



Experimental and theoretical studies on gas permeation through carbon molecular sieve membranes

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ABSTRACT

Carbon molecular sieve membranes were prepared from Kapton® polyimide film at different temperatures under vacuum. The micropore volume determined by CO₂ adsorption (273 K) increased with increasing carbonisation temperature and reached a maximum value of 0.34 cm³/g at a temperature of 1273 K. The gas permeances through the membranes increased with increasing carbonisation temperature with a maximum permeance at 873 K, but subsequently decreased with increasing temperature above 873 K. The samples carbonised at 873 K produced gas permeances of 16.89×10^{-10} , 10.10×10^{-10} and 9.80×10^{-10} mol/(m² s Pa) for O₂, N₂ and CH₄, respectively. The theoretical upper limit of the permeation rate for the gases with different masses was observed at the activation energy of 0 kJ/mol as determined by Knudsen diffusion mechanism. The magnitude and the distribution of the potential energy between gas molecules and carbon pore wall were strongly dependent on the membrane pore size. For the same pore diameter and internuclear separation, the order of the absolute values of the average potential energy was O₂ < N₂ < CH₄. The calculated gas permeances increased sharply with increasing pore diameter and the differences in the gas permeances among O₂, N₂ and CH₄ were significant for membrane pores smaller than 6 Å.

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1. Introduction

Increasing interest has focused on carbon molecular sieve membranes over the last few years. Such membranes are formed as a result of carbonisation/pyrolysis of polymeric substances (thin polymer film or hollow fibre) or carbonisation of polymer films deposited on porous (ceramic, graphite, alumina or stainless steel) supports under vacuum or inert atmospheres (helium, argon or nitrogen). The carbonisation, usually carried out at temperatures of 773–1273 K, removes most of the heteroatoms originally present in the polymeric macromolecules whilst leaving behind a stiff and cross-linked carbon matrix [1].

The transport properties of carbon molecular sieve membranes are highly dependent on their pore sizes and therefore various membrane preparation methods and characterisation techniques have been used. Shiflett et al. prepared high-selectivity nanoporous carbon membranes from polyfurfuryl alcohol through ultrasonic deposition [2–4]. A carbon mass to surface area value between 3.4 and 3.6 mg/cm² was found to result in the highest permselectivities, and this corresponded to a critical membrane thickness of 22 ± 1 μm [3]. Multiple peaks in the pore size distribution were

observed with membrane pores ranging from 4.0 to 10 Å but mostly centring around 4.5–5.0 Å [4]. Sircar and his coworkers developed adsorption selective carbon membranes [5–7]. The selective carbon layer, formed after coating for 5 times and carbonised at a final temperature of 1273 K under nitrogen, had a thickness of 2.5 μm and a mean pore size of 5–6 Å. Sedigh et al. studied the transport and morphological characteristics of carbon membranes prepared by pyrolysis of polyetherimides coated on porous γ-alumina tubes [1,8]. The mesoporous structure of the original γ-alumina layer was modified as the polymer solution penetrated into the pores and the selective thin carbon membrane was formed inside the γ-alumina layer. The average pore dimension in the mesoporous region decreased from about 50 Å for the original γ-alumina layer to 38 Å and a sharp peak at 3.6–3.8 Å was found in the microporous region. The gas permeances and the separation factors were greatly dependent on the number of coating/carbonisation cycles. Steel and Koros prepared carbon molecular sieve membranes from Matrimid® polyimide [9]. By applying the density functional theory method to CO₂ (at 273K) adsorption isotherms, a multi-mode distribution of the pores ranging from 4 to 9.5 Å within the membranes was observed. Increasing the pyrolysis temperature from 823 K to 1073 K, the integral pore volume fraction of the pores in the range of 4–6.8 Å apparently increased.

