Supplementary Information for:

**A robust ethane-trapping metal-organic framework with a high capacity for ethylene purification**

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1. Synthesis of MUF-15

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

\([\text{Co}_3(\mu_3\text{-OH})(\text{ipa})_{2.5}(\text{H}_2\text{O})]\) (MUF-15): A mixture of \(\text{Co(OAc)}_2\cdot4\text{H}_2\text{O}\) (0.125 g, 0.5 mmol), isophthalic acid (\(\text{H}_2\text{ipa}\), 0.166 g, 1.0 mmol), MeOH (6 mL), and \(\text{H}_2\text{O}\) (0.5 mL) were sonicated for 10 min and sealed in a 25 ml Teflon-lined autoclave and heated at 120 °C for two days. After cooling to room temperature, the resulting purple plate crystals were washed with methanol several times and dried under vacuum (Yield ca. 0.081 g, 78% based on cobalt). Guest-free MUF-15 was obtained by heating under high vacuum at 120 °C for 20 h. Anal. calcd. (found) for \([\text{C}_{20}\text{H}_{13}\text{Co}_3\text{O}_{12}]\cdot\text{H}_2\text{O}\): C, 37.53 (37.47); H, 2.36 (2.87); N, 0.00 (0.00).

Large scale synthesis of MUF-15: \(\text{Co(OAc)}_2\cdot4\text{H}_2\text{O}\) (0.75 g, 3.0 mmol) and \(\text{H}_2\text{ipa}\) (0.664 g, 4.0 mmol) were mixed in MeOH (40 mL) and \(\text{H}_2\text{O}\) (3 mL) and sonicated for 30 min. The solution was sealed in a 100 mL Teflon-lined autoclave and heated at 120 °C for two days. After cooling to room temperature, the resulting purple plate crystals were washed with methanol several times and dried under vacuum (Yield ca. 0.42 g, 66% based on cobalt).

![Figure S1. An optical micrograph of MUF-15](image)

\([\text{Co}_3(\text{OH})(\text{ipa})_{2.5}(\text{H}_2\text{O})(\text{DMF})]\) (OMOF-2) was synthesized using a reported procedure. The resulting block purple crystals were washed with dichloromethane several times and guest-free MOF was obtained by heating these under high vacuum at 140 °C for 20 h.

OMOF-2 is structurally very similar to MUF-15 but it has an additional coordinated DMF molecule. The adsorption performance and characterization results of OMOF-2 is also presented here for the sake of comparison. Its ethane/ethylene separation performance is vastly inferior to that of MUF-15.

2. \(^1\text{H NMR spectroscopy analysis of digested MOF samples}\)

For \(^1\text{H NMR spectroscopy}, guest-free crystals were digested using the following protocol: 150 µL of a 35% DCI solution in D$_2$O was mixed with 500 µL of DMSO-\(d_6\) to give a DCI/DMSO-\(d_6\) stock solution. Around 5 mg of OMOF-2 was digested in 150 µL of this stock solution together with 450 µL of DMSO-\(d_6\). 5 mg of MUF-15 was also digested in 5 mL of NaOD/D$_2$O. Spectra were acquired immediately following dissolution. The resulting spectra are presented below.
Figure S2. $^1$H NMR spectrum of MUF-15 digested in D$_2$O/NaOD.

Figure S3. $^1$H NMR spectrum of digested OMOF-2 in DCI/DMSO-$d_6$.

3. Single-crystal and powder X-ray diffraction

A Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator (Cu$_{\text{K}}$ 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\textsuperscript{2} SHELX\textsuperscript{3} (under OLEX\textsuperscript{4}) was used for structure solution and refinement. The Solvent Mask function in OLEX was used to mask out contributions from guest molecules occluded in the framework pores. As-synthesized samples were washed several times with methanol before being mounted on the instrument. All the data were collected at room temperature.

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 20 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-15 remains unchanged after: (i) activation at 120 °C under vacuum, (ii) gas adsorption isotherm measurements, (iii) gas breakthrough experiments and (iv) exposure to an air with relative humidity of 80% for a week.

