Supplementary Information

Confined flexibility release enabled non-equilibrium stage in mixed-matrix membranes: unprecedented selectivity for olefin/paraffin deep separation

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1. Experimental Methods

1.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA, Mn=700) and 2, 2-dimethoxy-2phenylacetophenone (DMPA) were obtained from Sigma-Aldrich (China). 2methylimidazole (mIm, 98%) was purchased from Aladdin. Zinc hydroxide (Zn(OH)₂, 99%) was purchased from Tianjin Heowns Biochem Co., Ltd. Methanol (99.9%) and isopropanol (99.9%) were supplied from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

1.2. Synthesis of P-ZIF-8 nanocrystals

In a typical synthesis, Zn(OH)₂ (0.01 mol) and mIm (0.048 mol) were mixed and manually ground in a mortar for about 10 min at room temperature. Then several drops of methanol solution of PEGDA (1.0 mol/L) were added into the above mixture while kept grinding for another 120 min at room temperature. Finally, the resulting powder was washed with methanol and used for membrane fabrication without drying to avoid the aggregation of fillers. The pristine ZIF-8 sample was also synthesized following the same procedure, except that pure methanol instead of PEGDA/methanol solution was added to the mixture after 10 min of grinding.

1.3. Fabrication of ZIF-8/XLPEO membranes

The XLPEO membranes were prepared using the ultraviolet (UV)-induced curing method.^[S1] Typically, the PEGDA precursor was dissolved in isopropanol to form a 50 wt% solution, and 0.1 wt% DMPA photo-initiator was then added into the solution. After being stirred for 1 h, about 0.5 mL of the pre-polymerization solution

was cast between two quartz plates and then exposed to the 302 nm UV light for 60 s at room temperature under air condition in a UVP crosslinker (CL-1000M, Analytik Jena US). The membrane thickness was controlled by spacers and the total radiation energy was 270 mJ/cm². After the curing process, the formed membranes were peeled off from the quartz plate and soaked in isopropanol for 3 days to allow any sol (low molecular weight polymer) to diffuse out of the gels (three-dimensional networks). The membranes were finally vacuum-dried at 60 °C for 3 days. The MMMs were prepared following the same procedure, except for the dispersion of P-ZIF-8 nanoparticles in isopropanol through sonication before the addition of PEGDA. The loadings of the MOFs were calculated as

MOF loading (wt%) =
$$\left[\frac{wt_{MOF}}{wt_{MOF} + wt_{polymer}}\right] \times 100\%$$
 (S1)

1.4. Characterization

Powder X-ray diffraction (PXRD) analyses of the MOF powders and membranes were recorded on a Bruker D2 X-Ray Diffractometer using Cu K α radiation source with a wavelength of 1.54 Å at room temperature. Fourier transform infrared spectroscopy (FTIR) analysis was performed in a Bruker TENSOR II FTIR spectrophotometer. The spectra were collected in the range of 2000-400 cm⁻¹. An attenuated total reflectance (ATR) mode was applied during the measurement of the prepared membranes. The glass transition temperature (T_g) for each membrane was determined using a differential scanning calorimeter (NETZSCH DSC 200 F3 Maia[®]) under nitrogen at a heating and cooling rate of 1 K/min in a temperature range of -100 to 60 °C. To measure the Brunauer-Emmett-Teller (BET) surface area of the MOFs, the samples were degassed overnight at 150 °C and then characterized using nitrogen adsorption at 77 K on an Micrometritics ASAP 2020 automated gas sorption analyzer. Adsorption kinetics profiles of C_3H_6 and C_3H_8 for the pristine ZIF-8 sample and the 60 wt% ZIF-8/XLPEO membrane sample were obtained with a BSD-DVS multistation gravimetry vapor sorption analyzer (BeiShiDe Instrument) at 25 °C. The samples were degassed at 120 °C for 6 h before tests. High-angle annular dark fieldscanning transmission electron microscope (HAADFSTEM) and corresponding energy dispersive spectrometer (EDS) images of the synthesized P-ZIF-8 nanoparticles were captured with a TALOS F200X instrument. High resolution images of the cross-section of the prepared membranes were obtained using a Gemini SEM 500 scanning electron microscope (SEM). The samples were fractured in liquid nitrogen and glued on the sample holder with conductive tape.

1.5. Gas permeation

Mixed gas permeation tests were performed in a custom-built stainless steel permeation cell using the Wicke-Kallenbach technique. A mixture of propylene and propane (50/50 vol%) was used as feed gas to characterize the separation properties of the prepared membranes. The total feed gas flux was 100 mL/min and the transmembrane pressure was controlled at 3 bar with a back pressure valve at the feed side. The component of the permeate gas was on-line analysed by a well-calibrated gas chromatograph with high precision (Agilent 7890) and Helium was used as sweep gas (5 mL/min) to carry the permeate gas into the instrument. For each membrane, at least three different samples were measured to obtain the average permeation data. Gas permeabilities were calculated with the following equation:

$$P_{\text{perm},i} = \frac{l}{\Delta p_i \times A} \times \frac{\mathrm{d}V_i}{\mathrm{d}t} \times 10^{10}$$
(S2)

where $P_{\text{perm},i}$ is the permeability of component *i* (*i* = propylene or propane) in units of Barrer, *l* is the thickness of the membrane (cm), and *A* is the effective permeation area of the samples (cm²). Δp_i and dV_i/dt represent the partial pressure drop (cmHg) and volumetric flow rate (cm³/s) of component *i* through the membrane samples, respectively.

The separation factors for propylene/propane mixture (α) were obtained by

$$\alpha = \frac{y_{C_3H_6}/y_{C_3H_8}}{x_{C_3H_6}/x_{C_3H_8}}$$
(S3)

where $y_{C_3H_6}/y_{C_3H_8}$ and $x_{C_3H_6}/x_{C_3H_8}$ are the mole ratios of propylene to propane in the permeate gas and the feed gas, respectively. It should be mentioned that since the fraction of feed gas that permeates the membrane (i.e. the flow-rate ratio of the permeate gas to the feed gas) in this work was always below 1%, the component of the feed gas is considered the same as the component of the retentate gas, and used in the calculation to simplify the permeation measurements.

2. Computational Methods

In this work, the periodic model of ZIF-8 structure has been constructed from the experimental X-ray powder diffraction (XRD) data collected from the Cambridge Crystallographic Data Centre. The finite size cluster model was built by directly cleaving from the super cell of optimized periodic ZIF-8 structure. To minimize the

boundary effects in the cluster model calculations, the unsaturated nitrogen atoms in the cluster model was saturated with hydrogen atoms. As for the ZIF-8/XLPEO model, six PEGDA fragment were chelated on each Zn atom of the cluster model of ZIF-8.

All DFT calculations were performed using the OUICKSTEP program within the CP2K code with employing mixed Gaussian and planewave basis sets.^[S2] Exchangecorrelation (xc) functional, namely, the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation was used.[S3] The valence electron wavefunction was expanded in a double-zeta basis set with polarization functions^[S4] along with an auxiliary plane wave basis set with an energy cutoff of 360 Ry, and the core electrons were represented with norm-conserving Goedecker-Teter-Hutter pseudopotentials.^{[S5-} ^{S7]} To account for van der Waals (vdW) interactions, the DFT-D3 scheme^[S8] with an empirical damped potential term was added into the energies obtained from exchangecorrelation functional in all calculations. The AIMD simulations were performed in the canonical ensemble (NVT) for ZIF-8 and PEGDA fragment chelated ZIF-8 systems at 300 K. The temperature of the AIMD-simulated systems was controlled using a Nosé thermostat. To mimic the constrain effect of the periodic structure, all of the Zn atoms of the ZIF-8 cluster model were fixed. Production runs were 15 ps long and a time step of 0.5 fs, where the first 3 ps was used for equilibrium and the last 12 ps was used for statistical analysis.

3. Figure and Tables



Fig. S1. (a) XRD patterns, (b) FTIR spectra, (c) N₂ adsorption isotherms at 77 K, and (d) XPS Zn 2p spectra of the synthesized ZIF-8 and P-ZIF-8 nanoparticles. (e) TEM and corresponding EDS images of the synthesized P-ZIF-8 nanoparticles.



Fig. S2. Cross-sectional SEM images of ZIF-8/XLPEO membranes with different filler loadings.



Fig. S3. Permeability and separation factor evolution of XLPEO membranes containing different loadings of filler particles for equimolar C_3H_6/C_3H_8 . Permeation tests were performed at 30 °C.



Fig. S4. Simulated 6MR dihedral swing angle (left) and corresponding aperture size (right) of ZIF-8 and PEGDA fragment chelated ZIF-8 as a function of time from the AIMD trajectories at 300 K.



Fig. S5. Permeability and separation factor evolution of 60 wt% ZIF-8/XLPEO membrane for

equimolar C₃H₆/C₃H₈ under different temperatures.



Fig. S6. Permeability and separation factor evolution of 60 wt% ZIF-8/XLPEO membrane for equimolar C_2H_4/C_2H_6 under different temperatures.

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