Supplementary Information for:

A Multipurpose Metal-Organic Framework for the Adsorption of Acetylene: Ethylene Purification and Carbon Dioxide Removal

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Table S1. Physicochemical characteristics of different gases relevant to their separation.\textsuperscript{1-3}

<table>
<thead>
<tr>
<th>Gas</th>
<th>Boiling point (K)</th>
<th>Molecular dimensions (Å)</th>
<th>Polarizability (Å(^3))</th>
<th>Dipole moment (\times 10^{19}) esu cm(^2)</th>
<th>Quadrupole moment (\times 10^{26}) esu cm(^2)</th>
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<tbody>
<tr>
<td>C(_2)H(_2)</td>
<td>188.4</td>
<td>3.32(\times)3.34(\times)5.7</td>
<td>3.33-3.93</td>
<td>0</td>
<td>+7.5</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>216.5</td>
<td>3.18(\times)3.33(\times)5.36</td>
<td>2.91</td>
<td>0</td>
<td>-4.3</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>169.4</td>
<td>3.28(\times)4.18(\times)4.84</td>
<td>4.25</td>
<td>0</td>
<td>+1.5</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>184.5</td>
<td>3.81(\times)4.82(\times)4.08</td>
<td>4.43-4.47</td>
<td>0</td>
<td>+0.65</td>
</tr>
</tbody>
</table>

1. Synthesis of MUF-17

All starting reactants and solvents were obtained from commercial sources and used without further purification.

\[
\text{[Co}_5(\mu_3-\text{OH})_2(\text{aip})_4(\text{H}_2\text{O})_2]\text{, MUF-17}
\]

\([\text{Co}_5(\mu_3-\text{OH})_2(\text{aip})_4(\text{H}_2\text{O})_2]\) (MUF-17): A mixture of Co(OAc)\(_2\).4H\(_2\)O (0.125 g, 0.5 mmol), 5-aminoisophthalic acid (H\(_2\)aip, 0.046 g, 0.25 mmol), MeOH (7 mL), and H\(_2\)O (0.5 mL) were sonicated for 20 min and sealed in a 50 mL Schott bottle and heated at 85 °C for 24 hours. After cooling the oven to room temperature, the resulting purple crystals were isolated by decanting off the mother liquor, then washed with methanol several times and dried under vacuum. Yield ca. 0.062 g, 92% (based on H\(_2\)aip). Anal. calcd. (found) for [Co(5\(\mu_3\)-OH)\(_2\)(aip)\(_4\)(H\(_2\)O)\(_2\)]: C, 35.58 (35.32); H, 3.71 (3.70); N, 5.18 (4.79). Guest-free MUF-17 could be obtained by heating under high vacuum at 130 °C for 20 h.

Cost estimate: 1 kg of H\(_2\)aip = 15USD; 1 kg of Co(OAc)\(_2\).4H\(_2\)O = 10USD. Therefore, 2 kg of Co(OAc)\(_2\).4H\(_2\)O (20USD) requires 736 g of H\(_2\)aip (11USD) and produces 1 kg of MUF-17 for approx. USD30.

Figure S1. An optical micrograph of MUF-17.
Synthesis of MUF-17 for single crystal X-ray diffraction studies:

A mixture of Co(OAc)$_2$·4H$_2$O (0.125 g, 0.5 mmol), H$_2$aipBoc (0.281 g, 1 mmol), MeOH (6 mL), and H$_2$O (0.5 mL) were sonicated for 20 min and sealed in a Teflon-lined bomb and heated at 120 °C for 3 days. After cooling the oven to room temperature, the resulting product was isolated by decanting off the mother liquor, then washed with methanol several times and dried under vacuum to give ~0.3 g of MUF-17 as a dark purple solid. Appropriate single crystals were chosen for SCXRD studies.

