Supporting Information

Highly permeable and selective zeolitic imidazolate framework ZIF-95 membrane for hydrogen separation

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**Experimental details:**

Materials: Chemicals were used as received: zinc nitrate tetrahydrate (>99%, Merck), 5-chlorobenzimidazole (cbIM, >96%, ABCR), 3-aminopropyltriethoxysilane (APTES, 98%, Abcr), toluene (Acros), N, N-Dimethylformamide (DMF, water<50 ppm, Acros). Porous $\alpha$-Al$_2$O$_3$ disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as supports.

**APTES modification of the support surface:** Porous $\alpha$-Al$_2$O$_3$ disks were treated with APTES (0.2 mM in 10 mL toluene) at 110 °C for 2 h under argon, leading to APTES monolayer deposited on the $\alpha$-Al$_2$O$_3$ support surface. 1

**Synthesis of ZIF-95 membrane:** The ZIF-95 membrane was prepared by a solvothermal reaction of zinc nitrate tetrahydrate and cbIMI in DMF according to the previous report. 2 The APTES-treated or APTES-free $\alpha$-Al$_2$O$_3$ supports were placed horizontally in a Teflon-lined stainless steel autoclave which was filled with synthesis solution, and heated at 120 °C in air oven for 3 days. After solvothermal reaction, the ZIF-95 membranes were washed with DMF several times, and then dried in air at 100 °C over night.

**Characterization of ZIF-95 membrane:** Scanning electron microscopy (SEM) micrographs were taken on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 µA. using the same SEM microscope at 20 kV and 20 µA. The X-ray diffraction (XRD) patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuKa radiation at 40 kV and 40 mA.

**Permeation of single gas and separation of mixed gases:** For the single gas and mixture gas permeation, the supported ZIF-95 membrane was sealed in a permeation module with silicone O-rings.
The feed gases were fed to the top side of the membrane, and sweep gas was fed on the permeate side to keep the concentration of permeating gas low providing a driving force for permeation. Before gas permeation, the as-synthesized ZIF-95 membrane was on-stream activated to remove guest DMF at 325 °C with a heating rate of 0.2 °C min⁻¹ by using an equimolar H₂-CO₂ mixture in the Wicke-Kallenbach permeation apparatus (Figure S2). The activation is completed at 325 °C for 24 h. and then before measurements of every single gas permeation and mixture separation, the membrane was in-situ heated at 325°C for 24 h under sweep gas to remove the adsorbed CO₂. The sweep gas N₂ (except for the N₂ permeation measurement where CH₄ was used as sweep gas) was fed on the permeate side to keep the concentration of permeating gas as low as possible thus providing a driving force for permeation. On both sides of the membranes was atmospheric pressure. The fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromatograph (HP6890) was used to measure the gas concentrations, as shown in Figure S2. The separation factor \( \alpha_{i,j} \) of a binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i, j) in the retentate, as show in Eq. 1.

\[
\alpha_{i,j} = \frac{y_{i,Perm} / y_{j,Perm}}{y_{i,Ret} / y_{j,Ret}}
\]

Simulation Models and Methods: The adsorption of H₂/CO₂ mixture in ZIF-95 was examined by molecular simulation. The model structure of ZIF-95 was adopted from experimentally determined X-ray crystallographic data. To estimate the charges of ZIF-95 framework atoms, a fragmental cluster (Figure S1E) was cleaved and saturated by lithium. The electrostatic potentials around the cluster were calculated by density-functional theory (DFT). It has been widely recognized that first-principles derived charges fluctuate appreciably when a small basis set is used; however, they tend to converge beyond 6-31G(d) basis set. Consequently, 6-31G(d) basis set was used in the DFT calculation for all the atoms except Zn metals, for which LANL2DZ basis set was used with effective pseudopotentials. The DFT calculation used the Lee-Yang-Parr correlation functional (B3LYP) and was carried out with Gaussian 03. The
concept of atomic charges is solely an approximation and no unique straightforward method is currently available to rigorously determine atomic charges. In this study, the atomic charges were estimated by fitting to the electrostatic potential using the CHelpG scheme. 

