Supporting Information

Zr-MOFs incorporated thin film nanocomposite-Pebax 1657 membranes dip coated on polymethylpentyne layer for efficient separation of CO_2/CH_4

Mohammad Mozafari, Reza Abedini, Ahmad Rahimpour*

Department of Chemical Engineering, Babol Noushirvani University of Technology, Shariati
Ave., Babol 4714871167, Iran.

*Corresponding author: ahmadrahimpour@nit.ac.ir (A. Rahimpour)

S1. Experimental section

S1.1. Gas permeation test for PMP support characterization

The gas permeation test has been performed to characterize the PMP support surface parameters including pore size and porosity. The process of gas permeation test is started by passing the nitrogen gas (N_2) through the membrane followed by measuring the gas flow which is permeated and came out from the another side, this measurement was carried out by a soap bubble flow meter. To achieve the structural parameters, conventional gas permeation testing model was utilized (Eq. 1).

$$P = P_P + P_K = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{r_{P,m}\,\varepsilon}{RT\,L_P} + \frac{1}{8\mu}\frac{r_{P,m}^2\,\varepsilon}{RT\,L_P}p \tag{1}$$

$$P = A + Bp \tag{2}$$

where P is the total gas permeance ($mol\,m^{-2}Pa^{-1}s^{-1}$). Gas permeance in flow regimes of Poiseuille and Knudsen were shown by P_P and P_K, respectively ($mol\,m^{-2}Pa^{-1}s^{-1}$). R is the universal gas constant ($8.314\,J\,mol^{-1}K^{-1}$). The absolute temperature is indicated by T (K). M is the gas molecular weight ($kg\,mol^{-1}$). $r_{P,m}$ is the mean pore radius (m). μ is the viscosity of gas ($Pa\,s$), ε is the surface porosity, L_P is the effective pore length (m) and p is the mean pressure (Pa) (calculated by $(\frac{P_u + P_d}{2})$, where P_u is upstream pressure and P_d is downstream pressure). Using plot of P versus p and computing its intercept (A) and slope (B), as well as usnig Eq. 3 and 4, the mean pore size and the effective surface porosity can be determined [1, 2].

$$r_{P,m} = \frac{16B}{3\,A}\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \tag{3}$$

$$\frac{\varepsilon}{L_p} = \frac{8\mu RTB}{r_{P,m}^{2}} \tag{4}$$

The characterization results for PMP support membrane are listed in Table S1.

Table S1. Result of PMP support characterization test.

	PMP support membrane
Mean pore size (nm)	103.1
Effective surface porosity (m^{-1})	68.0
Gas permeation rate @ 1 bar (GPU)	4016

S2. Results and discussion

S2.1. Effect of drying temperature on pure gas permeabilities

The fabricated neat TFC membrane was dried at different temperatures (35, 45 and 55 °C) for 10 h to investigate the drying procedure influence on membrane gas separation performance. The results of gas separation performance of the neat TFC membrane (PP-X) are presented in Fig. S1, which X indicated the temperature of drying process. As can be seen in Fig. 9, the CO_2 and CH_4 permeabilities of membrane dried at 35 °C is a little bit higher than two other membranes dried at 45 and 55 °C , while it has the lower CO_2/CH_4 selectivity compared to the membrane dried at 55 °C. By comparing the separation properties of each membrane, it can be concluded that the PP-55 membrane showed the better gas separation performance.