2. Single-crystal and powder X-ray diffraction

As-synthesized samples were washed several times with methanol before being mounted on the instrument. All the data were collected at room temperature. A Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator (Cu Kα radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image plate detector was used to collect SCXRD and PXRD data. The SCXRD data were integrated, scaled and averaged with FS Process.$^4$ SHELX$^5$ (under OLEX$^6$) was used for structure solution and refinement.

For PXRD measurements, unless otherwise noted, samples were kept damp with solvent prior to and during measurements. The two-dimensional images of the Debye rings were integrated with 2DP to give 2θ vs I diffractograms. Predicted powder patterns were generated from single crystal structures using Mercury. Powder diffraction patterns (shown below) revealed that the structure of MUF-17 remains unchanged after: (i) activation at 130 °C under vacuum, (ii) gas adsorption isotherm measurements, (iii) gas breakthrough experiments, and (iv) exposure to an air with relative humidity of >80% for 12 months.

![Figure S2. PXRD patterns of MUF-17 showing that its structure remains unchanged after activation at 130 °C under vacuum (red), after isotherm measurements (green), after breakthrough experiments (dark blue), and after exposure to air with relative humidity of >80% for at least 12 months (orange).]
<table>
<thead>
<tr>
<th>Crystal data and structure refinement for MUF-17.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CCDC deposition number</strong></td>
</tr>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
</tr>
<tr>
<td><strong>α/°</strong></td>
</tr>
<tr>
<td><strong>β/°</strong></td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>ρcalc/g.cm⁻³</strong></td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
</tr>
<tr>
<td><strong>Data range for refinement</strong></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
</tr>
</tbody>
</table>
3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q50 instrument. Measurements were made on approximately 5 mg of activated sample under a N₂ flow with a heating rate of 5 °C/min. Activated samples were kept at atmosphere after activation. Weight loss at low temperatures are attributed to the removal of water vapor trapped in the pores.

![TGA curve of MUF-17](image)

Figure S3. TGA curve of MUF-17.

4. Structure, physical properties and pore shape

The Zeo++² code and RASPA2 were used to characterize the geometric features of the framework by calculating the pore volume (with the use of a helium probe), surface area (with the use of a H₂ probe), pore limiting diameter (i.e., the diameter of smallest opening along the pore) and largest cavity diameter (i.e., the diameter of the largest sphere that can fit within the pores). Accelrys Materials Studio 7.0 software package was performed to visualize the MOF structure and pore topology.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometric surface area (RASPA2)</td>
<td>323 m²/g</td>
</tr>
<tr>
<td>BET surface area (from experimental CO₂ isotherm/273 K)</td>
<td>247 m²/g</td>
</tr>
<tr>
<td>BET surface area (from experimental N₂ isotherm/77 K)</td>
<td>211 m²/g</td>
</tr>
<tr>
<td>Crystallographic density</td>
<td>1.65 g/cm³</td>
</tr>
<tr>
<td>Pore volume (RASPA2)</td>
<td>0.20 cm³/g</td>
</tr>
<tr>
<td>Pore volume (from experimental CO₂ isotherm/273 K)</td>
<td>0.14 cm³/g</td>
</tr>
<tr>
<td>Largest cavity diameter (Zeo++)</td>
<td>4.63 Å</td>
</tr>
<tr>
<td>Pore limiting diameter (Zeo++)</td>
<td>3.15 Å</td>
</tr>
</tbody>
</table>
Figure S4. (a,b) One dimensional zigzag channels and the overall pore structure of MUF-17 illustrated by a calculated Connolly surface using a probe of diameter of 1 Å, (c) pore limiting and large cavity dimensions (Co, dark blue; N, light blue; O, red; C, grey; and H, white).
5. Gas adsorption measurements and calculations

5.1. Single gas adsorption isotherm measurements

The adsorption isotherms were measured with a volumetric adsorption apparatus (Quantachrome-Autosorb-iQ2). Ultra-high purity gases were used as received from BOC Gases. The as-synthesized samples were washed with dry methanol several times and 50-100 mg was transferred into a pre-dried and weighed sample tube and heated at rate of 10°C/min to a temperature of 130 °C under a dynamic vacuum at 10^{-6} Torr then held for 20 hours. Accurate sample masses were calculated using degassed samples after the sample tube was backfilled with nitrogen. The low temperature at 77 K was controlled by a Dewar filled with liquid N\textsubscript{2}. Around room temperature, the bath temperature was precisely controlled with a recirculating control system containing a mixture of ethylene glycol and water. The surface area was determined from the CO\textsubscript{2} (273 K) adsorption isotherm by application of the BET model.

