Membrane Separation for Gases: Materials, Preparation Methods and Transport Mechanism

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***Abstract*—Gas adsorption and permeation of CO_2 gas were measured on two carbon molecular sieve membranes over a wide pressure range. The two membrane samples were fabricated under similar conditions but with different degrees of carbonization. The pressure dependence of the permeation time lag was investigated and it is found that the diffusion coefficient takes a stronger functional dependence on loading than the Darken relation and this dependence increases with the degree of carbonization.**

***Keywords*— Diffusion, permeation, adsorption, carbon molecular sieve membrane; gas separation**

I. Introduction

Carbon molecular sieve membranes (CMSMs) are prepared from the controlled pyrolysis of polymer precursors. The mico-structure of a CMSM is determined by the carbonization parameters such as temperature ramping rate, thermal soak time, final temperature, polymer precursor used, etc.(i,ii) It is well known that diffusion coefficient is dependent on the adsorbed concentration. The Darken relation provides a popular correlation but many exceptions exist.(iii,iv) Stronger functional dependence has been reported for the diffusion in microporous media such as CMSM. Wang et al. measured CO2 sorption and permeation in a CMSM carbonized at 950°C, and found that the diffusion coefficients derived from both the transit permeation and the steady state permeation flux present strong dependence over a wide pressure range.(v, vi). Do attributed such kind of anomaly to the structural heterogeneity of the adsorbents.(vii,viii) Ruthven investigated effect of isotherm and loading on the concentration dependence of the diffusion coefficient (ix).

II. Theory

The diffusion flux of the adsorbed phase, can be written as:

$$J_\mu = -D_\mu \frac{\partial C_\mu}{\partial r} \tag{1}$$

Where C_μ is the adsorbed-phase concentration, D_μ is the apparent diffusion coefficient which is related to the diffusion coefficient at zero loading, D_μ^0, via the isotherm:

$$\frac{D_\mu}{D_\mu^0} = \left(\frac{\partial \ln P}{\partial \ln C_\mu} \right)_T \tag{2}$$

In eq.(2), P is the bulk phase pressure in equilibrium with the adsorbed phase, and T is the temperature. D_μ^0 is assumed to be independent of surface loading and specific to adsorbate-surface system. Eq.(2) is the popular Darken relation and its actual functional dependence on the adsorbed concentration (loading) depends on the local isotherm. With the Langmuir isotherm $C_\mu = C_{\mu s} bP/(1+bP)$, Eq.(2) reduces to:

$$D_\mu = \frac{D_\mu^0}{1 - C_\mu / C_{\mu s}} = \frac{D_\mu^0}{1-\theta} \tag{3}$$

Eq.(3) is same as HIO model for a homogenous surface.(x)

With the Toth isotherm,

$$C_\mu = C_{\mu s}\, b_t P \Big/ \left[1 + (b_t P)^t\right]^{1/t}$$, eq.(2) will become:

$$D_\mu = \frac{D_\mu^0}{1-\theta^t} \tag{4}$$

where $C_{\mu s}$ is the adsorption capacity, b and b_t are the affinities, t is the surface heterogeneity, and θ is the surface loading. The use of Langmuir isotherm implicitly assumes a homogeneous surface while the choice of the Toth isotherm suggests a heterogeneous surface for both adsorption and diffusion processes. In addition to the Darken relation, two diffusion models were also employed in this study to investigate the experimental data. Model A was used by Wang et al[v] and Lagorsse et al.[Error! Bookmark not defined.] It is a modified HIO model allowing a flexible concentration dependence on the surface loading:

$$D_\mu = \frac{D_\mu^0}{\left(1 - C_\mu / C_{\mu s}\right)^n} = \frac{D_\mu^0}{(1-\theta)^n} \tag{5}$$

The value of 'n' in eq.(5) , as will be shown later, represents the heterogeneity for diffusion. Eq.(5) reduces to the Darken relation with the Langmuir isotherm and n=1,

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that is, a homogeneous surface for both adsorption and diffusion.