**Figure S4.** PXRD patterns of MUF-15 showing that its structure remains unchanged after activation at 120 °C under vacuum, after isotherm measurements, after breakthrough experiment and after exposure to an air with a relative humidity of 80% for one week.
Table S1. Crystal data and structure refinement for MUF-15.

| Property                  | Value                                                                 |
|---------------------------|----------------------------------------------------------------------|
| Formula                   | Co₃(µ₃-OH)(ipa)₂.₅(H₂O)                                               |
| Empirical formula         | C₂₀H₁₃Co₃O₁₂                                                          |
| Formula weight            | 622.09                                                               |
| Crystal system            | orthorhombic                                                         |
| Space group               | Pnna                                                                 |
| a/Å                       | 28.714(2)                                                            |
| b/Å                       | 21.1265(7)                                                           |
| c/Å                       | 10.9460(3)                                                           |
| α/°                       | 90                                                                   |
| β/°                       | 90                                                                   |
| γ/°                       | 90                                                                   |
| Volume/Å³                 | 6640.1(5)                                                            |
| Z                         | 8                                                                    |
| ρ calc/g cm⁻³             | 1.245                                                                |
| μ/mm⁻¹                    | 12.006                                                               |
| F(000)                    | 2480                                                                 |
| 2θ range for data collection/° | 12.044 to 70.24                                                     |
| Index ranges              | -21 ≤ h ≤ 21, -15 ≤ k ≤ 15, -8 ≤ l ≤ 8                              |
| Reflections collected     | 16306                                                                |
| Independent reflections   | 1426 [R int = 0.1075, R sigma = 0.0582]                               |
| Data/restraints/parameters| 1426/219/296                                                         |
| Goodness-of-fit on F²     | 1.160                                                                |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0878, wR₂ = 0.2481                                        |
| Final R indexes [all data]| R₁ = 0.1056, wR₂ = 0.2680                                          |
| Largest diff. peak/hole / e Å⁻³ | 0.72/-0.42                                                          |
4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 instrument. Measurements were made on approximately 5 mg of dried samples under a N\textsubscript{2} flow with a heating rate of 5 °C/min.

**Figure S5.** TGA curve of MUF-15 showing a 2.95% weight loss equivalent to calculated weight loss for one coordinated water molecule.

**Figure S6.** TGA curve of OMOF-2 showing a 14% weight loss equivalent to the calculated weight loss for one coordinated DMF and one coordinated water molecule.
5. Structure, physical properties and pore shape

The Zeo++ code and RASPA2 were used to characterize the geometric features of the crystal structure of MUF-15 by calculating the pore volume with the use of a helium probe atom, the pore limiting diameter (i.e., the diameter of smallest pore window), the largest cavity diameter (i.e., the diameter of the largest sphere that can fit within the pores), and the surface area accessible to a H$_2$ probe (a N$_2$ probe produce a surface area of zero) using the coordinated found by X-ray crystallography. The Accelrys Materials Studio 7.0 software package was used to visualize the MOF structure and pore topology.

**Table S2.** Some calculated and experimentally determined structural characteristics of MUF-15.

|                                |                          |
|--------------------------------|--------------------------|
| Geometric surface area calculated (RASPA2) | 1260 m$^2$/g            |
| BET surface area from experimental N$_2$ isotherm/77K | 1130 m$^2$/g            |
| Pore volume calculated (RASPA2)           | 0.46 cm$^3$/g            |
| Pore volume from experimental N$_2$ isotherm/77K | 0.51 cm$^3$/g           |
| Largest cavity diameter calculated (Zeo++) | 5.2 Å                   |
| Pore limiting diameter calculated (Zeo++)  | 3.6 Å                   |
Figure S7. Pore structure and void space of MUF-15 illustrated by Connolly surface using a probe of diameter of 1 Å along the x (a), y (b), z (c) axes, and a top view showing the connectivity of the pores (d) (Co, blue; O, red; C, grey; and H, white).
6. Gas adsorption measurements and calculations