![Figure S5](image-url)

**Figure S5.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of C\textsubscript{2}H\textsubscript{2} (black), C\textsubscript{2}H\textsubscript{4} (red) and CO\textsubscript{2} (blue) measured at 293 K for MUF-17.
Figure S6. Volumetric adsorption (filled circles) and desorption (open circles) isotherms of $\text{C}_2\text{H}_2$ (black), $\text{C}_2\text{H}_4$ (red) and $\text{CO}_2$ (blue) measured at 273 K for MUF-17.

Figure S7. Volumetric adsorption (filled circles) and desorption (open circles) isotherms of $\text{C}_2\text{H}_6$ (black), $\text{CH}_4$ (pink) and $\text{N}_2$ (green) measured at 293 K for MUF-17.
**Figure S8.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of C\textsubscript{2}H\textsubscript{6} (black), CH\textsubscript{4} (pink) and N\textsubscript{2} (green) measured at 273 K for MUF-17.

**Figure S9.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of N\textsubscript{2} and H\textsubscript{2} measured at 77 K for MUF-17.
5.2. Sorption performance of MUF-17 over multiple cycles and after exposure to air and water

The stability and recyclability of MUF-17 was investigated by measuring $\text{C}_2\text{H}_2$ isotherms at 293 K in multiple cycles (repeated measurements) and after exposing the MOF to an air with a relative humidity of >80% for 6 months (followed by activation).

![Graph showing isotherms](image)

**Figure S10.** $\text{C}_2\text{H}_2$ isotherms of MUF-17 at 293K measured on the same sample over multiple cycles.
Figure S11. C$_2$H$_2$ adsorption isotherm of MUF-17 at 293 K after exposing it to air with ~ 90% humidity for 8 months.

5.3. Calculation of BET surface areas

The BET surface area was calculated from the both CO$_2$ adsorption isotherm at 273 K and N$_2$ adsorption isotherms at 77 K according to the following procedures:

1) The isotherm region where $v(1 - P/P_0)$ increases versus $P/P_0$, where $v$ is the amount of CO$_2$ adsorbed, was identified.

2) Within this isotherm region, sequential data points that led to a positive intercept in the plot of $P/P_0$ against $v(1 - P/P_0)$, were found. This plot yields a slope $a$, and a positive intercept $b$. The amount of gas molecules adsorbed in the initial monolayer is $v_m = \frac{1}{a + b}$.

3) The BET surface area was calculated according to the following equation:

$$A_{BET} = v_m (\text{cm}^2 \text{g}^{-1}) \times \frac{1 (\text{mol})}{22400 (\text{cm}^3)} \times \sigma_o (\text{Å}^2) \times N_A (\text{mol}^{-1}) \times 10^{-20} (\text{m}^2)$$

Where $N_A$ is Avogadro’s constant, and $\sigma_o$ is the cross-sectional area of a probe molecule, which is 21.8 and 18.2 Å$^2$ for CO$_2$ and N$_2$, respectively.
Figure S12. CO$_2$ adsorption isotherm at 273 K and BET surface area plots for MUF-17.

