properties and Constants</strong></td>
<td></td>
</tr>
<tr>
<td>Adsorbent density, ( \rho_s ) (kg/m$^3$)</td>
<td>1312</td>
</tr>
<tr>
<td>Column Wall density, ( \rho_w ) (kg/m$^3$)</td>
<td>7800</td>
</tr>
<tr>
<td>Specific heat capacity of gas phase, ( C_{p,g} ) (J/mol/K)</td>
<td>22.43</td>
</tr>
<tr>
<td>Specific heat capacity of adsorbed phase, ( C_{p,a} ) (J/mol/K)</td>
<td>22.43</td>
</tr>
<tr>
<td>Specific heat capacity of adsorbent, ( C_{p,s} ) (J/mol/K)</td>
<td>1070</td>
</tr>
<tr>
<td>Thermal conductivity of the wall, ( k_w ) (J/m/K/s)</td>
<td>16</td>
</tr>
<tr>
<td>Inside heat transfer coefficient, ( h_{in} ) (J/m$^2$/K/s)</td>
<td>25</td>
</tr>
<tr>
<td>Outside heat transfer coefficient, ( h_{out} ) (J/m$^2$/K/s)</td>
<td>400</td>
</tr>
<tr>
<td>Universal gas constant, ( R_g ) (m$^3$ Pa/mol/K)</td>
<td>8.314</td>
</tr>
</tbody>
</table>

**S3.3 Characterization of silica gel pores**

The characterization of silica gel pores was done using Quantachrome Autosorb iQ3 instrument. The pore size distribution shown in Figure S3 confirms that the fraction of the total pore volume contributed by the pores below 20 Å in diameter is not significant. The adsorption and desorption isotherms shown in Figure S4 present negligible hysteresis. This should also
confirm that pore connectivity is not an issue in the silica gel sample under study. Monte Carlo and DFT simulation results for nitrogen adsorption in cylindrical pores at 77 K presented in the literature indeed support that it is possible to have very small to practically no hysteresis in the pore diameter range of 18 to 30 Å\textsuperscript{26,27}.

Figure S3: Pore size distribution of silica gel measured on Quantachrome Autosorb iQ3 using non-local density functional theory (NLDFT)-for N\textsubscript{2} on silica at 77K based on cylindrical pore model for analysing the data.

Figure S4: Adsorption and Desorption isotherm of N\textsubscript{2} at 77K on silica gel sample measured on Quantachrome Autosorb iQ3.
S3.4 Simulation of single component CO$_2$ breakthrough runs

Figure S5: A representative result showing the best fit (line) of a breakthrough run (symbols) using LDF constant ($k$) as the decision variable. For experimental details, see runs S4 and S5 in Table 2 of the main text. Adsorption column 1 (detailed in Table S3) was used for these runs.

Table S4: Surface diffusivity ($D_s$) values extracted from CO$_2$ breakthrough runs.¶

<table>
<thead>
<tr>
<th>Run</th>
<th>LDF constant ($k$) (s$^{-1}$)</th>
<th>$D_g$ (cm$^2$/s)</th>
<th>$D_K$ (cm$^2$/s)</th>
<th>$D_s$ (cm$^2$/s)</th>
<th>Non-linearity ($\frac{q_0}{q_s}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>0.029</td>
<td>0.0106</td>
<td>0.0017</td>
<td>7.25×10$^{-5}$</td>
<td>0.045</td>
</tr>
<tr>
<td>S5</td>
<td>0.025</td>
<td>0.0092</td>
<td>0.0017</td>
<td>6.13×10$^{-5}$</td>
<td>0.037</td>
</tr>
<tr>
<td>S6</td>
<td>0.02</td>
<td>0.0104</td>
<td>0.0017</td>
<td>7.22×10$^{-5}$</td>
<td>0.061</td>
</tr>
<tr>
<td>S7</td>
<td>0.037</td>
<td>0.0083</td>
<td>0.0018</td>
<td>8.73×10$^{-5}$</td>
<td>0.027</td>
</tr>
<tr>
<td>S8</td>
<td>0.058</td>
<td>0.0072</td>
<td>0.0018</td>
<td>1.29×10$^{-4}$</td>
<td>0.014</td>
</tr>
</tbody>
</table>

¶ See Table S3 in the Supporting Information for adsorbent and adsorption column details.