6.1. Properties of ethane and ethylene and related gases

Table S3. Physicochemical characteristics of different gases relevant to their separation.7-9

|        | Boiling point (K) | Molecular dimensions (Å) | Polarizability (Å³) | Dipole moment ×10¹⁸ esu cm² | Quadrupole moment ×10²⁶ esu cm² |
|--------|------------------|--------------------------|---------------------|----------------------------|-------------------------------|
| CO₂    | 216.5            | 3.18×3.33×5.36           | 2.91                | -                          | -4.3                          |
| N₂O    | 184.6            | 3.03×3.04×5.32           | 3.03                | 0.16                       | -3.3                          |
| C₂H₂   | 188.4            | 3.32×3.34×5.70           | 3.33-3.93           | -                          | +7.5                          |
| C₂H₄   | 169.4            | 3.28×4.18×4.84           | 4.25                | -                          | +1.5                          |
| C₂H₆   | 184.5            | 3.81×4.82×4.08           | 4.43-4.47           | -                          | +0.65                         |

6.2. Single gas adsorption isotherm measurements at low pressures

Gas adsorption isotherms were measured with a volumetric adsorption apparatus (Quantachrome-Autosorb-iQ2). Ultrahigh-purity gases were used as received from BOC Gases. The as-synthesized samples were washed with anhydrous methanol several times and about 100 mg was transferred into a pre-dried and weighed sample tube and heated at rate of 10°C/min to a temperature of 120 °C under a dynamic vacuum with a turbomolecular pump for 20 hours. Accurate sample masses were calculated using degassed samples after sample tubes were backfilled with nitrogen. Surface areas were determined from the N₂ (77 K) adsorption isotherm collected by application of the BET model. Bath temperatures of 273 K and 293 K were precisely controlled with a recirculating control system containing a mixture of ethylene glycol and water. The low temperature (77 K) was controlled by a Dewar filled with liquid N₂.

Figure S8. Volumetric C₂H₆ adsorption (filled circles) and desorption (open circles) isotherms measured at different temperatures for MUF-15.
**Figure S9.** Volumetric C$_2$H$_4$ adsorption (filled circles) and desorption (open circles) isotherms measured at different temperatures for MUF-15.

**Figure S10.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of different gasses measured at 293 K for MUF-15. Slight hysteresis is seen in the C$_2$H$_2$ isotherm due to slow uptake kinetics, but this was not explored in detail.
**Figure S11.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of different gasses measured at 273 K for MUF-15.

**Figure S12.** Comparison of adsorption isotherms of C$_2$H$_6$, C$_2$H$_4$ and C$_2$H$_2$ at 293 K for MUF-15.
Figure S13. Volumetric C$_2$H$_6$ adsorption (filled circles) and desorption (open circles) isotherms of MUF-15 at 293K measured on the same sample over multiple cycles.

Figure S14. Volumetric C$_2$H$_6$ adsorption (filled circles) and desorption (open circles) adsorption isotherms of MUF-15 at 293 K before and after exposing a sample to a laboratory environment with ~80% humidity overnight.
Figure S15. Kinetic profiles of gas uptake by MUF-15 at 293 K upon exposing an evacuated sample to a dose of gas equal to its measured total adsorption of that gas at 760 torr.

Figure S16. Volumetric $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_4$ adsorption (filled circles) and desorption (open circles) isotherms measured at 293 K for OMOF-2. Its ethane/ethylene separation performance is vastly inferior to that of MUF-15.
6.3. Single gas adsorption isotherm measurements at high pressures

High-pressure adsorption isotherms were measured on a PCT Pro instrument from Setaram. About 0.4 g of activated sample (activated at 120 °C under vacuum overnight) was transferred into a 4 mL stainless steel sample holder inside a glove box under an Ar atmosphere, the sample mass was weighed using decrement method due to the insufficient measuring range of the balance for the sample holder. The sample holder was then transferred to the PCT Pro, connected to the instrument’s analysis station via an VCR fitting, and evacuated at 40 °C for at least 2 h. The sample holder was placed inside a stainless-steel recirculating dewar connected to a Julabo F12-E0 isothermal bath filled with Ethylene glycol aqueous solution (1:3, v/v), for which the temperature stability is ± 0.02 °C.

