Electronic Supplementary Information

Recovery of Xenon from Air over ZIF-8 Membranes

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Materials and Methods

1. Membrane Synthesis

1.1 Preparation of membrane solution

ZIF-8 membranes were prepared with the method derived from our previous study. [1] Two solutions were used for the membrane synthesis gel. Solution A contained 0.2 g of zinc chloride (Acros, 97%) and 0.3 g of sodium formate (Sigma, > 99%) dissolved in 10 g of methanol (Fisher scientific, 99.9%). Solution B contianed 0.96 g of 2-methylimidazole (Sigma-Aldrich, 99%) dissolved in 10 g of methanol. Each solution was stirred separately for 15 minutes at room temperature. Then both solutions were mixed and stirred for an extra 30 minutes.

1.2 ZIF-8 membranes fabrication

Asymmetric porous alumina tubes (Inopor GmbH) were used as supports for ZIF-8 membrane growth in this study, which have an inside diameter of 0.7 cm and an outside diameter of 1.1 cm with a pore size of 100 nm. Teflon tape was wrapped around the outer surface of the support to prevent membrane growth on the external surface. The support's effective permeation area was ~7.5 cm^2. The support was placed with the gel in a stainless steel autoclave (4713 General Purpose Pressure Vessel, 45 mL, Parr Instrument) and solvothermally treated in a conventional oven at 120 °C for 3, 4, and 10 hours.

The autoclave was heated at a rate of 25 ˚C/min and cooled at a rate of 0.5 ˚C /min during and after the solvothermal treatment. The support was removed and the teflon tape unwrapped after solvothermal treatment. The support was then washed with methanol. To activate, the resulting 1-layered membrane was immersed in 25 mL of methanol for 1 day. A second and third (if needed) layer and a third layer (if needed) were applied following the aforementioned process. The membranes were stored at ~ 80 °C before gas permeation testing. Table S1 shows the detailed synthesis conditions for the membranes reported in Table 1.

For the 1-layered M1 membrane, a healing process was conducted between the first and the second layer. The method was slightly modified from previous study. [2] The membrane was wrapped with Teflon tape and transferred to a Teflon liner with a ligand solution composed of 2.27 g of 2-methyimidazole in 20 mL of D.I. water, where it remained for 1 hour to saturate the support. A solution containing 0.11 g of zinc nitrate hexahydrate (Sigma, ≥99.0% KT) in 20 mL of D.I. water was added to the liner. For the final healing process, the liner was placed in an oven at 30 °C for 6 h. The healed membrane was washed in methanol and stirred for 3 days and dried at 60 °C for 6 h. Then the second layer was added to them membrane at 120 C for 3 hours.

Table S1. General synthesis conditions of ZIF-8 membranes of this study

Membrane ID	Number of layers	General synthesis conditions
M1	2	1st layer: 120˚C for 10 hours Healing process was conducted 2nd layer: 120˚C for 3 hours
M2	2	1st layer: 120˚C for 10 hours 2nd layer: 120˚C for 4 hours
M3	3	1st layer: 120˚C for 10 hours 2nd layer: 120˚C for 4 hours 3nd layer: 120˚C for 3 hours