![Figure S1E](image)

**Figure S1E.** A fragmental cluster of ZIF-95 used to calculate atomic charges. The dangling bonds connected to N were saturated by Li. Color code: Zn, pink; N, blue; C, grey; H, white; Cl, green.

The adsorption isotherms of CO$_2$, CH$_4$ and N$_2$ in ZIF-95 were predicted and compared with available experimental data. CO$_2$ was represented as a three-site molecule and its intrinsic quadrupole moment was described by a partial-charge model. A united-atom model was used for CH$_4$ with the Lennard-Jones (LJ) potential parameters from the TraPPE force field. N$_2$ was mimicked by two-site models with a bond length of 1.10 Å. The dispersion interactions of the framework atoms in ZIF-95 were represented by the universal force field (UFF). Similar to recent studies, the well depths of the framework atoms were scaled by a factor (0.6). The cross LJ interaction parameters between ZIF-95 and adsorbates were evaluated by the Lorentz-Berthelot combining rules. As shown in Figure S5, the predicted isotherms of CO$_2$, CH$_4$ and N$_2$ match well with experimental data.
References


Fig. S1. Scheme of the fabrication of ZIF-95 molecular sieve membrane as carbon dioxide captor for H$_2$/CO$_2$ separation.
Figure S2. SEM images of the ZIF-95 membrane prepared on the APTES-modified asymmetric macroporous $\alpha$-Al$_2$O$_3$ disk: (a-c) top views, (d) cross-section. The circle in (c) indicates the “folded filters” structure.
Figure S3

Fig. S3. SEM image of the ZIF-95 layer prepared on the non-APTES-modified Al₂O₃ support.
**Figure S4**

**Legend:**

**MFC:** mass flow controller  
**PC:** permeation cell with mounted membrane  
**GC:** gas chromatograph  
**f:** volumetric flow rate  
**p:** pressure

Fig. S4. Measurement equipment for both single and mixed gas permeation.
Figure S5

Fig. S5. The comparison of the experimental and simulated adsorption isotherms of CO$_2$, CH$_4$ and N$_2$ in ZIF-95 at 25 °C.
Fig. S6. The simulated adsorption isotherms of equimolar H$_2$/CO$_2$ mixture in ZIF-95 at 25 °C.
Fig. S7. Mixed gas permeances and H$_2$/CO$_2$ selectivity of the ZIF-95 membrane as function of the operating temperatures at 1 bar.
Figure S8

**Fig. S8.** The adsorption isotherms of CO₂ in ZIF-95 as function of the operating temperature.
Fig. S9. Mixed gas permeances and H$_2$/CO$_2$ selectivity of the ZIF-95 membrane as function of the operating time at 325 °C and 1 bar.
Fig. S10. XRD patterns of the as-prepared ZIF-95 membrane prepared on the APTES-modified α-Al₂O₃ support (a), and the spent ZIF-95 membrane after the measurement of gas separation at 325 °C. (●): Al₂O₃ support, (not marked): ZIF-95.
**Fig. S11.** Hydrothermal stability measurement of the ZIF-95 membrane for the separation of an equimolar H$_2$/CO$_2$ mixture with adding of 3 mol% steam at 325 °C.
Table S1 Single and mixed gases permeances (mol/m²·s·Pa⁻¹) and separation factors for the ZIF-95 membrane at 325 °C and 1 bar with 1:1 binary mixtures of H₂ with CO₂, N₂, CH₄ and C₃H₈.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Knudsen constant</th>
<th>Permeances(i) (mol/m²·s·Pa⁻¹)</th>
<th>Permeances(j) (mol/m²·s·Pa⁻¹)</th>
<th>Ideal Separation factor</th>
<th>Permeances(i) (mol/m²·s·Pa⁻¹)</th>
<th>Permeances(j) (mol/m²·s·Pa⁻¹)</th>
<th>Separation factor</th>
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<tr>
<td>H₂/CO₂</td>
<td>4.7</td>
<td>2.46 x 10⁻⁶</td>
<td>7.04 x 10⁻⁸</td>
<td>34.9</td>
<td>1.95 x 10⁻⁶</td>
<td>7.59 x 10⁻⁸</td>
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<td>H₂/N₂</td>
<td>3.7</td>
<td>2.46 x 10⁻⁶</td>
<td>2.27 x 10⁻⁷</td>
<td>10.8</td>
<td>2.18 x 10⁻⁶</td>
<td>2.16 x 10⁻⁷</td>
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<td>H₂/CH₄</td>
<td>2.8</td>
<td>2.46 x 10⁻⁶</td>
<td>1.61 x 10⁻⁷</td>
<td>15.3</td>
<td>2.04 x 10⁻⁶</td>
<td>1.85 x 10⁻⁷</td>
<td>11.0</td>
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<tr>
<td>H₂/C₃H₈</td>
<td>4.7</td>
<td>2.46 x 10⁻⁶</td>
<td>3.69 x 10⁻⁸</td>
<td>66.8</td>
<td>1.93 x 10⁻⁶</td>
<td>3.23 x 10⁻⁸</td>
<td>59.7</td>
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Table S2. Comparison of H₂/CO₂ selectivity versus H₂ permeability for ZIF-95 membrane with the previously reported MOF membranes.