To eliminate the influence of fluctuations in room temperature, the manifold was set as 40 °C. He was used to determine the void volume in the sample holder by using the method of expanding from the dosing manifold to the evacuated sample holder and recording the change in pressure, assuming He adsorption is negligible. The PCT Pro is equipped with a 15 bar transducer (accuracy of ± 0.12% of the reading) for the measurements up to 10 bar. By default, the direct method was used to calibrate the void volume. Ultrahigh grade (99.999%) of C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and He were used for all the adsorption measurements. The background adsorption was measured with empty holder at 273 and 298 K by the direct method. The background correction on all isotherms was performed with the “subtract” function directly within Origin.

Figure S17. High pressure C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} adsorption (filled circles) and desorption (open circles) isotherms of MUF-15 at 298 K.
6.4. Calculation of BET surface areas

BET surface areas were calculated from N\textsubscript{2} adsorption isotherms at 77 K according to the following procedures\textsuperscript{10}:

1) The isotherm region where \( v(1 - P/P_0) \) increases versus \( P/P_0 \), where \( v \) is the amount of N\textsubscript{2} adsorbed, was identified.

2) Within this isotherm region, sequential data points that led to a positive intercept in the plot of \( \frac{P/P_0}{v(1 - P/P_0)} \) against \( P/P_0 \) 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:

\[
A_{BET} = v_m(\text{cm}^3\text{g}^{-1}) \times \frac{1}{22400(\text{cm}^3)} \times \sigma_0(\text{Å}^2) \times N_A(\text{mol}^{-1}) \times 10^{-20} \text{m}^2\text{Å}^{-2}
\]

Where \( N_A \) is Avogadro’s constant, and \( \sigma_0 \) is the cross-sectional area of a N\textsubscript{2} molecule, which is 16.2 Å\textsuperscript{2}.

![Figure S18. Volumetric N\textsubscript{2} adsorption (filled circles) and desorption (open circles) isotherms measured at 77 K for MUF-15 and OMOF-2.](image_url)
Figure S19. $N_2$ adsorption isotherm at 77 K and BET surface area plots for MUF-15.

Figure S20. $N_2$ adsorption isotherm at 77 K and BET surface area plots for OMOF-2.
6.5. Isosteric heats of adsorption

Isosteric heat of adsorption ($Q_{st}$) values were calculated from isotherms measured at 288K, 293K and 298 K for ethane and ethylene; 273K and 293 K for CO$_2$ and CH$_4$ on MUF-15 and 273 K and 293 K for ethane and ethylene on OMOF-2. The isotherms were first fit to a viral equation:

\[
\ln P = \ln N + \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]

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 required 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 S21. Virial equation fit for C$_2$H$_6$ adsorption isotherms of MUF-15.
Figure S22. Virial equation fit for C$_2$H$_4$ adsorption isotherms of MUF-15.

Figure S23. Virial equation fit for CO$_2$ adsorption isotherms of MUF-15.
Figure S24. Virial equation fit for CH₄ adsorption isotherms of MUF-15.

Figure S25. Virial equation fit for C₂H₂ adsorption isotherms of MUF-15.
**Figure S26.** Isosteric heat of adsorption plots as a function of gas uptake for the adsorption of different guests by MUF-15.

6.6. IAST selectivity calculations for binary gas mixtures

Mixed gas adsorption isotherms and gas selectivities for 5 different mixtures of C$_6$H$_6$/C$_2$H$_4$ (25/75, 50/50, 10/90, 1/99, 0.1/99.9) were calculated at 293 K based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz$^{12}$. The pylAST package$^{13}$ was used to perform the IAST calculations. In order to predict the sorption performance of MUF-15 toward the separation of binary mixed gases, the single-component C$_6$H$_6$ and C$_2$H$_4$ adsorption isotherms were first fit to a dual site angmuir 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 S24 and S25. These parameters were used subsequently to carry out the IAST calculations.
Figure S27. Dual-site Langmuir fits of the MUF-15 isotherms at 293 K.