Figure S13. N$_2$ adsorption isotherm at 77 K and BET surface area plots for MUF-17.
5.4. Isosteric heats of adsorption

Isosteric heat of adsorption ($Q_{st}$) values were calculated from isotherms measured at 273K, 283K and 293 K for CO$_2$. The isotherms were first fit to a virial equation:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i$$

Where $N$ is the amount of gas adsorbed at the pressure $P$, $a$ and $b$ are virial coefficients, $m$ and $n$ are the number of coefficients require to adequately describe the isotherm. To calculate $Q_{st}$, the fitting parameters from the above equation were used for the following equation:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N_i$$
**Figure S14.** Virial equation fits for C$_2$H$_2$ adsorption isotherms of MUF-17.

**Figure S15.** Virial equation fits for C$_3$H$_6$ adsorption isotherms of MUF-17.
Figure S16. Virial equation fits for CO$_2$ adsorption isotherms of MUF-17.

Figure S17. Isosteric heat of adsorption plotted as a function of gas uptake for the adsorption of C$_2$H$_2$, C$_2$H$_4$ and CO$_2$ by MUF-17.
5.5. IAST selectivity calculations for binary gas mixtures

Mixed gas adsorption isotherms and gas selectivities for different mixtures of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} at 293 K and 273 K were calculated based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz\textsuperscript{10}. The pyIAST package\textsuperscript{11} was used to perform the IAST calculations. In order to predict the sorption performance of MUF-17 toward the separation of binary mixed gases, the single-component C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} adsorption isotherms were first fit to a dual site Langmuir model as below:

\[
q = \frac{q_1 b_1 P}{1 + b_1 P} + \frac{q_2 b_2 P}{1 + b_2 P}
\]

Where \(q\) is the uptake of a gas; \(P\) is the equilibrium pressure and \(q_1, b_1, q_2\) and \(b_2\) are constants. The fitting parameters are shown in Figure S\textsuperscript{18} and S\textsuperscript{19}. These parameters were used afterwards to carry out IAST calculations.

![Figure S18. Dual-site Langmuir fits of the MUF-17 isotherms at 293 K.](image-url)
**Figure S19.** Dual-site Langmuir fits of the MUF-17 isotherms at 273 K.

**Figure S20.** Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 50/50 mixture of C2H2/C2H4 at 293 K.
Figure S21. Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 1/99 mixture of C₂H₂/C₂H₄ at 293 K.

Figure S22. Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 0.1/99.9 mixture of C₂H₂/C₂H₄ at 293 K.
Figure S23. Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 50/50 mixture of C₂H₂/C₂H₄ at 273 K.

Figure S24. Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 50/50 mixture of C₂H₂/CO₂ at 293 K.
**Figure S25.** Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 1/99 mixture of C₂H₂/CO₂ at 293 K.

**Figure S26.** Mixed-gas isotherms and selectivity of MUF-17 predicted by IAST for a 0.1/99.9 mixture of C₃H₈/CO₂ at 293 K.
6. Breakthrough separation experiment

6.1. Breakthrough experiments

A home-built breakthrough apparatus was used to measure the gas separation performance of the MOFs under dynamic conditions (Fig. S32). The performance and accuracy of this apparatus was established by reproducing breakthrough results reported in the literature and consistent results were obtained.12-14

In a typical breakthrough experiment, 1.2 g of activated MUF-17 was placed in an adsorption column (6.4 mm in diameter × 11 cm in length) to form a fixed bed. The adsorbent was activated at 130 °C under high vacuum for 12 hours and then the column was left under vacuum for another 3 hours while being cooled to 20 °C. The column was then purged under a 20 mL/min flow of He gas for 1 hr at 1.1 bar prior to the breakthrough experiment. A gas mixture containing either C2H2/C2H4 or C2H2/CO2 with different compositions along with He as a carrier was introduced to the column at 1.1 bar and 20 °C. A total feed flowrate of 6 mL/min was set for the experiments with 50/50 and 1/99 mixtures of gasses, and the flowrate of He in the feed was kept constant at 3 mL/min for all the experiments. The operating pressure was controlled at 1.1 bar with a back-pressure regulator. The outlet composition was continuously monitored by the mass spectrometer until complete breakthrough was observed. The adsorbent was regenerated under vacuum for 40-50 minutes at 60 °C between each cycle.
Figure S28. A schematic of the experimental column breakthrough apparatus.

