Supplementary information for

High flux high-silica SSZ-13 membrane for CO$_2$ separation

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Fig. S1 SEM images of the macroporous α-alumina support surface (left) and layer of SSZ-13 seed crystals after two dip-coating steps (right).
**Fig. S2** Scheme of separation setup and membrane module.

1. Gas bottles  
2. Mass-flow controllers  
3. Stainless steel saturator  
4. 4-way valves  
5. Oven  
6. Membrane module  
7. Back-pressure regulator  
8. Flow meter (digital or bubble)  
9. Online GC

**Calculation of permeance**

Due to use of hollow fiber membranes the composition of the feed flow may change along the membrane length. To account for that we used log-mean pressure difference calculated as follows:
\[(\Delta p_i)_n = \frac{(p_{feed}^i - p_{perm}^i) - (p_{ret}^i - p_{perm}^i)}{\ln\left(\frac{p_{feed}^i - p_{perm}^i}{p_{ret}^i - p_{perm}^i}\right)}\]

Retentate, permeate and feed flows and compositions were measured for every experiment and the values were applied for the above calculation.

The back-permeation of sweep gas was neglected in this work. It may, however, significantly influence the membrane performance, especially at lower pressures [J.M. van der Graaf, et al. J. Membr. Sci., 1998, 144, 87-104 and J. van der Bergh et al., J. Membr. Sci., 2008, 16, 35]. Hence, we are currently investigating this effect, to be published in a follow-up publication [C. Gücüyener et al., Modeling permeation of binary gas mixtures across an SSZ-13 zeolite membrane, in preparation]
Fig. S3 TGA curves of SSZ-13 powder (Si/Al=100) calcined in air at 700°C for 5 h (red); calcined in oxygen at 450°C for 80 h (green) and as-synthesized (blue). Heating rate 5 K/min, air flow 40 ml/min.

Table S1 Weight loss of different SSZ-13 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss (400°C-750°C), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined at 700°C</td>
<td>0.6</td>
</tr>
<tr>
<td>Calcined at 450°C</td>
<td>2.3</td>
</tr>
<tr>
<td>As-synthesized</td>
<td>22.0</td>
</tr>
</tbody>
</table>

Detemplation extent: 92.3%
Fig. S4 SEM image of a crack formed on the membrane surface after calcination at 550°C in artificial air flow.
Fig. S5 CO₂/CH₄ equimolar mixture separation in a pressure gradient mode with no sweep gas (dashed lines - single component permeance and ideal selectivity, solid lines - mixture separation results; conditions: 0.6 MPa feed pressure, atmospheric pressure at permeate side, total feed flow rate 200 ml/min.).
**Fig. S6** CO$_2$/N$_2$ equimolar mixture separation in a pressure gradient mode without sweep gas (dashed lines - single component permeance and ideal selectivity, solid lines - mixture separation results; conditions: 0.6 MPa feed pressure, atmospheric pressure on permeate side, total flow rate 200 ml/min)

In the pressure mode at 6 bar total feed pressure without using a sweep gas results were very similar to those obtained in the sweep-gas mode for both mixtures separations. The flux at lower pressures and especially in the presence of water was not high enough to provide reliable GC analysis. Thus, sweep-gas mode was chosen as the standard in this work.

The temperature dependencies presented in Figures S5 and S6 reveal the following trends. For the single component permeation the CO$_2$ permeance decreases with temperature, as a result of the decreasing concentration in the membrane. For CH$_4$ the permeance is nearly constant, which may be caused by the combined influence of activated diffusion and permeation through defects. The nitrogen permeance passes through a maximum which can be the result of a slightly activated diffusion process and a decreasing concentration in the membrane, similarly as for MFI and DDR membranes. [F. Kapteijn et al., *AIChE J.*, 2000, **46**, 1096 and J. van der Bergh et al., *J. Membr. Sci.*, 2008, **16**, 35]

For both mixtures the selectivity monotonically decreases and evolves to that of the ideal selectivity at higher temperatures. For CO$_2$/CH$_4$ the mixture selectivity is lower, due to an increased permeance of methane, suggesting an interaction with the faster permeating carbon dioxide. For the CO$_2$/N$_2$ selectivity this ‘entrainment’ of N$_2$ seems even stronger at lower temperatures, resulting in an appreciable lower selectivity at low temperatures, passing through a weak maximum as a function of temperature.

The preparation of SSZ-13 membranes on the supports with higher permeation area can ensure permeation flows high enough to perform the separation in the pressure gradient mode at lower pressures [Canan Gücüyener et al., *Modeling permeation of binary gas mixtures across an SSZ-13 zeolite membrane*, in preparation].
Fig. S7 Influence of total flow rate on SSZ-13 membrane separation of an equimolar CO$_2$/CH$_4$ mixture (conditions: 293 K, 0.6 MPa feed pressure, atmospheric pressure on permeate side, 200 ml/min of sweep gas).