Figure S28. Dual-site Langmuir fits of the OMOF-2 isotherms at 293 K.
**Figure S29.** Mixed-gas isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 50/50 C$_2$H$_6$/C$_2$H$_4$ at 293 K.

**Figure S30.** Mixed-gas isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 25/75 C$_2$H$_6$/C$_2$H$_4$ at 293 K.
Figure S31. Mixed-gas isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 10/90 \( \text{C}_2\text{H}_6/\text{C}_3\text{H}_8 \) at 293 K.

Figure S32. Mixed-gas isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 1/99 \( \text{C}_2\text{H}_6/\text{C}_3\text{H}_8 \) at 293 K.
**Figure S33.** Mixed isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 0.1/99.9 \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) at 293 K.

**Figure S34.** Mixed isotherms and selectivity of MUF-15 predicted by IAST for a mixture of 25/75 \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) at 293 K (High pressure single gas isotherms were used for IAST selectivity calculations).
7. Breakthrough separation experiments

7.1. Mass spectrometer calibration and fragmentation peaks

A SRS UGA200 mass spectrometer was used to continuously analyse the composition of the outlet gasses. It was first calibrated for the gases under investigation by introducing them at known pressures. A mass of 30 was used for ethane, 2 for helium and 28 for ethylene. It should be noted that the ethane spectrum also generates a peak at mass 28 with an intensity 47% of that of the total peak. Therefore, to calculate the composition of ethylene, the contribution of this fragment peak from ethane was subtracted.

7.2. Breakthrough experiments

A home-built breakthrough apparatus was used to measure gas separations under dynamic conditions (Fig. S36). The performance and accuracy of this apparatus was established by reproducing breakthrough results reported in the literature, and consistent results were obtained.\textsuperscript{14-16}

In a typical breakthrough experiment, 1 g of an activated sample of MUF-15 was placed in an adsorption column (6.4 mm in diameter × 11 cm in length) to form a fixed bed. The adsorbent was activated \textit{in situ} at 120 °C under high vacuum for 6 hours and then the column was left under vacuum for another 2 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 each breakthrough experiment. A gas mixture containing different mixtures of C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and He gas was introduced to the column at 1.1 bar and 20 °C at 8 mL/min. The flow rate of inert He gas in all the experiments was kept constant at 4 mL/min. 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 15-20 minutes between each cycle.
Figure S36. A schematic of the column breakthrough experimental setup.
**Figure S37.** Experimental breakthrough curves for a mixture of 25/75 ethane/ethylene at 1.1 bar and 293 K over 12 consecutive cycles. The adsorbent was regenerated between cycles by leaving the column under vacuum for 15-20 minutes.

**Figure S38.** Overlay of experimental breakthrough curves for a mixture of 25/75 ethane/ethylene at 1.1 bar and 293 K for 12 cycles. The helium curve has been removed from the figure.
Figure S39. Experimental breakthrough curves for a mixture of 50/50 ethane/ethylene at 1.1 bar and 293 K over three consecutive cycles. The adsorbent was regenerated between cycles by leaving the column under vacuum for 15-20 minutes.

Figure S40. Overlay of experimental breakthrough curves of a mixture of 50/50 ethane/ethylene at 1.1 bar and 293 K for 3 cycles. The helium curve has been removed from the figure.
**Figure S41.** Experimental breakthrough curves for a mixture of 10/90 ethane/ethylene at 1.1 bar and 293 K over three consecutive cycles. The adsorbent was regenerated between cycles by leaving the column under vacuum for 15-20 minutes.