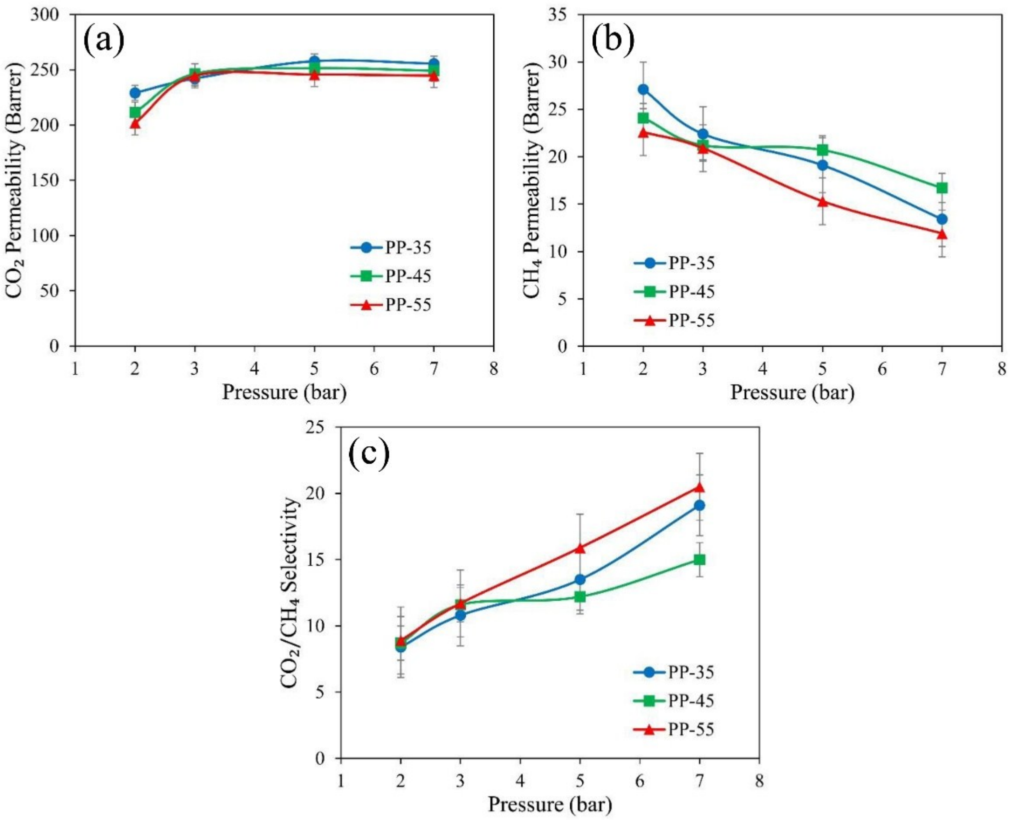

Figure S1. (a) Permeability of CO_2, (b) permeability of CH_4 and (c) CO_2/CH_4 ideal selectivity of neat TFC membrane at different temperature of drying process versus pressure.

S2.2. Effect of feed pressure on mixed gas separation

The result of effect of pressure on the performance of membranes for gas mixture separation is plotted in Fig. S2. The trend of CO_2 permeability and selectivity of membranes for mixed gas was similar to pure gas with considering this fact that the CO_2 permeability and CO_2/CH_4 selectivity for mixed gas were lower than the pure gas CO_2 permeability and ideal selectivity. The efficient performance (CO_2 permeability of 245.3 Barrer and CO_2/CH_4 selectivity of 29.4) was achieved for PPUN-1.5 membrane at pressure of 7 bar.