Kapton® polyimide has been used as a raw material to prepare carbon membranes. Hatori et al. reported the preparation of carbon

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films from Kapton® polyimide through phase inversion technique. These carbon films showed a homogenous fine pore structure and the pores were macropores [10]. Petersen et al. prepared asymmetric capillary carbon membrane by coagulation of a polyamic acid solution which was imidized to a Kapton capillary and finally pyrolysed to a capillary carbon membrane [11]. The capillary carbon membranes showed permselectivities of 2000 and 1000 for He/N₂ and H₂/N₂ respectively at 0 °C, and 170 for He/N₂ at 250 °C. By carbonisation of Kapton® type polyimide at 500–700 °C under vacuum, Fuertes et al. obtained carbon composite membranes [12]. These membranes showed permselectivities of 16 and 4 for CO₂/CH₄ and O₂/N₂, respectively, with CO₂ and O₂ permeabilities of 92 and 45 Barrers, respectively. Wang et al. characterised carbon molecular sieve membranes from Kapton® polyimide film using CO₂ adsorption and gas permeation measurements [13]. It was found that surface diffusion was the predominant mass transfer mechanism for CO₂ permeation in the membranes, and the surface diffusivity of CO₂ showed much stronger concentration dependence than that described by the traditional Higashi–Ito–Oishi (HIO) model.

Theoretical studies of single gas permeation and gas separation in carbon membranes have been carried out using different methods. In the published works, a model of a slit-shaped carbon pore is commonly used. Considered as a semi-infinite graphite slab, the carbon pore wall consists of parallel graphite planes with an interplanar spacing of 0.335 nm and with a carbon atom density of 114 nm⁻³. The porous carbon membrane may contain a range of pore sizes from nano- to meso- to micropores. The main resistance to gas permeation is attributed by the interconnected nano- and mesopores [14]. In the non-equilibrium molecular dynamics (NEMD) simulations of H₂/CH₄ separation, Vieira-Linhares and Seaton observed that the pores between 6.3 and 10 Å showed selective adsorption of methane. Pores smaller than 6 Å showed molecular sieving effect whilst pores bigger than 10–12 Å showed poor selectivities [15]. At a feed pressure of 11.3 bar, a maximum selectivity of about 170 of CH₄ over H₂ was obtained; this maximum selectivity corresponded to a pore size of 7 Å. Xu et al. reported that the separation of CO₂/CH₄ was dependent on the porosity [14]. Using molecular dynamics simulations, they found that the amount of gases adsorbed increased with increasing porosity and reached a maximum at a porosity of 0.45–0.5. Beyond this porosity, the amount of gases adsorbed decreased with increasing porosity. The selectivity increased with increasing porosity due to the improved CO₂ flux and nearly constant CH₄ flux. A maximum selectivity of about 14 was achieved at a porosity of 0.6. In the study of Furukawa and Nitta, the carbon membranes were modelled with three different pore shapes, i.e., a diamond path (DP), a zigzag path (ZP) and a straight path (SP) [16]. The gas permeations through the DP and ZP membranes were suppressed by the potential barriers inside the pores whilst the gas permeation through the SP membrane was only controlled by the potential barriers at the pore exit. For the separation of CH₄/C₂H₆ using the three different pore shapes, the calculated CH₄/C₂H₆ selectivities were higher than the ideal separation factors derived from the ratio of CH₄ permeabilities over C₂H₆ permeabilities but were lower than the separation factors based on adsorption equilibrium.

MacElroy and Boyle simulated the transport of binary mixtures of H₂ and CH₄ through carbon membranes with varying thickness using the NEMD technique [17]. If the pores controlling the separation process were short, the pore entrance/exit resistances to the mass transfer would be significant. The transport of strongly adsorbing CH₄ molecules was nearly not affected by the cross-coefficient of diffusion. Strano and Foley considered the membrane permeability as the contribution of highly selective membrane pores in conjunction with less selective cylindrical defect pathways [18]. By applying the model to the published results, they found that the carbon membranes having high numbers of defects showed

a quadratic dependence of flux on pressure and the O₂/N₂ selectivity varied with O₂ permeability. According to Gilron and Soffer, the pure gas permeance through the carbon membranes displayed molecular weight and temperature dependencies expected from Knudsen diffusion even though the pore size distribution was below 0.55 nm [19].

