Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Way, J. Douglas and Roberts, Daryl L.(1992) 'Hollow Fiber Inorganic Membranes for Gas Separations', Separation Science and Technology, 27: 1, 29 — 41
To link to this Article: DOI: 10.1080/01496399208018863
URL: http://dx.doi.org/10.1080/01496399208018863

SEPARATION SCIENCE AND TECHNOLOGY, **27**(1), pp. 29–41, 1992

Hollow Fiber Inorganic Membranes for Gas Separations*

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Abstract

Pure gas permeabilities of He, H_2, CO_2, N_2, and CO were measured for microporous silica hollow fiber membranes as a function of temperature. The transport mechanism for gas permeation is clearly non-Knudsen since several heavier gases permeate faster than lighter gases. An excellent correlation is obtained between permeability and kinetic diameter of the penetrant. The proposed mass transfer mechanism is a combination of surface diffusion and molecular sieving. High ideal separation factors (permeability ratios) are observed at 343 K for H_2/N_2 and H_2/CO of 163 and 62.4, respectively, which compare very favorably with polymeric and molecular sieve gas separation membranes.

INTRODUCTION

There is increasing interest to develop high temperature, high pressure membrane technology to perform a variety of gas separations such as acid gas removal from synthetic gas streams found in coal-fired power generation systems, hydrogen recovery in petrochemical production, and CO/H_2 ratio adjustment in the production of oxychemicals. The temperatures encountered in these processes are far above the operating temperature

*Presented at Sixth Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 25, 1989.

range for most organic membrane materials which is typically 423–473 K for polymers such as silicone rubber, polysulfone, and cellulose esters. Materials such as silica, ceramics, and carbon are potential membrane materials for gas separations at high temperatures or in aggressive chemical environments (*8*). This paper presents gas transport data for microporous silica hollow fibers at high pressure as a function of temperature.

The application of microporous membranes to the separation of gases and vapors has been extensively reviewed by Hwang and Kammermeyer (*9*), especially the literature pertaining to transport in microporous Vycor glass membranes. Gas transport in microporous Vycor glass is controlled by Knudsen diffusion or, in the case of condensible vapors, a combination of Knudsen diffusion and surface diffusion (*11*). More recently, Okubo and Inoue reported the chemical modification of microporous Vycor-type glass membranes to improve the mixture separation factor for He over O_2 from the Knudsen value of 3 to 6.

Koresh and Sofer (*14*, *15*) reported molecular sieve carbon (MSC) membranes prepared by pyrolysis of polymer films. These membranes have ideal separation factors much higher than those predicted for Knudsen diffusion (e.g., He/O_2 and O_2/N_2 selectivities of 20 and 8.0, respectively). Heat treatment of the MSC membranes in O_2 was used to increase the pore size and resulted in a decrease in the ideal separation factors for He/O_2 and O_2/N_2 to 2.8 and 0.92, respectively. These values are close to those expected from a Knudsen diffusion mechanism. Koresh and Sofer attribute the high selectivity prior to pore opening to a molecular sieving or size discrimination effect similar to the mechanism of MSC adsorbents.

EXPERIMENTAL

The fibers were manufactured by melt extrusion followed by leaching as described by Hammel and coworkers (*5*, *6*). PPG Industries provided microporous hollow fiber silica membranes for use in this work. The diameter of the hollow fibers was approximately 100 μm. Physical adsorption of N_2 was used to characterize the hollow fibers, and analysis of the N_2 adsorption data using the BET isotherm indicated that virtually all of the pores were less than 20 Å in diameter.

Permeability measurements were made using single hollow fiber membranes potted in one end of $\frac{1}{8}$-in. stainless steel tubes using quick-setting epoxy resin (Devcon Corporation, Danvers, Massachusetts). The permeate end of the fiber was left open, and the other end of the fiber was sealed using the epoxy potting compound. The length of the hollow fibers in the test cells was approximately 14 cm. The single hollow fiber test cells were installed in $\frac{1}{4}$-in. diameter stainless steel pressure vessels with double-end shut off quick connect fittings at the high pressure feed inlet and residue outlet ports. Cajon Ultra-torr O-ring fittings were used to connect the low pressure permeate stream to the tubing system which is shown in Fig. 1.

The flow system in Fig. 1 was used to measure pure gas permeabilities for silica hollow fiber membrane test cells. The temperature of the test cells is controlled by a gravity convection oven. A pure gas at 21.4 atm flows through the hollow fiber test cell to a backpressure regulator, fine metering valve, and a bubble flowmeter. Ultrahigh purity (99.999%) He, H_2, and N_2, 99.99% CO_2, and 99.5% CO were used as feed gases without further purification. The permeate gas flow rate was measured as a function of membrane temperature using a capillary bubble flowmeter. The pure gas permeability was calculated from the hollow fiber dimensions, permeate flow rate, and feed pressure by using the equation

$$Q_i = \frac{q_i(\mathrm{STP}) \ln\left(\frac{r_o}{r_i}\right)}{2\pi L \Delta p_i} \tag{1}$$

where: q_i = volumetric flow rate of species i at STP
Q_i = permeability of species i