Figure S29. Experimental breakthrough curves for a mixture of 50/50 C₂H₂/C₂H₄ at 1.1 bar and 293 K.
Figure S30. Experimental breakthrough curves for a 50/50 mixture of C₂H₂/C₂H₄ at 1.1 bar and 293 K over 10 consecutive cycles. The adsorbent was regenerated between cycles by leaving the column under vacuum for 40-50 minutes at 60 °C.

Figure S31. Experimental breakthrough curves for a 1/99 mixture of C₂H₂/C₂H₄ at 1.1 bar and 293 K.
Figure S32. Experimental breakthrough curves for a 50/50 mixture of $C_2H_2$/CO$_2$ at 1.1 bar and 293 K.

Figure S33. Experimental breakthrough curves for a 1/99 mixture of $C_2H_2$/CO$_2$ at 1.1 bar and 293 K.

6.2. Regeneration profile

The desorption behaviour of $C_2H_2$, CO$_2$ and C$_2$H$_4$ from the adsorption column was also investigated. Once the adsorbent was saturated with an equimolar mixture of $C_2H_2$/C$_2$H$_4$ or $C_2H_2$/CO$_2$, the column was purged with a helium flow of 5 mL/min for 11 mins at 20 °C at 1 bar, while monitoring the effluent gas. The column was then heated to 80 °C with a ramp of 10 °C/min for 18 mins. Finally, the column was heated to 130 °C with the same ramping rate for 30 min before cooling to 20 °C. A breakthrough measurement was then performed, which showed that the absorbent had been fully regenerated.
Figure S34. Desorption behaviour of the C₂H₂/C₂H₄ mixture adsorbed in MUF-17 following a breakthrough experiment. The column was heated at 1 bar under a helium flow of 5 mL/min. C₂H₄ was fully removed from the bed by purging with helium for 10 min at 130 °C. C₂H₂ is completely desorbed from the column upon heating to 130 °C for 30 min. A further breakthrough test confirmed the full regeneration of the adsorbent.

Figure S35. Desorption behaviour of MUF-17 following a breakthrough separation of a C₂H₂/CO₂ mixture. The column was heated at 1 bar under a helium flow of 5 mL/min. CO₂ was fully removed from the bed by purging with helium for 18 min at 80 °C. C₂H₂ is also almost completely desorbed from the column upon heating to 130 °C for 30 min. A further breakthrough test confirmed the full regeneration of the adsorbent.
7. Breakthrough curve simulations

7.1. Mathematical modelling

Considering a fixed bed adsorption column of length L filled with MUF-17, following assumptions were made to develop a mathematical model\textsuperscript{15–17} that could be solved using proper numerical methods to calculate the concentration of gasses at different elapsed times along the bed.

![Schematic diagram of a fixed adsorption bed](image)

**Figure S36.** Schematic diagram of a fixed adsorption bed

The following assumptions were made:
- The dynamic behaviour of the fluid obeys an axial dispersion plug flow model in the bed.
- The gradient of the concentration along the radial and angular directions are neglected.
- The flow velocity is varied along the bed and it is calculated from the total mass balance equation.
- The gas property is described by the Peng-Robinson equation of state.
- Diffusion and adsorption into the particles is assumed as a lump kinetic transfer model.
- The mass transfer rate is represented by the linear driving force model.
- The pressure drop is considered along the bed using the Ergun equation.
- The adsorption columns operate under isothermal conditions.
- Mixed gas isotherms calculated by IAST method were fitted by single site Langmuir model and fitting parameters were used for breakthrough curves simulations.