In this paper, carbon molecular sieve membranes were prepared by pyrolysing flat polyimide films. CO₂ adsorption at 273 K was used to determine the pore volume of the carbon membranes. The gas permeation properties of the carbon membranes were analyzed by means of experimental and theoretical methods.

2. Theory

The transport properties of gas molecules in microporous membranes may be represented by Knudsen, configurational diffusion and/or surface diffusion. Therefore, the gas permeation rate can be a function of both diffusion coefficient and the concentration of the penetrant. For nonadsorbable gases such as O₂ and N₂, the concentration of the penetrant is primarily determined by the gas phase inside the membrane. For adsorbable gases such as CO₂, the concentration of the penetrant is determined by the concentration of the adsorbed phase. The permeability coefficient of a penetrant can thus be expressed by [20]

$$\bar{P}^0 = D_{c,ads} \frac{d \ln p}{d \ln C_{ads}} \frac{\theta}{\tau} \frac{dC_{ads}}{dp} + \frac{\theta}{\tau} \frac{D_{c,gas}}{RT} \quad (1)$$

$$D_{c,ads} = \rho_g d_p \left(\frac{8RT}{\pi M} \right)^{1/2} e^{-\Delta E_{ads}/RT} \quad (2)$$

$$D_{c,gas} = \rho_g d_p \left(\frac{8RT}{\pi M} \right)^{1/2} e^{-\Delta E_{gas}/RT} \quad (3)$$

where $D_{c,ads}$ and $D_{c,gas}$ are the corrected diffusion coefficients (m²/s) in the adsorbed and gas phases respectively, θ is the porosity, τ is the tortuosity, p is the pressure, C_{ads} is the adsorbed-phase concentration, R is the gas constant, T is the temperature, M is the molecular mass of the penetrant, ρ_g is the geometrical probability or the probability that the gas molecules jump into the desired direction, d_p is the pore diameter, ΔE_{ads} is the apparent activation energy of diffusion in the adsorbed phase, and ΔE_{gas} is the apparent activation energy of diffusion in the gas phase.

For nonadsorbable gases, the first term in Eq. (1) is negligibly small and the permeability of the penetrant is determined exclusively by the transport in the gas phase. Thus, the permeability of nonadsorbable gases such as CH₄, O₂ and N₂, is

$$\bar{P}^0 = d_p \rho_g \left(\frac{8}{\pi MRT} \right)^{1/2} \frac{\theta}{\tau} e^{-\Delta E_{gas}/RT} \quad (4)$$

The gas permeance for the nonadsorbable gases is

$$P = \frac{\bar{P}^0}{l} = \frac{d_p \rho_g}{l} \left(\frac{8}{\pi MRT} \right)^{1/2} \frac{\theta}{\tau} e^{-\Delta E_{gas}/RT} \quad (5)$$

where l is the thickness of the membrane. The activation energy of diffusion ΔE_{gas} can be estimated from the interactions between the diffusant and the pore [20]. Fig. 1 shows the schematic diagram of the slit-shaped carbon pore model. The pore width, H , is the internuclear distance (along the z -axis) between carbon atoms in opposite walls. Each pore comprises n parallel layers of carbon atoms separated by an internuclear distance, Δ , and each layer plane has an atom density ρ_a . The total interaction potential between a gas molecule and one wall of the model pore is given by [21]:

$$u_{sf}(z) = 2\pi \rho_a \varepsilon_{sf} \sigma_{sf}^2 \left\{ \sum_{j=0}^{n-1} \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{z+j\Delta} \right)^{10} - \left(\frac{\sigma_{sf}}{z+j\Delta} \right)^4 \right] \right\} \quad (6)$$

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