S3.5 CO$_2$ temperature profiles

Temperature profiles at two different locations along the column length for highest concentration breakthrough run of CO$_2$ (Run S6, for experimental details, see run S6 in Table 2 of the main text) are shown in Figure S6. The maximum temperature rise observed was around 1°C for this run. It was even lower for other lower concentration runs (Run S4 and S5).
Figure S6: Best fit temperature profiles for CO$_2$. The solid (—) and broken (----) lines are simulation results for T1 (bottom) and T2 (top) thermocouples respectively. For experimental details, see run S6 in Table 2 of the main text. Adsorption column 1 (detailed in Table S3) was used for these runs.

**S3.6 Simulation of mixture breakthrough runs**

Figure S7: Experimental breakthrough profiles (symbols) for confirmation of transport mechanism of CO$_2$ in a binary CO$_2$/$N_2$ mixture in silica gel pores and comparison with model prediction. The solid (—), dotted (…) and broken (----) lines are simulation results for a combination of Knudsen and surface, Knudsen and Molecular diffusion control respectively. For experimental details, refer to Table 3. Adsorption column 1 (detailed in Table S3) was used in these runs.
S4 Parametric study to identify the experimental conditions for establishing N\textsubscript{2} equilibrium in binary mixture (CO\textsubscript{2}/N\textsubscript{2})

The bed was initially saturated with N\textsubscript{2}/CO\textsubscript{2} mixture and then N\textsubscript{2} was desorbed in CO\textsubscript{2}. Simulations were carried out for different starting initial concentrations of N\textsubscript{2} and CO\textsubscript{2} in the bed (Table S5) and it was seen that the displacement effect of N\textsubscript{2} by CO\textsubscript{2} was more evident with high initial concentration of N\textsubscript{2} (Figure S6).

Table S5: Process conditions for various binary breakthrough runs in which the silica gel bed was initially saturated with CO\textsubscript{2}/N\textsubscript{2} mixture and then desorbed with pure CO\textsubscript{2}.§

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed Flow rate (SLPM)</th>
<th>Initial condition</th>
<th>N\textsubscript{2} (%) in feed</th>
<th>CO\textsubscript{2} (%) in feed</th>
<th>Inlet Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Velocity (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.3</td>
<td>Saturated with 100% N\textsubscript{2}</td>
<td>0</td>
<td>100</td>
<td>1.1</td>
<td>25</td>
<td>3.90</td>
</tr>
<tr>
<td>P2</td>
<td>0.3</td>
<td>Saturated with 80% N\textsubscript{2} and 20% CO\textsubscript{2}</td>
<td>0</td>
<td>100</td>
<td>1.1</td>
<td>25</td>
<td>3.90</td>
</tr>
<tr>
<td>P3</td>
<td>0.3</td>
<td>Saturated with 60% N\textsubscript{2} and 40% CO\textsubscript{2}</td>
<td>0</td>
<td>100</td>
<td>1.1</td>
<td>25</td>
<td>3.90</td>
</tr>
<tr>
<td>P4</td>
<td>0.3</td>
<td>Saturated with 40% N\textsubscript{2} and 20% CO\textsubscript{2}</td>
<td>0</td>
<td>100</td>
<td>1.1</td>
<td>25</td>
<td>3.90</td>
</tr>
<tr>
<td>P5</td>
<td>0.3</td>
<td>Saturated with 20% N\textsubscript{2} and 80% CO\textsubscript{2}</td>
<td>0</td>
<td>100</td>
<td>1.1</td>
<td>25</td>
<td>3.90</td>
</tr>
</tbody>
</table>

§ See Table S3 in the Supplementary Information for adsorbent and adsorption column details.
Figure S8: Simulations profiles for N$_2$. The solid (—) and broken (----) lines are simulation results for single component Langmuir and extended Langmuir isotherm model respectively. For process parameter details, refer to Table S5.
References