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

\[
\varepsilon \frac{\partial C_i}{\partial t} = - \frac{\partial (uC_i)}{\partial z} + \varepsilon D_{ax,i} \frac{\partial^2 C_i}{\partial z^2} - (1 - \varepsilon) \rho_s \frac{\partial q_i}{\partial t}
\]

\[
\varepsilon \frac{\partial C}{\partial t} = - \frac{\partial (uC)}{\partial z} - (1 - \varepsilon) \rho_s \sum_{i=1}^{n_c} \frac{\partial q_i}{\partial t}
\]

Where \(C_i\) and \(q_i\) are, respectively, concentration of components in the gas phase and in the adsorbed phase, \(z\) is the axial coordinate in the bed, \(D_{ax,i}\) is the effective axial dispersion coefficient, \(u\) is the superficial gas velocity, \(\rho_s\) is the adsorbent density, \(n_c\) is the number of the adsorbed components in the mixture and \(\varepsilon\) is the bed voidage. The value of \(D_{ax}\) was calculated through the following equation\textsuperscript{18}:

\[
\frac{\varepsilon D_{ax,i}}{D_{m,i}} = 20 + 0.5 Sc_i Re
\]
Where $Re$ is the Reynolds number and $Sc$ is the Schmidt number and $D_{m,i}$ is the molecular diffusivity of component $i$ in the mixture which was calculated by following equation:

$$D_{m,i} = \frac{1 - y_i}{\sum_{x=1}^{n} \frac{y_i}{D_{i,x}}}$$

Where $y_i$ is the mole fraction of component $i$ and $D_{i,x}$ is molecular diffusivity of component $i$ in component $x$ which was calculated by Wile-Lee equation\(^{19}\). Referring to the assumptions, the solid linear driving force (LDF) model is used to describe the mass transfer rate of the gas and solid phase\(^{20}\):

$$\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i)$$

Where $k_i$ is the overall mass transfer coefficient, and a lumped parameter considering three different mass transfer resistances associated with film, macropore and micropore zone. As the overall mass transfer coefficient is in proportion to the steepness of breakthrough curves, the accurate value of it was obtained empirically by tuning its value until the steepness of the predicted and experimental breakthrough curves were the same. This mass transfer coefficient tuned in this way was later used to predict breakthrough curves for other feed mixtures and operating pressures. $q_i^*$ is the equilibrium concentration of $i$th component in the adsorbed phase and is related to the concentration in the gas phase through isotherms. The IAST method was used to predict mixed gas isotherms and they were fitted by a Dual-Site Langmuir model. The pressure drop is defined by Ergun’s equation as\(^{21}\):

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

Where $P$ is the local pressure at the $z$ axial coordinate, $\mu$ is the gas viscosity, $\phi$ is the shape factor and $\rho$ is the gas density. Identical conditions to the experimental breakthrough measurement, including operating pressure, feed flowrate, temperature, bed size and amount of MOF, were used as input for simulations. All the parameters used for the simulations are tabulated in Table S4.

### Table S4. Adsorption column parameters and feed gas metrics used for the simulations for MUF-17.

<table>
<thead>
<tr>
<th>Adsorption bed</th>
<th>Dual-Site Langmuir fitting</th>
</tr>
</thead>
<tbody>
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<td>Length: 110 mm</td>
<td>Figures above</td>
</tr>
<tr>
<td>Diameter: 6.4 mm</td>
<td></td>
</tr>
<tr>
<td>Amount of adsorbent in the bed: 1.2 g</td>
<td>Total flow rate (including He): 6 mL/min</td>
</tr>
<tr>
<td>Bed voidage: 0.85</td>
<td>Temperature: 293 K</td>
</tr>
<tr>
<td>Adsorbent average radius: 0.05 mm</td>
<td>Pressure: 1.1 bar</td>
</tr>
<tr>
<td>$k_{CO2}$: 6.12 s(^{-1})</td>
<td>Carrier gas (He) flow rate: 3 mL/min</td>
</tr>
<tr>
<td>$k_{C2H2}$: 5.95 s(^{-1})</td>
<td>Purge gas: He with a flow rate of 20 mL/min</td>
</tr>
<tr>
<td>$k_{C2H4}$: 6.02 s(^{-1})</td>
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</tbody>
</table>

