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Rapid communication

The structural characterization of a CMS membrane using Ar sorption and permeation

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ABSTRACT

The sorption and permeation properties of argon were measured on a CMS membrane at different temperatures and a range of permeation pressures. The structural information of the membrane sample was derived from the analysis of adsorption isotherms at different temperatures. Further discrimination between through pores and blind pores is carried out by analyzing the permeation kinetics, from which we derive that the majority of the pore volumes are contributed by the blind pores.

1. Introduction

Carbon molecular sieve (CMS) membranes are prepared from the controlled pyrolysis of such polymeric precursors as: polyimide, phenolic and cellulosic resins, polyfurfuryl alcohol, or mixed matrix polymers, etc. [1–3]. The micro-structure of the membrane is known to be 'turbostratic' [4], i.e., graphitic microdomains are randomly embedded in amorphous carbons to form slit-shaped micropores which provide a 'sieving' effect at molecular level [5,6]. Due to these structural characteristics, diffusion anomalies (diffusion coefficient presents stronger/weaker functional dependence on loading than the classical Darken relation [7]) have been commonly observed in gas permeation processes at both transient and steady states [8–11] and these anomalies were found to be dependent on the structure of the membrane (particularly the existence of blind pores) and the molecular properties of adsorbates [12]. As the 'sorption–diffusion' is the mechanism for gas permeation in such membranes [2], it is desirable that we characterize the sorption as well as the diffusion properties of a membrane sample using a reference gas, and based on which the prediction/estimation can be made for other gas(es). Helium gas was popularly used in characterizing gas permeation in microporous media, which is spherical, non-polar and fast penetrating. However, helium, being a small molecule ($\sigma = 2.6$ Å), cannot effectively probe large micropores and the sorption properties as it is virtually non-adsorbing at room temperature. In contrast, Ar is larger in size ($\sigma = 3.54$ Å) and strong in sorption (comparable to N_2) so it is potentially a good candidate to probe a microporous membrane for its sorption and diffusion properties. The popular approach to characterize a porous media is to simulate the observed isotherm using the local pore isotherm (or density) generated with various theories (such as DFT or GCMC), and to derive the pore size/volume distributions. Such approaches are theoretically sound, but give no information about the pore connectivity which is critical to the separation performance of a porous membrane. This article will describe the characterization of a CMS membrane using the sorption as well as the permeation properties of argon.

2. Theory

The porous structure of a membrane can be derived from the analysis of multiple adsorption isotherms with the mathematical model proposed by Nguyen and Do [13,14]. The blind pore characteristics of the membrane can be characterized via the transient permeation kinetics using the mathematical model proposed by Wang [12]. Details of those two models can be found in the original publications, and we only briefly present the essential features of the models here.

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The observed isotherm is the contribution of local isotherms (assumed to be Langmuir) of all pores:

$$C_\mu(p)=\int_0^\infty C_{\mu s}(r)\frac{b_{pore}(r)p_{pore}(r)}{1+b_{pore}(r)p_{pore}(r)}f(r)\ dr \tag{1a}$$

where r is the pore size, p is pressure, b is sorption affinity, C_μ is adsorbed phase concentration, and $C_{\mu s}$ is the sorption capacity. The subscript '*pore*' represents the property in *pore phase*. The pore pressure is related to the bulk pressure via:

$$p_{pore}=p\exp\left(\frac{-E_{pore}^{g}}{RT}\right) \tag{1b}$$

where T is temperature, E_{pore}^{g} is potential energy of the gas phase molecules confined in the pore interior. The sorption affinity of the pore, b_{pore}, is related to the sorption affinity on a flat surface (represented by a graphite sheet), b_s:

$$b_{pore}=b_s\ \exp\left(\frac{E_{pore}-E_s}{RT}\right) \tag{1c}$$

with $b_s=(\beta/\sqrt{MT})\exp(E_s/RT)$where E_s is sorption heat on a flat surface, E_{pore} is sorption energy in a pore (related to the sorption potential at the mid-plane). M is the molecular weight, β is a parameter characterizing the solid surface. The model parameters can be calculated from molecular and surface properties of adsorbate/adsorbent with the assumptions that micropores are slit-shaped while adsorbate–pore interaction is dispersive [13]. This model was used by Nguyen et al and Lagorsse et al. [15] to characterize the structure of CMS membranes.