2. Characterization

2.1 Powder X-Ray Diffraction

ZIF-8 crystal powder, synthesized with the same process for membrane synthesis, were collected for Powder X-ray diffraction (PXRD) analysis, which was conducted with an X'Pert PRO MPD X-Ray Diffraction System operated at 45 kV and 40 mA with Cu Kα1 radiation (λ=1.54059 Å). ZIF-8 membranes were broken and coated with gold for SEM imaging on a JEOL JSM-7000F scanning electron microscope.
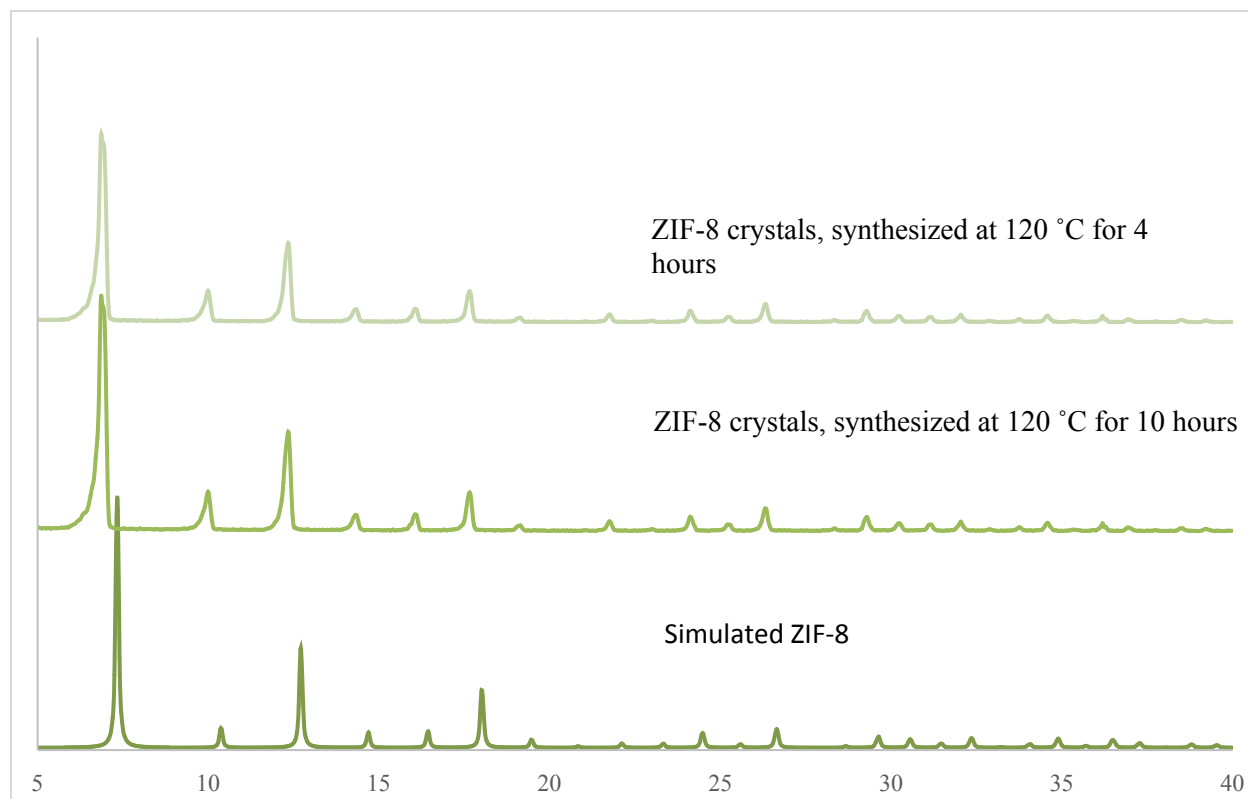
Figure S1. XRD patterns of ZIF-8 powders synthesized using the membrane gel. Simulated ZIF-8 pattern is shown for comparison.

2.2 Gas Permeation Measurement

Gas mixture permeations were measured in a continuous flow system. The membrane was mounted in a stainless steel module and sealed at each end with silicone O-rings. Fluxes were measured using a bubble flow meter. For mixture separation, premixed air (N_2 and O_2)/Xe=90:10 mixture molar composition (General Air, 99.999%) was used as feed gas. The composition of air was 79% N_2 and 21 % O_2. The total feed flow rate was 40 mL/min. The feed pressure was 223 kPa, and the pressure in the permeate side was 85 kPa for a transmembrane pressure of 138 kPa. The compositions of the feed, retentate and permeate streams were measured, after attaining the steady state, using a gas chromatograph (SRI instruments, 8610C) equipped with a thermal conductivity detector and HAYESEP-D packed column. The oven, injector and detector temperatures in the GC were kept at 40 °C, 120 °C and 150 °C, respectively. All selectivities are permselectivities (ratios of permeances). The permeances were calculated as the fluxes divided by the partial pressure driving forces. Because the module has a cross-flow design, a logarithm of the mean partial pressure drop was used to calculate the driving force. Specifically, the permeance of the component *i*, P_i, was calculated using:

$$P_i = \frac{J_i}{\Delta p_{\ln,i}} \tag{1}$$

where J_i is the flux through the membrane for component *i*. For the cross-flow configuration, one component preferentially permeates through the membrane, so the partial pressures in the feed and retentate sides are quite different. Therefore, a log-mean pressure drop, $\Delta p_{\ln,i}$, was calculated by:

$$\Delta p_{\ln,i} = \frac{(p_{f,i} - p_{r,i})}{\ln[(p_{f,i} - p_{p,i})/(p_{r,i} - p_{p,i})]} \tag{2}$$

where $p_{f,i}$, $p_{r,i}$, and $p_{p,i}$ are partial pressures for component *i,* in feed, retentate, and permeate sides, respectively. The permeability is defined as the permeance multiplied by membrane thickness. The separation selectivity, $\alpha_{i/j}^{sep}$, is the ratio of the permeances of components *i* and *j* in the mixture.

Effective diffusion coefficients for these gases were estimated using Fick's law $= -D\frac{\partial C}{\partial x}$. For the calculation of diffusion coefficients (*D*), the following assumptions were made: ideal gas, steady state, one-dimension gas transport, and constant membrane thicknesses. The molar gas diffusion flux *J* (mol/m²s), was calculated as the permeance of each gas multiplied by the log-mean pressure difference $\Delta p_{\ln,i}$. The gas concentration gradient (∂C in mol/m³) was calculated as the difference in molar concentrations between the gas in the feed side and permeate side. ∂x is membrane thickness. All these parameters were extracted from experimental data.

Table S2. Supporting data of estimated diffusivities for Air/Xe gas mixture over ZIF-8 membranes at room temperature.

Membrane ID	Air concentration gradient (mol/m³)	Air diffusion flux x10⁻³ (mol/m²s)	Diffusivity(air) x10⁻¹⁰ (m²/s)	Xe concentration gradient (mol/m³)	Xe diffusion flux x10⁻⁵ (mol/m²s)	Diffusivity(Xe) x10⁻¹¹ (m²/s)
M1	47.9	3.59	9.73	8.45	6.23	9.59
M2	48.1	4.52	12.2	8.29	7.44	12.6
M3	47.8	4.55	25.7	8.53	11.8	37.4

2.3 Calculation of Isosteric heat of Adsorption (Q_{st}):

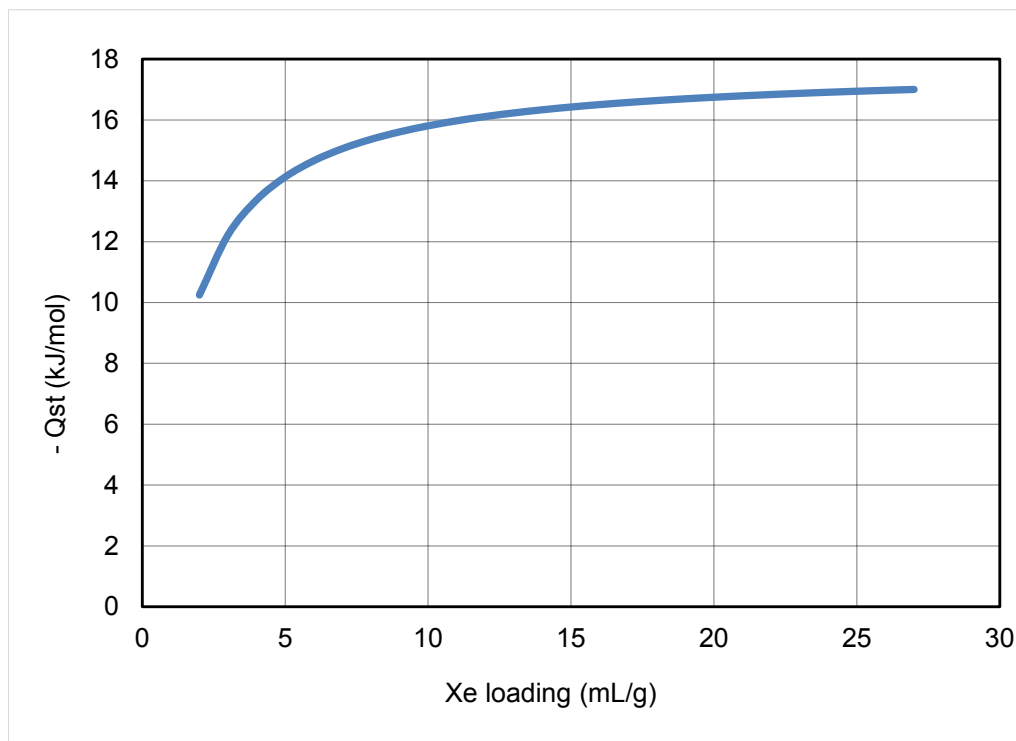The Q_{st} values for Xe and N_2 gases were calculated using Virial method (Figures S2 and S3).

