Supporting Information

Efficient separation of ethylene from acetylene/ethylene mixtures by a flexible-robust metal-organic framework

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Table of Contents

1. Experimental section ........................................................................................................2
   1.1 Synthesis and characterization of ELM-12 ...............................................................2
   1.2 Breakthrough experiments ......................................................................................3
2. Calculation of the separation potential of ELM-12 ......................................................4
   2.1 Fitting of pure component isotherms ..................................................................... 4
   2.2 IAST calculations of adsorption selectivities ........................................................5
3. Breakthrough curves for C₂H₂/C₂H₄ separation ...........................................................7
4. Adsorption cycling experiments for ELM-12 ...............................................................8
5. Separation cycling experiments for ELM-12 ..............................................................9
6. Structural stability experiments for ELM-12 ..........................................................10
1. Experimental section

1.1 Synthesis and characterization of ELM-12

Fig S1. (a, b) Schematic diagram of the structure of ELM-12. (c) Powder X-ray diffraction (PXRD) patterns of synthesized ELM-12 sample. (d) PXRD patterns of guest-free and C$_2$H$_2$-loaded ELM-12 samples. (Cu, green; C, gray; O, red; H, white; S, yellow; F, blue).
1.2 Breakthrough experiments

The breakthrough curves were measured on a homemade apparatus for gases mixtures C$_2$H$_2$/C$_2$H$_4$ (1/99 and 50/50) at 298 K and 1 bar. The gas flows were controlled at the inlet by a mass flow meter as 2 mL/min, and a gas chromatograph (TCD-Thermal Conductivity Detector) continuously monitored the effluent gas from the adsorption bed. Prior to every breakthrough experiment, we activated the sample by flushing the adsorption bed with helium gas for 2 hours at 373 K. Subsequently, the column was allowed to equilibrate at the measurement rate before we switched the gas flow.

Fig. S2 Breakthrough experiment apparatus.
2. Calculation of the separation potential of ELM-12

2.1 Fitting of pure component isotherms

The experimentally measured excess loadings for \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) at temperatures of 273 and 298 K for ELM-12 were fitted with the dual-Langmuir-Freundlich isotherm model

\[
q = q_{A,\text{sat}} \frac{b_A P_v^{q_A}}{1 + b_A P_v^{q_A}} + q_{B,\text{sat}} \frac{b_B P_v^{q_B}}{1 + b_B P_v^{q_B}}
\]

(1)

with \( T \)-dependent parameters \( b_A \) and \( b_B \)

\[
b_A = b_{A0} \exp \left( \frac{E_A}{RT} \right), \quad b_B = b_{B0} \exp \left( \frac{E_B}{RT} \right)
\]

(2)

The parameters are provided in table S1.

For all other MOFs, the isotherm data are taken from Cui et al.\(^1\)

<table>
<thead>
<tr>
<th>Site A</th>
<th>Site B</th>
</tr>
</thead>
<tbody>
<tr>
<td>q(_{A,\text{sat}}) (mol kg(^{-1}))</td>
<td>q(_{B,\text{sat}}) (mol kg(^{-1}))</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>0.65</td>
<td>2.5</td>
</tr>
<tr>
<td>1.45</td>
<td></td>
</tr>
</tbody>
</table>

Table S1. Dual-Langmuir-Freundlich fitting parameters for \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) isotherms.

Reference

2.2 IAST calculations of adsorption selectivities

We consider the separation of binary C₂H₂/C₂H₄ mixtures. The adsorption selectivity for C₂H₂/C₂H₄ separation is defined by

\[
S_{\text{ads}} = \frac{q_1}{p_1} / \frac{q_2}{p_2}
\]

Eq. (3)

\(q_1\), and \(q_2\) are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures \(p_1\), and \(p_2\).

**Fig. S3** IAST calculations of the adsorption selectivity of C₂H₂/C₂H₄ (50/50) mixtures on ELM-12.
Notation

\( b_A \)  Langmuir-Freundlich constant for species \( i \) at adsorption site A, \( \text{Pa}^{-\nu_A} \)

\( b_B \)  Langmuir-Freundlich constant for species \( i \) at adsorption site B, \( \text{Pa}^{-\nu_B} \)

\( c_i \)  molar concentration of species \( i \) in gas mixture, \( \text{mol} \text{ m}^{-3} \)

\( c_{i0} \)  molar concentration of species \( i \) in gas mixture at inlet to adsorber, \( \text{mol} \text{ m}^{-3} \)

\( E \)  energy parameter, \( \text{J} \text{ mol}^{-1} \)

\( L \)  length of packed bed adsorber, \( \text{m} \)

\( p_i \)  partial pressure of species \( i \) in mixture, \( \text{Pa} \)

\( p_t \)  total system pressure, \( \text{Pa} \)

\( q_i \)  component molar loading of species \( i \), \( \text{mol} \text{ kg}^{-1} \)

\( Q_{st} \)  isosteric heat of adsorption, \( \text{J} \text{ mol}^{-1} \)

\( t \)  time, \( \text{s} \)

\( T \)  absolute temperature, \( \text{K} \)

\( u \)  superficial gas velocity in packed bed, \( \text{m} \text{ s}^{-1} \)

Greek letters

\( \varepsilon \)  voidage of packed bed, dimensionless

\( \nu \)  Freundlich exponent, dimensionless

\( \rho \)  framework density, \( \text{kg} \text{ m}^{-3} \)

\( \tau \)  time, dimensionless
3. Breakthrough curves for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation

![Breakthrough curve diagram]

**Fig. S4** Experimental breakthrough curves of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (50/50) mixtures separation for ELM-12 materials at 298 K and 1 bar.
4. Adsorption cycling experiments for ELM-12

**Fig. S5** $\text{C}_2\text{H}_2$ (a) and $\text{C}_2\text{H}_4$ (b) adsorption cycles for ELM-12. After each adsorption process, sample was evacuated under $10^{-6}$ bar for 30 minutes.
5. Separation cycling experiments for ELM-12

Fig. S6 (a) Cycling column breakthrough curves of C$_2$H$_2$/C$_2$H$_4$ separation (1/99) for ELM-12 at 298 K and 1 bar. The breakthrough experiments were carried out at a flow rate of 2 mL/min. Regeneration with He flow (100 mL/min) for 30 minutes at 373 K.
6. Structural stability experiments for ELM-12

**Fig. S7** (a) PXRD and (b) breakthrough experiment of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} (1/99) mixture for ELM-12 samples (fresh sample and two-years aging sample), respectively.
<table>
<thead>
<tr>
<th>Crystal data</th>
<th>ELM-12 (Guest-free)</th>
<th>ELM-12 (C_2D_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>system</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
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<tr>
<td><strong>space group</strong></td>
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<td>C2/c</td>
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<tr>
<td><strong>MF</strong></td>
<td>C_{22}H_{16}CuF_{6}N_{4}O_{6}S_{2}</td>
<td>C_{24.43}H_{16}CuD_{2.43}F_{6}N_{4}O_{6}S_{2}</td>
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<tr>
<td><strong>b/Å</strong></td>
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<td>0.141a</td>
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<td><strong>refinement parameters</strong></td>
<td>R_1 = 0.1415, wR_2 = 0.3556</td>
<td>R_p = 0.0112, R_wp = 0.0135</td>
</tr>
</tbody>
</table>

*a Calculated on the basis of the MOF crystal structures using PLATON software.

**Table S2.** Comparison of the Crystallographic and Refinement Parameters for Guest-free ELM-12* and C_2D_2-loaded ELM-12.

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