<table>
<thead>
<tr>
<th>ZIF membranes</th>
<th>Pore size (nm)</th>
<th>Thickness (µm)</th>
<th>H₂ permeances (mol/m²·S·Pa⁻¹)</th>
<th>H₂ permeability* (Barrers)</th>
<th>H₂/CO₂ selectivity</th>
<th>References</th>
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<tr>
<td>ZIF-7</td>
<td>0.30</td>
<td>1.5</td>
<td>7.71 x 10⁻⁸</td>
<td>345</td>
<td>6.48</td>
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<td>ZIF-8</td>
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<td>5412</td>
<td>4.54</td>
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<td>ZIF-22</td>
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<td>40</td>
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<td>19832</td>
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<td>ZIF-69</td>
<td>0.44</td>
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<td>6.50 x 10⁻⁸</td>
<td>9707</td>
<td>2.7</td>
<td>4</td>
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<td>ZIF-90</td>
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<td>2.37 x 10⁻⁷</td>
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<td>7.3</td>
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<td>MIL-53</td>
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<td>5.01 x 10⁻⁷</td>
<td>11971</td>
<td>6.8</td>
<td>6</td>
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<td>KUUST-1</td>
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<td>ZIF-95</td>
<td>0.37</td>
<td>30</td>
<td>1.95 x 10⁻⁶</td>
<td>174732</td>
<td>25.7</td>
<td>This study</td>
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*Permeability is calculated as the membrane permeance multiplied by the membrane thickness. 1 Barrer = 3.348 x 10⁻¹⁶ mol m⁻² s⁻¹ Pa⁻¹.

Reference


**Table S3.** Separation performances of ZIF-95 membranes for the separation of H₂/CO₂ mixtures at 25 ºC and 1 bar.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>H₂ permeance (mol·m⁻²·s⁻¹·Pa⁻¹)</th>
<th>CO₂ permeance (mol·m⁻²·s⁻¹·Pa⁻¹)</th>
<th>H₂/CO₂ selectivity</th>
<th>Average selectivity</th>
<th>standard deviation of selectivity</th>
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<tr>
<td>M1</td>
<td>5.05 x 10⁻⁷</td>
<td>5.96 x 10⁻⁸</td>
<td>8.48</td>
<td>8.49</td>
<td>0.065</td>
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<td>M2</td>
<td>4.96 x 10⁻⁷</td>
<td>5.81 x 10⁻⁸</td>
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<tr>
<td>M3</td>
<td>5.11 x 10⁻⁷</td>
<td>6.05 x 10⁻³</td>
<td>8.45</td>
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