III. Experiment

CMSM samples were prepared by the controlled pyrolysis of Kapton polyimide thin film under high vacuum. The thermal treatment programs are similar but with different soaking temperatures. The first membrane sample was carbonized at 950°C (thereafter referred to as KP950) while the second sample was treated at 800°C (referred to as KP800). The carbonization parameters and some of the membrane properties are listed in Table 1.

Table 1: The Pyrolysis Parameters and the Properties of the Two Membrane Samples

Sample	Temp. (°C)	Soaking Time(hr)	Heating rate	Thickness (μm)
KP950	950	1	10°C/min	23
KP800	800	1	10°C/min	125

Previous studies showed that the membranes are pinhole-free and symmetric in structure (1). The pore volume evolution against temperature was previously investigated in details for a total of three membrane samples (KP600, KP800,and KP1000). The derived pore volume distributions are shown in Figure 1. It is seen that, as the pyrolysis temperature increases from 600˚C to 1000˚C, the membrane samples will develop more fractions of micropores below 4Å.

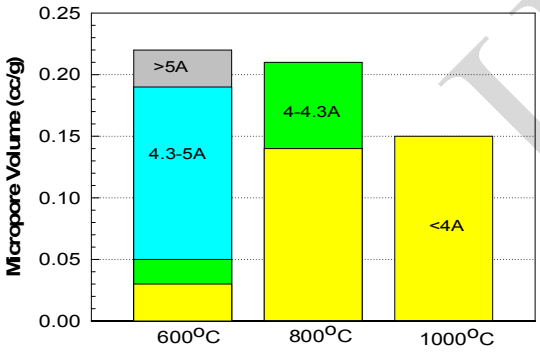


Figure 1: Pore Volume Distribution vs. Pyrolysis Temperature (KP600, KP800, and KP1000

CO_2 permeation experiments were conducted on a time-lag rig while the adsorption isotherms were measured on a volumetric rig for KP950[v] and a Cahn 2000 microbalance for KP800, respectively. The experimental setup and procedures can be found in the references [v, vi].

IV. Results and Discussion

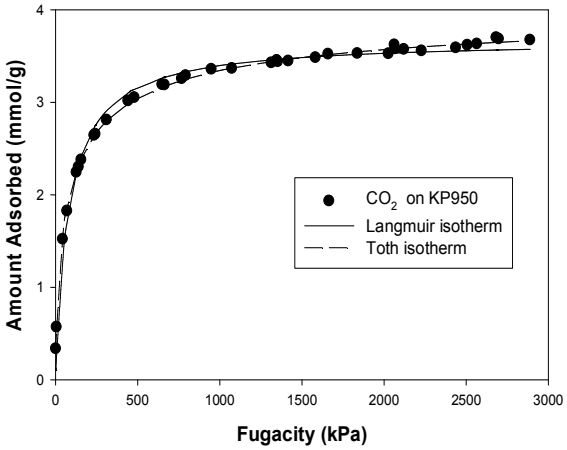


Figure 2: Adsorption Isotherm of CO2 on KP950 At 298K (Dots); Langmuir (—); Toth (--). .

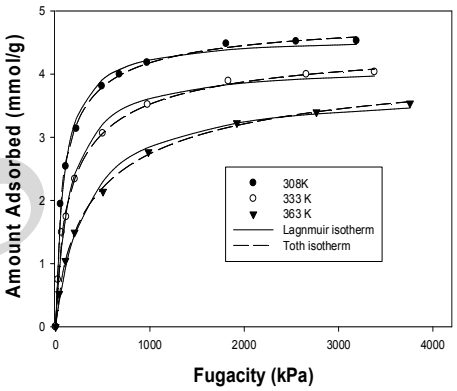


Figure 3: Adsorption Isotherm Of CO_2 On KP800 (Symbols); Langmuir (—); Toth (--).

Figure 2 shows CO_2 adsorption isotherm measured on KP950 at 298K (dots). As CO_2 is not an ideal gas at high pressure, the pressure reading is converted to fugacity. The isotherm data are fitted to the Langmuir isotherm (solid line) and Toth isotherm (dashed line), respectively.

The fitting is reasonably good for the Langmuir and good for the Toth isotherm. The fitting results are listed in Table 3 and Table 4, respectively. Figure 3 shows the CO_2 isotherms measured on KP800 at 308K, 333K and 363K, respectively, as symbols. The fittings are shown as solid lines for the Langmuir and dashed lines for the Toth isotherm.

Next, CO_2 permeation time lags measured on KP 800 were investigated. Figure 4b shows the permeation data at three temperatures (308K, 333K, and 363K) as symbols. It is seen that, model A (solid lines) again well simulates the data at each temperature with n ≈1.6 (The optimal parameters are listed in Table 3). Model B (dashed lines), however, shows a much too stronger dependence on the permeation pressure, as exemplified by the fittings of the time lag data at 308K and 333K, respectively.

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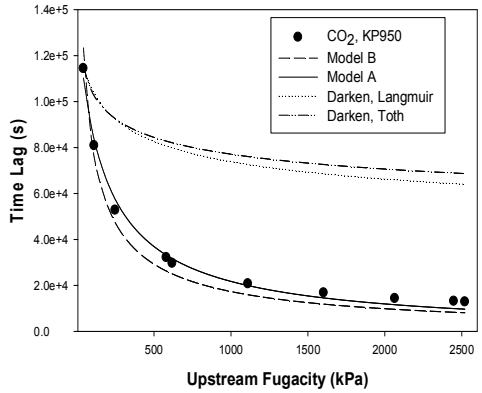


Figure 4a. Permeation time lag of CO_2 on KP950 at 298K. Experimental data (dots); Model A—; Model B --.

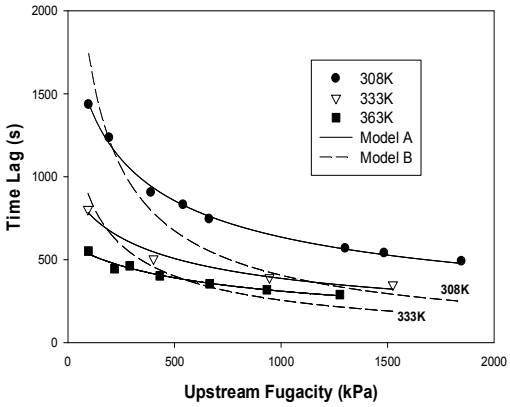


Figure 4b. Permeation time lag of CO_2 on KP800. Experimental data (symbols); Model A —; Model B --.

Compared with KP950, KP800 is the sample with less degree of carbonization and less heterogeneity for CO_2 adsorption. Therefore, it can be generally concluded that the anomaly of CO_2 diffusion depends on the structural heterogeneity of the molecular sieve membrane and an increase in the degree of carbonization will result in stronger concentration dependence for the apparent diffusion coefficient (n≈2.0 for KP950 vs n≈1.6 for KP800).

The different performance of model A and B deserves some attention and this leads us to explore more about the mechanisms and assumptions behind these two models. Both models attribute the structural heterogeneity as the source of diffusion anomaly but their approaches are very different.

V. CONCLUSION

The CO_2 diffusion coefficient in the carbon molecular sieve membranes presents strong functional dependence on loading than that described by the Darken relation over a wide pressure range and at multiple temperatures. This dependence is dictated by the surface heterogeneity of the membrane sample and increases with the degree of carbonization. The model of Wang et al is based on the traditional HIO model and modified with a correction factor of diffusional heterogeneity. The model is capable of addressing the diffusion anomalies in the samples with different degrees of carbonization and structure.

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