### 7.2. Numerical methods

Numerical solutions of the nonlinear parabolic PDEs derived from mass and momentum balance were conducted by an implicit method of lines using finite difference method for the spatial derivatives. Firstly, the second and first space derivatives were discreted by central and upwind- differential scheme (backward), respectively. In this way, the sets of partial equations were transformed to the sets of ODEs with respect to the time derivative terms. The length of the bed was divided into 50 increments and the set of equations were solved by the implicit Euler method with a time step of one second\(^{22}\).
Figure S37. Predicted breakthrough curves for a mixture of 50/50 of C₂H₂ (black)/C₂H₄ (red) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficients (k_C₂H₂: 5.95 s⁻¹, k_C₂H₄: 6.02 s⁻¹).

Figure S38. Predicted breakthrough curves for a mixture of 1/99 of C₂H₂ (black)/C₂H₄ (red) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficients (k_C₂H₂: 5.95 s⁻¹, k_C₂H₄: 6.02 s⁻¹).
Figure S39. Predicted breakthrough curves for a mixture of 50/50 of C$_2$H$_2$ (black)/CO$_2$ (blue) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficients ($k_{C_2H_2}$: 5.95 s$^{-1}$, $k_{CO_2}$: 6.12 s$^{-1}$).

Figure S40. Predicted breakthrough curves for a 1/99 mixture of C$_2$H$_2$ (black)/CO$_2$ (blue) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficients ($k_{C_2H_2}$: 5.95 s$^{-1}$, $k_{CO_2}$: 6.12 s$^{-1}$).
Figure S41. Predicted breakthrough curves for 0.1/99.9 mixtures of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (purple) and $\text{C}_2\text{H}_2/\text{CO}_2$ (orange) at 293 K and 1.1 bar after tuning the mass transfer coefficients ($k_{\text{C}_2\text{H}_2}: 5.95 \text{ s}^{-1}$, $k_{\text{C}_2\text{H}_4}: 6.02 \text{ s}^{-1}$, $k_{\text{CO}_2}: 6.12 \text{ s}^{-1}$). $\text{C}_2\text{H}_2$, which elutes from the column slowly, is shown as a solid line, while $\text{C}_2\text{H}_4$ and $\text{CO}_2$ are shown as dashed lines.

$\text{C}_2\text{H}_4$ productivity

The $\text{C}_2\text{H}_4$ productivity was defined by the breakthrough amount of ethylene (defined as a volume of gas at STP) from an adsorption bed packed with 1 kg of MOF. The breakthrough amount was calculated by integration of the breakthrough curves (for a mixture of 1/99 $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$) during a period from $t_1$ to $t_2$ during which the $\text{C}_2\text{H}_4$ purity is higher than or equal to a threshold value of 99.95%:

$$\text{(C}_2\text{H}_4)_{\text{Productivity}} = \int_{t_1}^{t_2} F_{\text{C}_2\text{H}_4,\text{out}} \, dt$$

Where $F_{\text{C}_2\text{H}_4,\text{out}}$ is the flowrate of effluent ethylene and $m_{\text{MOF}}$ is the amount of MOF packed in the bed.

8. Comparison with the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and $\text{CO}_2/\text{C}_2\text{H}_2$ separation performance of reported MOFs

The separation performance of MUF-17 were compared with benchmark MOFs reported in the literature for the separation of $\text{C}_2\text{H}_2$ from $\text{CO}_2$ and $\text{C}_2\text{H}_4$. Single gas isotherms, IAST selectivities and $Q_{\text{st}}$ values all were extracted from relevant literature.
Table S5. The separation parameters of MUF-17 compared with selected MOFs reported in the literature.

