Supporting information for
Deposition of chemical modified α-Al₂O₃ particles for high performance ZIF-8 membrane on a macroporous tube

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Contents

1. Experimental details.
2. Syntheses and Characterizations.
3. Results and Discussions.
4. Reference.

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1. Experimental details:

Materials:
Chemicals were used as received: zinc nitrate hexahydrate (>99%, Sinopharm Chemical Reagent Co., Ltd), 2-methylimidazole (Hmim, >99%, Rizhao Leadersh chemical Co., LT), 3-aminopropyltriethoxysilane (APTES, 98%, J&K Scientific Ltd.), α-Al₂O₃ particles (0.5μm, Dalian Luminglight Co., Ltd.). Porous α-Al₂O₃ tubes (Foshan Ceramics Research Institute of China: 13mm o.d., 9mm i.d., a nominal pore size of 3μm and porosity of 30–40%) were used as supports.

APTES modification on the α-Al₂O₃ particle surface:
5g α-Al₂O₃ particles having a particle size ranging from 0.5μm to 0.6μm were treated with 4ml APTES in 150ml toluene at 120°C for 24h under N₂ conditions, leading to APTES monolayer deposited on the α-Al₂O₃ particle surface.

Deposition of APTES-modified α-Al₂O₃ particles onto the tubular support:
Water suspension containing 3wt.% APTES-modified α-Al₂O₃ particles or APTES-free α-Al₂O₃ particles was used as coating solution respectively for the deposition of α-Al₂O₃ particle onto the support. Before hot dip-coating, the supports were calcined at 550°C for 6h and cooled down to room temperature for use with controlled heating and cooling rates of 2°C/min respectively. The hot dip-coating of α-Al₂O₃ particles onto the outer surface of the support was carried out by directly dipping the preheated support at 150°C oven into the coating solution for 20s followed by drying at 50°C overnight.

Counter diffusion synthesis of ZIF-8 membrane: (Fig. 1S)
0.146g of 2-methylimidazole (Hmim) solution dissolved in 25ml of methanol (solution A) and was supplied from the outer volume of the support, 0.066g of Zn(NO₃)₂⋅6H₂O dissolved in 4ml of methanol (solution B) was supplied from the inner volume of the support. The pre-treated support with one end sealed by Teflon cap was put vertically into a Teflon lined stainless steel autoclave along the wall followed by filling with solution A (about 18ml), the level of solution A should not exceed the top of the support at this moment. Immediately, solution B was filled into the inner volume of the support from the unsealed end, followed by sealing this end with Teflon cap and adding the rest A solution (about 7 mL) again to exceed the top of the support. The crystallization reaction was carried out at 150°C for 5h and the membrane was washed with pure methanol then dried in vacuum oven.
Figure 1S Schematic diagram of diffusion cell for ZIF-8 membrane preparation
2. Characterization

Scanning electron microscopy (SEM) images of the surfaces of membranes were taken with a KYKY2800B microscope at an acceleration voltage of 15 kV and a working distance of 10 mm after gold coating. X-ray diffraction (XRD) patterns were collected on a Philips Analytical X-ray diffractometer using Cu Kα radiation (30 mA and 40 kV).

The gas permeation properties of the ZIF-8 membranes was investigated using single gases of H₂ (0.289 nm), CO₂ (0.33 nm) and N₂ (0.364 nm) in a permeation set up as shown in Figure 2S. The values in brackets are the kinetic diameters of the various gases, respectively. The membrane was placed in a home-made stainless steel module with a cylindrical geometry. Rubber gaskets were used as sealing between the membrane and the module. The feed stream was pressurized, while downstream pressure was maintained at atmospheric pressure. The pressure difference through the membrane was maintained at 0.05MPa in the single gas permeation test. Before the measurement of each gas species, the permeation apparatus was purged with the respective gas to avoid the disturbance from previous gas permeation during measurements. The permeance \( P_i \) for the permeating gas \( i \) is defined as:

\[
P_i = \frac{N_i}{\Delta P_i A},
\]

where \( N_i \) is the permeating flux of component \( i \) (mol/s), \( \Delta P_i \) is the transmembrane pressure difference of component \( i \) (Pa), and \( A \) is the membrane area (m²). The separation factor \( a_{ij} \) is defined as the ratio of the permeance \( P_i \) and \( P_j \):

\[
a_{ij} = \frac{P_i}{P_j}.
\]

Figure 2S Schematic diagram of the gas permeation apparatus. (1) Feed gas cylinder, (2) filter, (3) mass flow controller, (4) non-return valve, (5) shut-down valve, (6) pressure gauge, (7) back pressure regulator, (8) permeation cell, (9) soap bubble film flow meter and (10) gas chromatograph.
3. Results and Discussions

3.1 Calculation of the surface areas of the Al₂O₃ particles deposited on the support and the corresponding tubular support covered by Al₂O₃ particles:

Models:

**Al₂O₃ particle:**
Model assumes the particle geometry is sphere. Weight of the deposited Al₂O₃ particle: particle radium, \( r = 250 \text{ nm} \), \( m = 0.007 \text{ g} \), the density of the \( \rho = 3.9 \text{ g·cm}^{-3} \).

\[
S_1 = \frac{3m}{\rho r} = \frac{3 \times 0.007 \text{ g}}{3.9 \text{ g·cm}^{-3} \times 2.5 \times 10^{-5} \text{ cm}} = 215.39 \text{ cm}^2
\]

**the tubular support:**
Model assumes the pore is sphere. Aperture : \( r = 1 \times 10^{-4} \text{ m} = 9.521 \text{ g} \), \( \varepsilon = 0.35 \).

\[
S_2 = \frac{2\pi l [\left(\frac{r_1}{2}\right)^2 - \left(\frac{r_2}{2} - d\right)^2]}{\ln r}
= 2 \times 0.3 \times 3.14 \times 5 \text{ cm} \times \left[\left(\frac{1.3 \text{ cm}}{2}\right)^2 - \left(\frac{1.3 \text{ cm}}{2} - 0.0002 \text{ cm}\right)^2\right]
= 28.56 \text{ cm}^2
\]
3.2 SEM images of the Al₂O₃ support and ZIF-8 membranes on the bare support or the pretreated Al₂O₃ support by deposition of APTES-free Al₂O₃ particles:

**Figure 3S.** SEM images of a tubular porous Al₂O₃ support without any modification. (left: surface view; right: cross section)

**Figure 4S.** SEM images of ZIF-8 membrane on the pretreated support by deposition of APTES-free Al₂O₃ particles (left: surface view; right: cross section)

**Figure 5S.** SEM images of ZIF-8 membrane on the bare Al₂O₃ support without any modification (left: surface view; right: cross section)
3.3 Table S1: Comparison of separation performance of the obtained ZIF-8 membrane in this study for H\textsubscript{2}/N\textsubscript{2} and H\textsubscript{2}/CO\textsubscript{2} systems with other porous H\textsubscript{2} separation membranes reported.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore size (nm)</th>
<th>Gas separation performance</th>
<th>H\textsubscript{2} CO\textsubscript{2} permeance [molm\textsuperscript{-2}s\textsuperscript{-1}Pa\textsuperscript{-1}]</th>
<th>reference</th>
<th>Separation index [c]</th>
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<tr>
<td>Zeolite X</td>
<td>0.74</td>
<td>4.5</td>
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<td>Silicate-1</td>
<td>0.55</td>
<td>1.84</td>
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<td>ZSM-5</td>
<td>0.55</td>
<td>-</td>
<td>9.3×10\textsuperscript{13}</td>
<td>[6s]</td>
<td>- 1.35×10\textsuperscript{-6}</td>
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<tr>
<td>Matrix AlPO\textsubscript{4}</td>
<td>-</td>
<td>9.7</td>
<td>1.1×10\textsuperscript{-7}</td>
<td>[7s]</td>
<td>0.00096 -</td>
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<td>SAPO-34</td>
<td>0.38</td>
<td>1.3</td>
<td>3.0×10\textsuperscript{-8}</td>
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<td>LTA AlPO\textsubscript{4}</td>
<td>0.4</td>
<td>7.6</td>
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<td>NaA</td>
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<td>- 14.4</td>
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<td>Silica 0.38-0.55</td>
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<td>[12s]</td>
<td>1.3 12.6</td>
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<td>-</td>
<td>100\textsuperscript{[a]}</td>
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<td>[13s]</td>
<td>- 0.442-0.883</td>
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<td>Silica (CVD)</td>
<td>--</td>
<td>--</td>
<td>1000</td>
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<td>CMS</td>
<td>--</td>
<td>45</td>
<td>2.0×10\textsuperscript{-6}</td>
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<tr>
<td>Pd</td>
<td>-</td>
<td>∞</td>
<td>3.3×10\textsuperscript{-6}</td>
<td>[16s]</td>
<td>- ∞</td>
</tr>
<tr>
<td>Pd</td>
<td>-</td>
<td>&gt;70000</td>
<td>8.4×10\textsuperscript{-6}</td>
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<td>11.6\textsuperscript{[a]}</td>
<td>[5a]</td>
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<td>15.44\textsuperscript{[a]}</td>
<td>This work</td>
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</table>

[a] Ideal separation factor. [b] Knudsen diffusion. [c]: $\pi = (P_{H2} \times (selectivity-1)) \times$ permeate pressure.
4. Reference:


16s. Z. Zhang, C. Salem, R.S. Magliozzo and J.F. Rusling, *Chem. Commun.*, 2001, **177**.