

**Supporting information for**

**Enhanced hybrid membrane of ZIF-8 and zeolite T for CO<sub>2</sub>/CH<sub>4</sub> separation**

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## 1. Experimental Details

### **Materials:**

Chemicals used: Zinc chloride ( $\text{ZnCl}_2$ , Sigma Aldrich), 2-Methyl-imidazole ( $\text{C}_4\text{H}_6\text{N}_2$ , Sigma Aldrich), Sodium formate ( $\text{NaCOOH}$ , Sigma Aldrich), Methanol ( $\text{CH}_3\text{OH}$ , R&M Chemicals), fumed silica ( $\text{SiO}_2$ , Sigma Aldrich), sodium aluminate ( $\text{NaAlO}_2$ , Sigma Aldrich), sodium hydroxide ( $\text{NaOH}$ , Merck), and potassium hydroxide ( $\text{KOH}$ , Merck). Laboratory made porous  $\alpha\text{-Al}_2\text{O}_3$  disc with diameter of 25mm and thickness of 3mm and 30-40% porosity were used as membrane supports.

### ***Vacuum Thermal Seeding and Secondary Growth of ZIF-8 membrane***

Seeding precursor was prepared by dissolving zinc chloride (0.75g), 2-methyl-imidazole (2.60g), and sodium formate (1.50g) in 40mL of methanol solution. The final solution of the seeding precursor displayed molar ratio of  $1\text{ZnCl}_2:5.8\text{Hmim}(2\text{-methyl-imidazole}):4\text{HCOONa}$  (sodium formate):180Methanol. Prior to vacuum thermal seeding, the  $\alpha\text{-Al}_2\text{O}_3$  support was heated in furnace at  $250^\circ\text{C}$  for 30 minutes. This was followed by a quick transfer of the  $\alpha\text{-Al}_2\text{O}_3$  supports ( $\sim 230^\circ\text{C}$ ) to the vacuum suction apparatus where the seeds precursor was dropped on the hot  $\alpha\text{-Al}_2\text{O}_3$  supports under vacuum suction. The seeded  $\alpha\text{-Al}_2\text{O}_3$  support was returned to the furnace ( $250^\circ\text{C}$ ) for another 15 minutes. "Vacuum thermal seeding" process was repeated three times to completely cover the  $\alpha\text{-Al}_2\text{O}_3$  support surface with seeds precursor.

Precursor solution for secondary growth of ZIF-8 membrane was prepared by dissolving zinc chloride (1.5g), 2-methyl-imidazole (5.20g), and sodium formate (3.0g) in 80mL of methanol with molar ratio of  $1\text{ZnCl}_2:5.8\text{Hmim}:4\text{HCOONa}:180\text{Methanol}$ . The vacuum thermal seeded support was then placed in the Teflon cup with the precursor solution. After hydrothermal synthesis at  $110^\circ\text{C}$  for 6 hours, the autoclave was cooled down naturally to room temperature and the collected membrane was washed thoroughly with excess amount of methanol.

### ***Preparation of Zeolite T membrane***

Zeolite T seed precursor were prepared by dissolving corresponding amount of fumed silica, sodium aluminate, sodium hydroxide, and potassium hydroxide in de-ionized water with molar composition of  $1\text{SiO}_2:0.04\text{Al}_2\text{O}_3:0.26\text{Na}_2\text{O}:0.09\text{K}_2\text{O}:14\text{H}_2\text{O}$ . The mixture was stirred for 3 hours followed by aging overnight until a homogeneous precursor was obtained. This was followed by hydrothermal synthesis of the precursor solution at  $110^\circ\text{C}$  for 30 hours. The hydrothermal precursor was then collected and subjected to several repetitions of centrifugation with washing steps. The recovered seed were then dried and further grinded to form fine zeolite T seed powders. Zeolite T seed powders were then seeded on the  $\alpha\text{-Al}_2\text{O}_3$  support *via* dip coating. The seeded  $\alpha\text{-Al}_2\text{O}_3$  support was then brought into contact with the zeolite T precursor solution ( $1\text{SiO}_2:0.04\text{Al}_2\text{O}_3:0.26\text{Na}_2\text{O}:0.09\text{K}_2\text{O}:14\text{H}_2\text{O}$ ) followed by hydrothermal synthesis at  $110^\circ\text{C}$  for 45 hours. The collected membrane was washed with a copious amount of de-ionized water.

### ***Hybrid Membrane Preparation***

The hybrid membrane was prepared by fabricating zeolite T on the ZIF-8 membrane. Initially, vacuum thermal seeding were performed on the  $\alpha\text{-Al}_2\text{O}_3$  support followed by secondary growth of ZIF-8 membrane. Then, zeolite T seeds were deposited on the  $\alpha\text{-Al}_2\text{O}_3$  supported

ZIF-8 membrane *via* simple dip coating. Zeolite T membrane was synthesized through secondary growth on the ZIF-8 membrane forming a hybrid structure.