To avoid influence of a concentration-polarization effect the flow rate of 200 ml/min was chosen as the standard for the permeation and separation tests.
Fig. S8 CO₂, CH₄ and N₂ adsorption isotherms of SSZ-13 powder (Si/Al=80).
Estimated dual site Langmuir adsorption parameters of CO$_2$, CH$_4$ and N$_2$ for SSZ-13 (Si/Al =80); including their 95% confidence intervals.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th># of sites</th>
<th>$q_{\text{mol,A}}$ mol kg$^{-1}$</th>
<th>$-\Delta H_A$ kJ mol$^{-1}$</th>
<th>$K_{0,A}$ $10^{-7}$ kPa$^{-1}$</th>
<th>$q_{\text{mol,B}}$ mol kg$^{-1}$</th>
<th>$-\Delta H_B$ kJ mol$^{-1}$</th>
<th>$K_{0,B}$ $10^{-7}$ kPa$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>2</td>
<td>3.78±0.75</td>
<td>32.0±1.70</td>
<td>0.03±0.03</td>
<td>4.32±0.75</td>
<td>24.8±0.72</td>
<td>6.73±2.97</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2</td>
<td>1.46±0.26</td>
<td>19.3±1.49</td>
<td>2.99±2.07</td>
<td>7.50±0.26</td>
<td>10.6±0.19</td>
<td>23.4±5.52</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2</td>
<td>3.05±0.16</td>
<td>19.7±0.59</td>
<td>0.43±0.22</td>
<td>2.66±0.14</td>
<td>17.9±0.11</td>
<td>20.5±1.02</td>
</tr>
</tbody>
</table>

Following cooling baths were employed to achieve the desired temperatures for adsorption:

- Adsorption at 195 K – Isopropanol/Ice
- Adsorption at 221 K – Ethylene glycol / Ethanol / Solid CO$_2$
- Adsorption at 234 K – Ethylene glycol / Ethanol / Solid CO$_2$
- Adsorption at 255 K – Kryo 20
- Adsorption at 273 K – Ice
- Adsorption at 298 K – Water
- Adsorption at 323 K – Heating

In addition, Ar physisorption tests at 87 K were performed on an SSZ-13 sample with an Si/Al ratio of 86 to evaluate its textural properties. BET surface of the sample is 632 m$^2$.g$^{-1}$ and microporous volume calculated by $t$-plot model is 0.25 cm$^3$.g$^{-1}$.
Computational details

In addition to description given in the main text, the interactions between the various molecules are described in a pair-wise fashion using the following parameters:

<table>
<thead>
<tr>
<th>Center i</th>
<th>Center j</th>
<th>R0 [Å]</th>
<th>D0 [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>O_z</td>
<td>3.895</td>
<td>0.2285</td>
</tr>
<tr>
<td>CH4</td>
<td>CH4</td>
<td>4.176</td>
<td>0.3150</td>
</tr>
<tr>
<td>CH4</td>
<td>C_CO2</td>
<td>3.637</td>
<td>0.1327</td>
</tr>
<tr>
<td>CH4</td>
<td>O_CO2</td>
<td>3.794</td>
<td>0.2245</td>
</tr>
<tr>
<td>CH4</td>
<td>N</td>
<td>3.951</td>
<td>0.1509</td>
</tr>
<tr>
<td>C_CO2</td>
<td>O_z</td>
<td>3.122</td>
<td>0.0998</td>
</tr>
<tr>
<td>C_CO2</td>
<td>C_CO2</td>
<td>3.098</td>
<td>0.0559</td>
</tr>
<tr>
<td>C_CO2</td>
<td>O_CO2</td>
<td>3.244</td>
<td>0.0946</td>
</tr>
<tr>
<td>C_CO2</td>
<td>N</td>
<td>3.412</td>
<td>0.0636</td>
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<tr>
<td>O_CO2</td>
<td>O_z</td>
<td>3.277</td>
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<td>O_CO2</td>
<td>O_CO2</td>
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<td>0.1600</td>
</tr>
<tr>
<td>O_CO2</td>
<td>N</td>
<td>3.569</td>
<td>0.1076</td>
</tr>
<tr>
<td>N</td>
<td>O_z</td>
<td>3.437</td>
<td>0.1158</td>
</tr>
<tr>
<td>N</td>
<td>N</td>
<td>3.727</td>
<td>0.0723</td>
</tr>
</tbody>
</table>
Fig. S9 Water adsorption isotherms of SSZ-13 samples of different synthesis Si/Al ratios at 298 K, measured by gravimetry.

A detailed description of the adsorption procedure can be found in [N. Kosinov et al. Microporous Mesoporous Mater. (2014) in press, doi: http://dx.doi.org/10.1016/j.micromeso.2014.03.034]
SF₆ is assumed to permeate exclusively through defects by Knudsen diffusion, and therefore the contribution of the defect permeance for other gases is calculated as:

\[ \Pi^i = \Pi^{SF_6} \cdot \sqrt{\frac{Mr(SF_6)}{Mr(i)}} \]

where \( \Pi^i \) – permeance of gas \( i \), \( Mr(i) \) – molecular mass of gas \( i \).