**Figure S42.** Overlay of experimental breakthrough curves of a mixture of 10:90 ethane/ethylene at 1.1 bar and 293 K for 12 cycles. The helium curve has been removed from the figure.
7.3. Regeneration profile

The desorption behaviour of ethane and ethylene from the adsorption column was also investigated. Once the adsorbent was saturated with an equimolar mixture of ethane and ethylene, the column was purged with a helium flow of 5 mL/min for 7 mins at 20 °C at 1.1 bar. Then column was then heated to 70 °C with a ramp of 10 °C/min for 23 mins. Finally it was heated to 130 °C with the same ramping for 12 min before cooling to 20 °C. A breakthrough measurement was then performed, which showed that the absorbent had been fully regenerated.

**Figure S43.** Desorption behaviour of the adsorbates through heating the column at 1.1 bar under a helium flow of 5 mL/min. Ethane and ethylene are both completely removed from the column upon heating to 70 °C. No adsorbates are removed upon further heating to 130 °C.
8. Breakthrough curve simulations

8.1. Mathematical modelling

Considering a fixed bed adsorption column of length L filled with MUF-15, following assumptions were made to develop a mathematical model\textsuperscript{17-19} that could be solved using proper numerical methods to calculate the concentration of gasses at different elapsed times along the 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 were 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 to obey the 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:

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

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

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, \(D_{ax}\) 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{20}:

\[
\frac{\varepsilon D_{ax,i}}{D_{m,i}} = 20 + 0.5 Sc_i Re
\]

Figure S44. Schematic diagram of a fixed adsorption bed.
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:

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

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. 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:

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

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, an accurate value for 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 concentration in the gas phase through isotherms. The IAST method was used to predict mixed gas isotherms and they were fitted by a Langmuir model. The pressure drop is defined by the Ergun’s equation:

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

Where $P$ is the local pressure at the $z$ axial coordinate, $\mu$ is the gas viscosity, $\varphi$ 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 S3.

### Table S4. Adsorption column parameters and feed characteristics used for the simulations.

| Adsorption bed | Feed |
|----------------|------|
| Length: 110 mm | Flow rate: 8 mL/min |
| Diameter: 6.4 mm | Temperature: 293 K |
| Amount of adsorbent in the bed: 1 g | Pressure: 1.1 bar |
| Bed voidage: 0.77 | Carrier gas (He) flow rate: In all the simulated breakthrough curves feed was diluted with 4 mL/min of helium unless otherwise stated. |
| Adsorbent average radius: 0.2 mm | Purge gas: He with a flow rate of 20 mL/min |
| $k_{\text{ethane}}$: 0.009 s$^{-1}$ | |
| $k_{\text{ethylene}}$: 0.013 s$^{-1}$ | |

**Langmuir fitting**

Figures S29-S34

### 8.2. 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 to 50 increments and the set of equations were solved by the Implicit Euler method with a time step of one second.\(^{24}\)

**Figure S45.** Predicted breakthrough curves for a mixture of 25/75 of C\(_2\)H\(_6\) (black) and C\(_2\)H\(_4\) (red) at 293 K and 1.1 bar compared with experimental breakthrough curves before tuning of the mass transfer coefficient.

**Figure S46.** Predicted breakthrough curves for a mixture of 50/50 of C\(_2\)H\(_6\) (black) and C\(_2\)H\(_4\) (red) at 293 K and 1.1 bar compared with experimental breakthrough curves before tuning of the mass transfer coefficient.
**Figure S47.** Predicted breakthrough curves for a mixture of 10/90 of C\(_2\)H\(_6\) (black) and C\(_2\)H\(_4\) (red) at 293 K and 1.1 bar compared with experimental breakthrough curves before tuning of the mass transfer coefficient.

**Figure S48.** Predicted breakthrough curves for a mixture of 25/75 of C\(_2\)H\(_6\) (black) and C\(_2\)H\(_4\) (red) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficient (\(k_{\text{ethane}}\): 0.009 s\(^{-1}\), \(k_{\text{ethylene}}\): 0.013 s\(^{-1}\)).
**Figure S49.** Predicted breakthrough curves for a mixture of 50/50 of C$_2$H$_6$ (black) and C$_2$H$_4$ (red) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficient ($k_{\text{ethane}}$: 0.009 s$^{-1}$, $k_{\text{ethylene}}$: 0.013 s$^{-1}$).