## 2. Characterizations

Field Emission Scanning Electron Microscopy (FESEM) images of the surface morphology and cross sectional area of membranes were taken with Hitachi SU8010. X-ray diffraction (XRD) patterns were collected on a D8 Advance X-Ray Diffractometer Bruker AXS using Cu K $\alpha$  monochromatized radiation.

### 2.1 CO<sub>2</sub> and CH<sub>4</sub> gas separation experiment

Binary and single gas separation testing was performed using a setup built in-house as shown in Figure 1. The prepared membrane was mounted in a custom-made stainless steel module with the membrane facing the high pressure side. Rubber gaskets were used as sealing material between the membrane and the module. The feed stream was pressurized, while downstream pressure was maintained at atmospheric pressure. 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 measurement was started when the permeate flow rates were considered to attain a steady state where it reached a constant value. CO<sub>2</sub> and CH<sub>4</sub> with a purity of 99.99% from Mox-Linde were used as the feed gases.

#### 2.1.1 Single gas permeation

Single gas permeation of the membranes were measured through the dead-end mode. The gas permeation properties of the prepared membranes was investigated using single gases of CO<sub>2</sub> (0.33nm) and CH<sub>4</sub> (0.38nm). The values in brackets are the kinetic diameters of the CO<sub>2</sub> and CH<sub>4</sub> gases, respectively. The gas permeances of the membranes were measured by a bubble flow meter. The permeance  $P_i$  for the permeating gas is defined in equation (1).

$$P_i = \frac{m}{M_w \Delta P A} \quad (1)$$

where  $m$  is the mass flow rate of permeated gas (kg/s),  $M_w$  is the molecular weight of permeated gas (kg/kmol),  $\Delta P$  is the pressure difference between the permeate and feed (Pa) and  $A$  is the effective membrane area (m<sup>2</sup>). The CO<sub>2</sub>/CH<sub>4</sub> selectivity was calculated by dividing the single gas permeance of CO<sub>2</sub> to single gas permeance of CH<sub>4</sub> as shown in equation (2).

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

where  $P_{CO_2}$  and  $P_{CH_4}$  are the gas permeances of CO<sub>2</sub> and CH<sub>4</sub>, respectively.

#### 2.1.2 Binary gas permeation

The feed gas flow rates are controlled by two different mass flow controllers (Brooks Instruments) to mix the gases in equimolar ratios. The feed and permeate streams were analyzed with a Agilent 7890A gas chromatograph. Separation measurements were conducted with 1:1 CO<sub>2</sub>/CH<sub>4</sub> gas mixtures with 100 sccm total feed flow. Mechanical feed

pressure up to 4 bar were used while maintaining the mechanical permeate pressure at 1 bar. The separation factor  $\alpha_{CO_2/CH_4}$  for binary gas mixture is defined in equation (3).

$$\alpha_{CO_2/CH_4} = \frac{y_{CO_2}/y_{CH_4}}{X_{CO_2}/X_{CH_4}} \quad (3)$$

where Y and X are the concentrations of CO<sub>2</sub> and CH<sub>4</sub> components in the permeate and retentate sides, respectively.

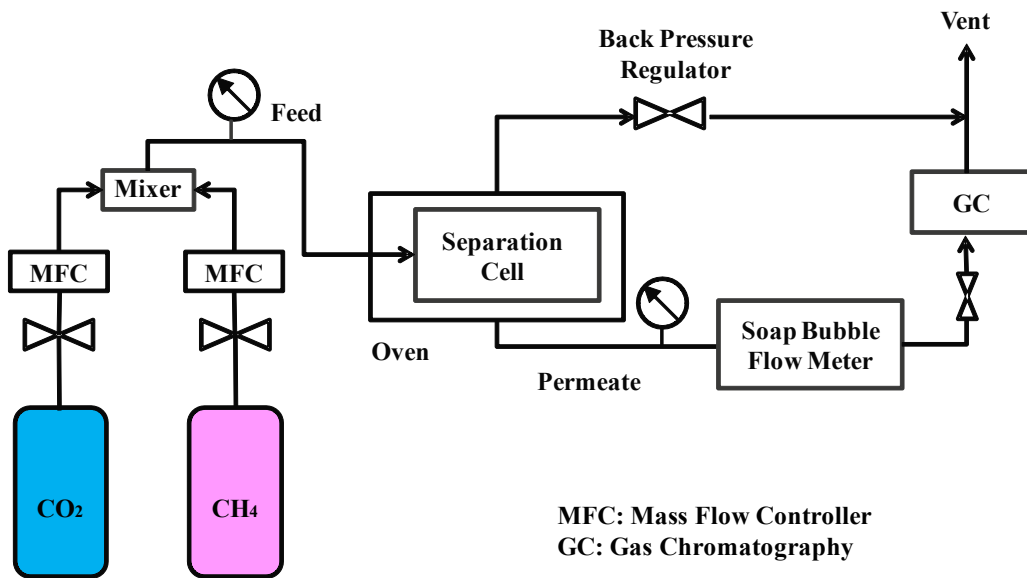


Figure 1 Gas permeation rig set-up for CO<sub>2</sub> and CH<sub>4</sub> separation.