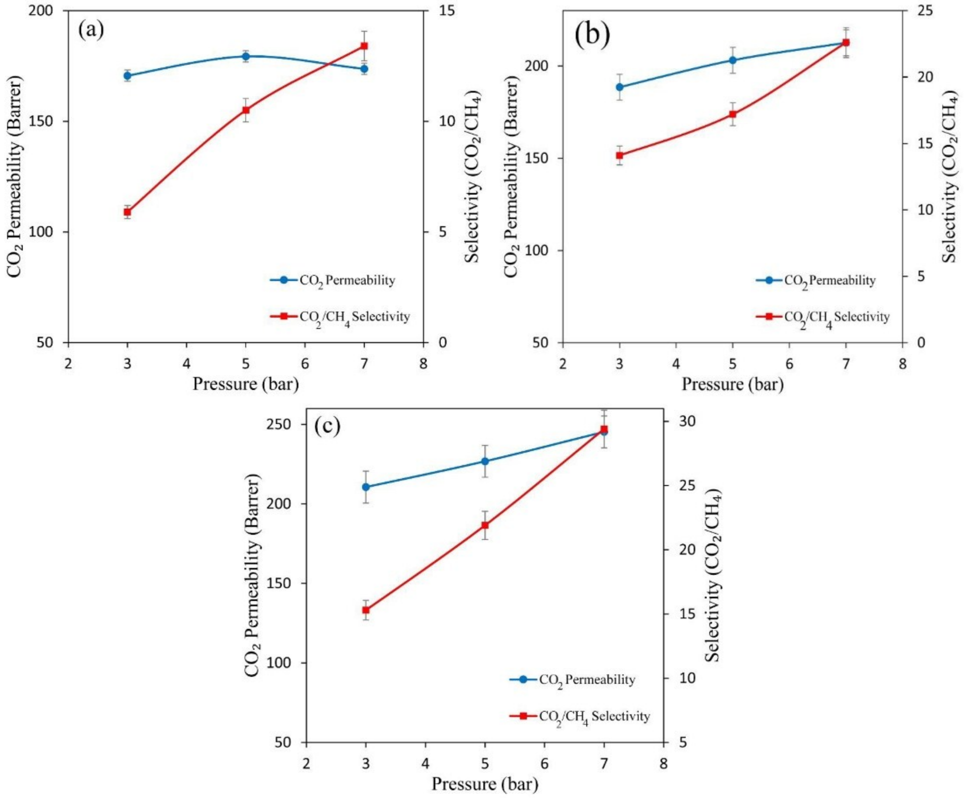

Figure S2. . Effect of pressure on CO_2 permeability and selectivity of mixed gas in TFC and TFN membranes, (a) PP, (b) PPU-2, (c) PPUN-1.5.

Fig. S3 represented the effect of pressure on the mixed gas separation performance of membrane under the humid condition. The effect of pressure on the trend of CO_2 permeability and CO_2/CH_4 selectivity at humid condition was similar to mixed gas permeability and real selectivity at dry condition. The optimum mixed gas separation performance (CO_2 permeability of 278.4 Barrer and CO_2/CH_4 real selectivity of 33.7) was achieved for PPUN-1.5 membranes under humid condition at pressure of 7 bar.

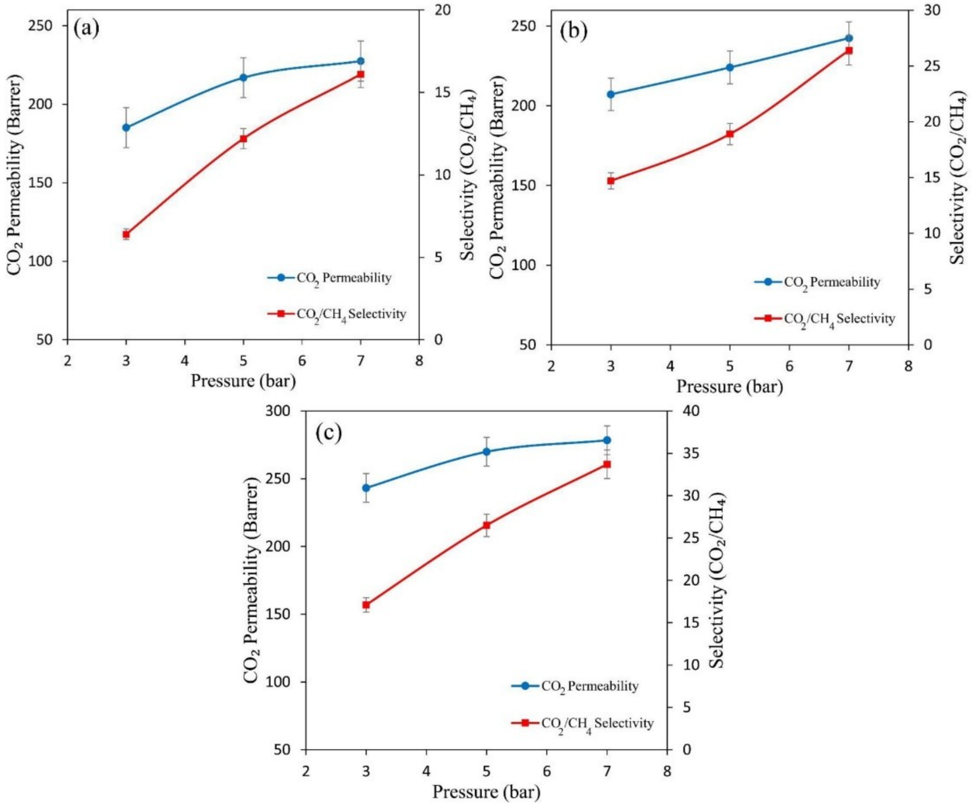

Figure S3. Effect of pressure on CO$_2$ permeability and selectivity in TFC and TFN membranes under humid conditions, (a) PP, (b) PPU-2, (c) PPUN-1.5.

Reference

1. S. Lee, G. Park, G. Amy, S.-K. Hong, S.-H. Moon, D.-H. Lee and J. Cho, *J. Membr. Sci.*, 2002, **201**, 191-201.
2. H. Yasuda and J. Tsai, *J. Appl. Polym. Sci.*, 1974, **18**, 805-819.