<table>
<thead>
<tr>
<th>MOF</th>
<th>( \text{C}_2\text{H}_2 ) uptake (^a) (cm(^3)/cm(^3))</th>
<th>( \text{C}_2\text{H}_2 ) uptake at 0.01 bar (cm(^3)/cm(^3))</th>
<th>( \text{C}_2\text{H}_4 ) uptake (^a) (cm(^3)/cm(^3))</th>
<th>( \text{C}_2\text{H}_4 ) uptake (^a) (cm(^3)/cm(^3))</th>
<th>( \text{CO}_2 ) uptake (^a) (cm(^3)/cm(^3))</th>
<th>IAST selectivity (^b) ((\text{C}_2\text{H}_2/\text{C}_2\text{H}_4))</th>
<th>IAST selectivity (^b) ((\text{C}_2\text{H}_2/\text{CO}_2))</th>
<th>( Q_\text{e} ) (\text{C}_2\text{H}_2 ) (^c) (kJ/mol)</th>
<th>( Q_\text{e} ) (\text{C}_2\text{H}_4 ) (^c) (kJ/mol)</th>
<th>( Q_\text{e} ) (\text{CO}_2 ) (^c) (kJ/mol)</th>
<th>( T ) (°C)</th>
</tr>
</thead>
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<tr>
<td>NOTT-300(^{23-24})</td>
<td>162.49</td>
<td>5.39</td>
<td>109.87</td>
<td>138.62</td>
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<td>-</td>
<td>32</td>
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<td>-</td>
<td>20</td>
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<td>SIFSIX-3-Ni(^{25-26})</td>
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<td>97.73</td>
<td>6.0</td>
<td>-</td>
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<td>30.3</td>
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<td>-</td>
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<td>92.31(^d)</td>
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<td>32</td>
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<td>[Ni(_2)(HCOO)(_3)](^{42})</td>
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<td>33.8</td>
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</tbody>
</table>

\(^a\) At a pressure of 1 bar. \(^b\) For an equimolar mixture of \(\text{C}_2\text{H}_2/\text{C}_2\text{H}_4\) or \(\text{CO}_2/\text{C}_2\text{H}_2\) and a total pressure of 1 bar. \(^c\) At low loading. \(^d\) At 298 K. \(^*\) Molecular sieving. \(^f\) Determined experimentally.
9. DFT calculations

Static binding energies for guest molecules in the MUF-17 framework were calculated using density functional theory (DFT) as implemented in the software package VASP 5.4.4. It is well-known that standard DFT methods based on generalized gradient approximation do not fully account for the long-range dispersion interactions between the framework and the bound adsorbates. Therefore, to accurately estimate static binding energies for the guest molecules within the MUF-17 framework, we implemented dispersion corrections using DFT-D3 method. Electron exchange and correlation were described using the generalized gradient approximation Perdew, Burke, and Ernzerhof (PBE) form, and the projector-augmented wave potentials were used to treat core and valence electrons. In all cases, we used a plane-wave kinetic energy cutoff of 600 eV and a Gamma-point mesh for sampling the Brillouin zone. The ionic coordinates were relaxed until the Hellman-Feynman forces were less than 0.02 eV/Å. The initial location of the guest molecule (one guest molecule per cell) in MUF-17 was obtained from a classical simulated annealing technique using classical force fields, as implemented in the sorption module in Materials Studio. In the simulated annealing method, the temperature was lowered stepwise, allowing the gas molecule to reach a desirable configuration based on different moves such as rotation, translation, and repositioning with preset probabilities of occurrence. This process of heating and cooling the system was repeated over several heating cycles to find the local minima. Forty heating cycles were performed where the maximum temperature and the final temperature were 10^5 K and 100 K, respectively. Static binding energies (ΔE) at 0 K in vacuum were calculated using the following expression

$$\Delta E = E_{\text{MOF+Guest}} - E_{\text{MOF}} - E_{\text{Guest}}$$

Where $E_x$ refers, respectively, to the total energies of the MOF + guest complex, the MOF alone, and the guest molecule.

Figure S42. The position of adsorbed C2H2 molecules in the narrowest channel neck in MUF-17 observed by DFT-D3 calculations.
References:


