The Experimental Verification of Reversed Selectivity for Gas Permeation in Nanoporous Membrane

*Zhou He, Ning Wang, and Kean Wang**
Department of Chemical Engineering, Khalifa University of Science & Technology, PO Box 2533, Abu Dhabi, United Arab Emirate

Abstract

The permeation of binary gas mixtures (H_2/CO_2 , He/CO_2) were measured on a microporous Carbon Molecular Sieve Membrane (CMSM). The transient permeation time lag and steady state permeation fluxes were measured and analyzed. It was found that the interactions (competitive adsorption/diffusion) between different gas molecules play dominant roles in the overall permeation processes, so that the true perm-selectivity/time lag of a binary mixture can be significantly different from the 'ideal' values calculated from the permeation properties of each pure species. Such interactions can even result in the 'reverse selectivity' for the binary mixture of (He/CO_2) [1,2]. For example, as the molar fraction of CO_2 increases from 50% to 75%, the membrane reversed its selectivity from 'He selective' to 'CO_2 selective', constituting an example of CMSM with the so-called 'surface flow selectivity', or the 'reverse selectivity'. This posts a serious challenge (as well as opportunity) for gas separation with membranes (e.g. carbon, zeolite, etc.) in which the adsorption and surface diffusion play important roles. Such phenomena were modeled and analyzed with the famous Maxwell-Stefan Equation.

Introduction

Membrane technology offers great advantages for natural gas (NG) processing. It is compact, easy to install and/or scale-up, and requires minimal resources such as space, energy input, labor and maintenance. These attributes make it particularly attractive in off-shore and remote gas fields[1]. Nowadays, membrane modules for CO_2 removal are commercially available and is the dominant technology in off-shore applications while becoming more competitive in on-shore applications [2]. However, improvements are needed to compete with the current technologies in large-scale, inland NG processing plants. Carbon Molecular Sieve Membrane or CMSM, has unique advantages for NG processing. It is produced from the controlled pyrolysis of polymeric precursors, with rigid graphite microstructure, superior selectivity, and thermal stability. For air (O_2/N_2) separation, the perm-selectivity of CMSM is 10 folds higher than in polymeric membranes at a similar flux [3]. Due to the microporous structural characteristics, a CMSM can separate a gas pair via either 'molecular sieving', which is based on the dimension (diffusion barrier) of different molecules, or 'surface flux selective'. Figure 1 shows the principle of N_2/CH_4 separation based on the two mechanisms. The membrane can be prepared to be selective (more permeable) to either N_2 or CH_4, with the former based on the mechanism of molecular sieving (or size exclusion, Figure 1a) while the later dictated by the surface flow (rate of surface diffusion, Figure 1b).

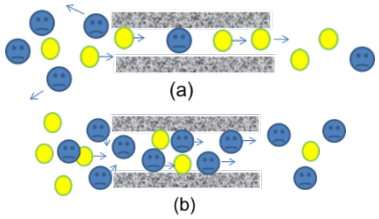

Figure 1 Schematic diagram of two mechanisms: (a) molecular sieving, (b) surface flow.

In this research, the CO_2/He, CO_2/H_2 system were investigated to compare the molecular sieving vs surface flux on a CMSM membrane [4].

Method

The pure gas permeation of the each species and binary mixture were measured on a CMSM 700 (Polyimide precursors pyrolyzed at 700°C), respectively, with a high pressure, improved time-lag device. The rig used a cold trap with liquid N_2 to separate permeates at downstream so that the fluxes and time lags of each components can be measured or calculated. The details of the experiments are given in the references [4,5].

Results and discussion

The permeation of 3 pure gases (He, H_2, and CO_2) were performed on the CMSM, respectively, at 25°C under various upstream permeation pressures (P_0). It is seen in Figure 2 that, the permeabilities of He and H_2 are largely independent of P_0. This is because that He is largely a non-adsorbing gas while H_2's isotherm is linear. It is further seen that H_2 permeation got a strong surface flux, because its permeability is more than doubled that of He (He is smaller

* Correspondence author. Email: kwang@pi.ac.ae. Tel: + 971 02 607 5116. Fax: + 971 02 607 5220

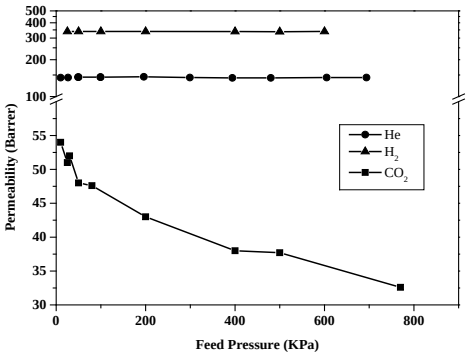

Figure 2. Experimental data on unary permeability of three gases at different permeation pressure

Table 1. The permeation properties (at T=25°C, P_0 = 1 bar) of 3 pure species

Gases	He	H_2	CO_2
Pe (barrer†)	143.00	330.00	45.80
Time lag (s)	1.30	2.78	1,160
D (cm^2/s)	2.50×10^{-6}	1.16×10^{-6}	2.7×10^{-9}
S (cmHg-1)	5.72×10^{-3}	2.84×10^{-2}	1.65
Ideal Perm-selectivity Pi/PHe	1.00	2.31	0.32

†-1 Barrer=1×10-10 [cm^3 (STP)•cm]/[cm^2•s•cmHg]

in molecular dimension than H_2, Table 1). On the other hand, CO_2 adsorbs strongly on the CMSM, so that its permeability showed a decreased trend with the increased P_0 , as reported in other studies [5].

Table 1 shows the permeation properties of each species, which were derived from permeation data measured with the time lag rig at the standard permeation conditions (P_0 = 1 bar, T = 25°C). As Helium is selected as the reference, the 'ideal' perm-selectivity for a species is represented by Pi/PHe.

The permeation experiments were conducted for 4 binary gas mixtures with different compositions (#A to #D). Table 2 summarizes the true permeabilities (P_e^T) for each species in their gas mixtures, which are compared to the ideal permeabilities (P_e^I) measured for each pure species at the same pressure (same partial pressure in the binary mixture) via the traditional time lag technology. Table 2 enables us to compare the measured true perm-selectivites $\left(\alpha_{2/1}^T = \frac{P_{e2}^T}{P_{e1}^T}\right)$ with the ideal perm-selectivities $\left(\alpha_{2/1}^I = \frac{P_{e2}^I}{P_{e1}^I}\right)$. It is seen in Table 2 that, in general:

1. The true permeability (P_e^T) of each species in gas mixture is significantly less than its ideal permeability (P_e^I). For example, with the gas mixture #B, a fraction of 25% He caused a decrease of 18% in the permeability of heavy species (CO_2).
2. The true selectivity ($\alpha_{2/1}^T$) is significantly different from the ideal values ($\alpha_{2/1}^I$) for all 4 gas mixtures, and is heavily dependent on the mixture composition. For example, $\alpha_{2/1}^{true}$ = 3.35 for #C mixture of CO_2 (0.5 bar) - H_2 (0.5 bar), but it reduced to 1.1 for #D mixture of CO_2 (2bar) - H_2 (0.5bar).
3. The competitive adsorption/diffusion dictates the performance of the CMS Membrane. It is seen that, as the molar fraction of CO_2 increases from 50% (#A) to 75% (#B), the membrane changed its selectivity from 'He selective' to 'CO_2 selective', or the 'reverse selectivity' [6]. This posts serious challenge (as well as opportunity) especially for gas separation in the inorganic membranes (e.g. carbon, zeolite, etc.) of which adsorption and surface diffusion play important roles.

Conclusion

In this research, the CO2/He, CO2/H2 system were investigated to compare the molecular sieving vs surface flux on a CMSM membrane. It's found that the true permeability (P_e^T) of each species in gas mixture is significantly less than its ideal permeability, and the true selectivity depends on the mixture composition severely. At last, competitive adsorption/diffusion was observed on the CMS membrane.

Acknowledgement

This project was supported by the research grant of GRC010/11010 from Gas Research Committee (GRC) of Abu Dhabi National Oil Company (ADNOC).

References:

[1] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, "Current status and development of membranes for CO_2/CH_4 separation: A review," International Journal of Greenhouse Gas Control, vol. 12, pp. 84-107, 2013.

[2] R. W. Baker and K. Lokhandwala, "Natural gas processing with membranes: An overview," Industrial & Engineering Chemistry Research, vol. 47, pp. 2109-2121, Apr 2008.

[3] W. J. Koros and R. Mahajan, "Pushing the limits on possibilities for large scale gas separation: which strategies?," Journal of Membrane Science, vol. 175, pp. 181-196, 2000.

[4] K. Wang, "Diffusion anomaly and blind pore character in carbon molecular sieve membrane," Chemical Engineering Science, vol. 62, pp. 3654-3659, Jul 2007.

[5] K. Wang, H. Suda, and K. Haraya, "The

characterization of CO2 permeation in a CMSM derived from polyimide," Separation and Purification Technology, vol. 31, pp. 61-69, Apr 2003.

[6] C. H. Lau, P. Li, F. Li, T.-S. Chung, and D. R. Paul, "Reverse-selective polymeric membranes for gas separations," Progress in Polymer Science, vol. 38, pp. 740-766, 2013/05/01/ 2013.