**Figure S50.** Predicted breakthrough curves for a mixture of 10/90 of C$_2$H$_6$ (black) and C$_2$H$_4$ (red) at 293 K and 1.1 bar compared with experimental breakthrough curves after tuning of the mass transfer coefficient ($k_{\text{ethane}}$: 0.009 s$^{-1}$, $k_{\text{ethylene}}$: 0.013 s$^{-1}$).
**Figure S51.** Predicted breakthrough curves for a mixture of 1/99 of C\textsubscript{2}H\textsubscript{6} (black) and C\textsubscript{2}H\textsubscript{4} (red) at 293 K and 1.1 bar using a mass transfer coefficient of $k_{\text{ethane}}$: 0.009 1/s and $k_{\text{ethylene}}$: 0.013 1/s.

**Figure S52.** Predicted breakthrough curves for a mixture of 0.1/99.90 of C\textsubscript{2}H\textsubscript{6} (black) and C\textsubscript{2}H\textsubscript{4} (red) at 293 K and 1.1 bar using a mass transfer coefficient of $k_{\text{ethane}}$: 0.009 1/s and $k_{\text{ethylene}}$: 0.013 1/s.
Figure S53. Predicted breakthrough curves for a mixture of 25/75 (black), 50/50 (red), 10/90 (blue), 1/99 (green) and 0.1/99.9 (orange) of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) at 293 K and 1.1 bar using mass transfer coefficients of \( k_{\text{ethane}}: 0.009 \, \text{s}^{-1} \) and \( k_{\text{ethylene}}: 0.013 \, \text{s}^{-1} \).

Figure S54. Predicted breakthrough curves at different operating pressures for a 25/75 mixture of \( \text{C}_2\text{H}_6/\text{C}_2\text{H}_4 \) at 298 K using mass transfer coefficients of \( k_{\text{ethane}}: 0.009 \, \text{s}^{-1} \) and \( k_{\text{ethylene}}: 0.013 \, \text{s}^{-1} \).
Figure S55. Productivity of ethylene at different operating pressures for a 25/75 mixture of C_2H_6/C_2H_4 at 293 K.
9. Comparison of separation performance for different MOFs

To unambiguously compare the separation performance of different materials, ethylene productivity, IAST selectivity and mixture uptakes (the amount of gas uptake taken by adsorbent in presence of other gasses, \( q_{i,mix} \)) for an equimolar mixture of ethane/ethylene and isosteric heats of adsorption for the top-performing ethane-selective MOFs reported in the literature were compared. 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 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%:

\[
\text{Productivity}_\text{C}_2\text{H}_4 = \int_{t_1}^{t_2} F_{\text{C}_2\text{H}_4,\text{out}} dt / m_{\text{MOF}}
\]

Where \( F_{\text{C}_2\text{H}_4,\text{out}} \) the flowrate of effluent ethylene and \( m_{\text{MOF}} \) is the amount of MOF packed in the bed. Ethylene productivity was calculated based on both experimental and simulated breakthrough curves (termed as Productivity\text{exp} and Productivity\text{sim}). Simulated breakthrough curves for an equimolar mixture of ethane/ethylene (without helium as a carrier gas) at 293 K and 1 bar were estimated using the method outlined earlier and assuming that gasses quickly reach their equilibrium uptake during the dynamic breakthrough process. The single gas isotherms presented in the references were used to calculate IAST selectivity and to simulate breakthrough curves. Experimental breakthrough curves presented in the references were used to calculate Productivity\text{exp}. It should be noted that experimental breakthrough curves data were extracted from these literature references using a plot digitizer program. Therefore, the Productivity\text{exp} values are estimates and not strictly based on threshold values of exactly 99.95% as we did not have the breakthrough data with sufficient precision. A summary of the separation performance of these MOFs is shown in Table S5.

| MOF    | \( T \) (°C) | \( P \) (bar) | \( Q_{\text{St,ethane}} \) (kJ/mol) | \( Q_{\text{St,ethylene}} \) (kJ/mol) | \( q_{\text{ethane,mixed}} \) (mmol/g) | \( q_{\text{ethylene,mixed}} \) (mmol/g) | Selectivity \((\text{C}_2\text{H}_6/\text{C}_2\text{H}_4)\) | Productivity\text{exp} \( (L/kg) \) | Productivity\text{sim} \( (L/kg) \) |
|--------|--------------|--------------|-----------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|---------------------------------|------------------|------------------|
| IRMOF-8\^[a\] | 25 | 1 | 52.5 | 50 | 2.16 | 1.25 | 1.7 | 20.3 | 2.5 |
| MAF-49\^[a\] | 43 | 1 | 61 | 48 | 1.21 | 0.44 | 2.7 | 17.2 | 5.3\^[a\] |
| MIL-142A\^[a\] | 25 | 1 | 27.2 | 26.2 | 2.1 | 1.39 | 1.51 | 15.9 | 6.7 |
| Ni(bdc)(ted)\^[a\] | 25 | 1 | 21.5 | 18.3 | 2.48 | 1.38 | 1.8 | 24.6 | - |
| PCN-245\^[a\] | 25 | 1 | 22.8 | 21 | 1.8 | 1 | 1.8 | 17.9 | 5.8 |
| ZIF-4\^[a\] | 20 | 1 | - | - | 1.56 | 0.73 | 2.15 | 18.5 | 6.6 |
| PCN-250\^[a\] | 25 | 1 | 23.2 | 21.1 | 2.96 | 1.6 | 1.85 | 30.4 | 10 |
| ZIF-7\^[a\] | 25 | 1 | - | - | 1.2 | 0.8 | 1.5 | 21 | 2 |
| ZIF-8\^[a\] | 22 | 1 | 17.2 | 16.1 | 1.26 | 0.7 | 1.8 | 13.4 | 0.4 |
| Cu(Qc)\^[a\] | 25 | 1 | 30 | 25.4 | 1.65 | 0.48 | 3.45 | 26.2 | 4.34\^[a\] |
| Fe\text{O}2dobdc\^[a\] | 25 | 1 | 66.8 | 36.5 | 2.53 | 0.57 | 4.4 | 45.02 | 19.3\^[a\] |
| MUF-15 \^[a\] | 20 | 1 | 29.2 | 28.2 | 3.13 | 1.6 | 1.96 | 34.2 | 14 |

\^[a\] The reported productivity value is 6.2 L/kg. \^[b\] The reported productivity value is 4.4 L/kg. \^[c\] The reported productivity value is 19.93 L/kg.
10. DFT calculations

Static binding energies for ethane and ethylene in MUF-15 framework were calculated using density functional theory (DFT) as implemented in the software package VASP 5.4.4.\(^3\) 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 gaseous adsorbates. To accurately estimate static binding energies for the guest molecules with MUF-15 framework, we implemented dispersion corrections using DFT-D3 method.\(^3\)\(^5\) Electron exchange and correlation were described using the generalized gradient approximation Perdew, Burke, and Ernzerhof (PBE)\(^3\)\(^6\) 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 ionic forces were less than 0.02 eV/Å. The initial location of the guest molecule (one guest molecule per cell) in the unit cell of MUF-15 was obtained from the classical simulated annealing technique using classical force field as implemented in sorption module in Materials Studio.\(^3\)\(^7\) 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 in 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 ($\Delta E$) at 0 K in vacuum and in solvent (both water and methanol) were calculated using the following expression

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

Where $E_x$ refers, respectively, to the total energies of the MOF + guest complex, the MOF alone, and guest molecule.
Figure S56. Comparison of the preferential \(\text{C}_2\text{H}_6\) (a) and \(\text{C}_2\text{H}_4\) (b) adsorption sites calculated by DFT. C−H···π interactions are shown in purple dashed bonds, highlighting vdw contacts between gas molecules and benzene rings (numbered as 1-3) (Co blue, C dark grey, H light grey, O red).

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