By matching the theoretical equation (Eq. (1)) to the experimental data of multiple isotherms, we can derive the pore size distribution *f*(*r*). This distribution includes open pores and blind pores, and it does not discriminate between these two types of pores and therefore it does not contain any information about pore connectivity (other models such as DFT, GCMC, HK, etc., have the same problem). To discriminate pores into through pores (which allow permeation flux at steady state) and blind pores (which adsorb permeates at transient state but present zero permeation flux at steady state), we resort to the transient permeation kinetics because the roles that these pores play are different [12]. The mass balance equation for gas permeation in a slab membrane with the thickness of l is

$$\varepsilon_T\frac{\partial C_\mu^T}{\partial t}+(1-\varepsilon_T)\frac{\partial C_\mu^B}{\partial t}=\frac{\partial}{\partial z}\left(\varepsilon_T D(C_\mu^T)\frac{\partial C_\mu^T}{\partial z}\right) \tag{2a}$$

where t is the time, z is diffusion coordinate, and ε is the porosity. The superscripts '*T*' and '*B*' represent the through pore and blind pore, respectively. D_μ is diffusion coefficient following the Darken type concentration dependence, $D_\mu=D_\mu^0(\partial\ln P/\partial\ln C_\mu)_T$, D_μ^0 is diffusion coefficient at zero surface loading. The overall sorption isotherm is then the combination of isotherms in blind and through pores, represented by Langmuir isotherms:

$$C_\mu(p)=\varepsilon_T C_\mu^T+(1-\varepsilon_T)C_\mu^B=\varepsilon_T C_{\mu s}^T\frac{b_T p}{1+b_T p}+(1-\varepsilon_T)C_{\mu s}^B\frac{b_B p}{1+b_B p} \tag{2b}$$

The analytical expression of permeation time lag (L) was derived from Eq. (2) using the method of Frisch and shown in Appendix A. Eq. (A.1) together with Eq. (2b) are used to compare with the permeation time lag data and isotherm data, respectively, to derive the contribution of blind pores and through pores.

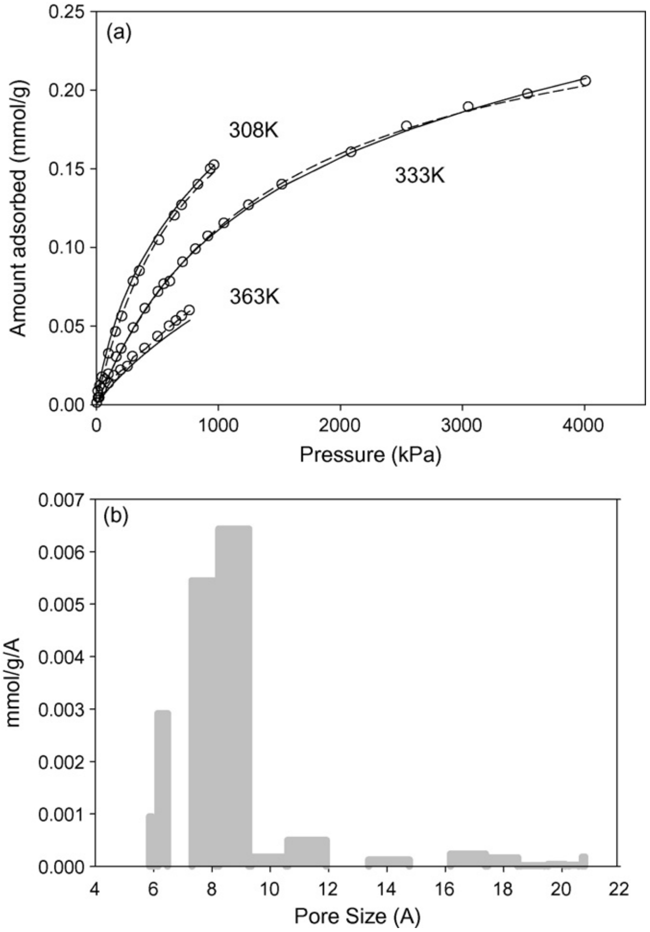

Fig. 1. (a) Ar isotherm (symbols) at 308 K, 333 K and 363 K; [— Eq. (1), - - - Eq. (2b)]. (b) The distribution of Ar sorption capacity in the membrane sample.

3. Experiment

A CMS membrane sample (denoted as KP800) was fabricated by the controlled pyrolysis of polyimide thin films under high vacuum and with a soaking temperature of 800 °C. The membrane was subject to the sorption as well as permeation experiments by molecules of different dimensions and properties [1]. The gas permeation properties of the membrane are listed in Table 1.

The isotherm data of Ar were collected using a Cahn 2000 microbalance. The permeation time lag and steady state flux were measured on a conventional time-lag rig [1,14].

4. Results and analysis

Fig. 1a shows the sorption isotherms (symbol) of Ar measured at 308, 333 and 363 K. Eq. (1) were used to fit all three isotherms

Table 1
Permeation properties of KP800 CMS membrane.

Pyrolysis temp. (°C)	Density (g/cc)	Thickness (μm)	Perm-selectivity				
			P_{He}/P_{CO_2}	P_{He}/P_{N_2}	P_{He}/P_{Ar}	P_{He}/P_{H_2}	P_{He}/P_{CF_4}
800	~1.99	125	0.67	22.28	22.30	0.31	∞

Note: perm-selectivity = P_{He} (permeability of helium)/P_i.