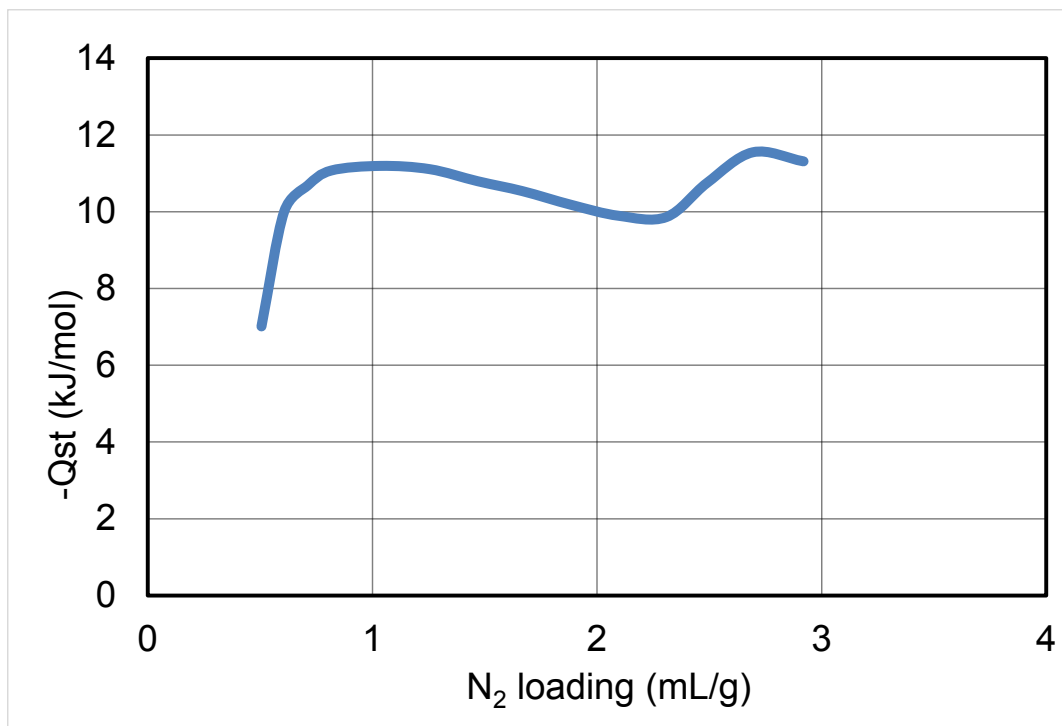**Figure S2.** Xe isosteric heat of adsorption (-Qst) for ZIF-8 calculated by Virial method.

Figure S3. N_2 isosteric heat of adsorption (-Qst) for ZIF-8 calculated by Virial method.

3.0 References

[1] T. Wu, X. Feng, S. K. Elsaidi, P. K. Thallapally, M. A. Carreon, *Ind. Eng. Chem. Res.* **2017**, *56*, 1682–1686

[2] H. T. Kwon, H.–K. Jeong *J. Am. Chem. Soc.* **2013**, *135*, 10763– 10768