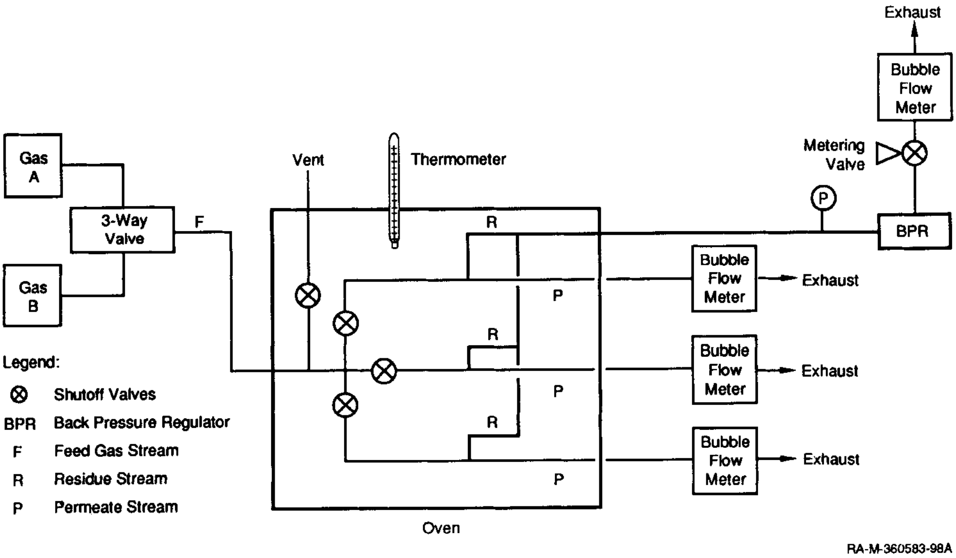

FIG. 1. Schematic diagram of apparatus for measuring single-component gas permeabilities.

TABLE 1
Pure Gas Permeabilities in Barrer Units Measured at 21.4 atm

Temperature (K)	He	H_2	CO_2	N_2	CO
298	13.5	17.5	—	0.140	0.568
313	163	101	21.4	0.773	—
343	568	285	53.2	1.75	4.56

r = inside (i) or outside (o) radius
L = fiber length
Δp_i = partial pressure difference of species i

Once the pure component permeabilities are known, ideal separation factors $\alpha(i/j)$ can be calculated from the ratio Q_i/Q_j.

Pure Gas Permeability Data

As shown in Table 1, pure component permeabilities for He, H_2, CO_2, N_2, and CO were measured at temperatures of 298, 313, and 343 K at a pressure of 21.4 atm. At temperatures above 300 K, the permeability of He was highest, followed by H_2, CO_2, CO, and N_2. The H_2 permeability was slightly larger than the He permeability at 298 K. The H_2 permeability at 313 K is 101 Barrer,* approximately one-half the permeability of a commercial cellulose acetate membrane. At the same temperature, the CO_2 permeability for this inorganic hollow fiber is 21.4 Barrer. The CO_2 permeability of a commercial cellulose acetate membrane is about 90 Barrer (*4*). The differences in permeability may be more than compensated by the higher surface area of hollow fiber modules compared to spiral wound membrane modules. Kesting (*12*) estimates that a hollow fiber module containing 100 μm diameter hollow fibers will have a surface area/volume ratio of 6,000 ft^2/ft^3, which is 20 times larger than a typical spiral wound cellulose acetate membrane module containing approximately 300 ft^2/ft^3 of membrane area.

Table 2 presents the ideal separation factors calculated from the pure gas permeabilities in Table 1. The ideal separation factors compare very favorably with literature values for polymer and molecular sieve carbon (MSC) membranes. Hayes (*7*) reported a range of ideal selectivities for He/N_2 and CO_2/N_2 separations with UV crosslinked polyimide membranes. For example, the polyimide sample with the highest He permea-

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*1 Barrer is 10^{-10} $cm^3(STP)/cm{\cdot}s{\cdot}cmHg$.

TABLE 2
Ideal Separation Factors, $\alpha(i/j)$

Temperature (K)	H_2/CO_2	H_2/CO	He/CO_2	CO_2/N_2	H_2/N_2	CO/N_2	He/N_2
298	—	30.8	—	—	125	4.06	96.4
313	4.72	—	7.62	27.7	131	—	211
343	5.36	62.5	10.7	30.4	163	2.61	325

bility had an $\alpha(He/N_2)$ of 137 and an $\alpha(CO_2/N_2)$ of 40 at 298 K. Schott et al. (*17*) reported an ideal separation factor of approximately 35 for H_2 over CO using a cellulose acetate spiral wound module for commercial H_2/CO ratio adjustment for the manufacture of oxochemicals. Koresh and Sofer (*14*, *15*) reported a He/N_2 separation factor of 22 for an MSC membrane.

All of the separation factors increase with increasing temperature except $\alpha(CO/N_2)$ which decreases from 4.06 to 2.61. This difference could indicate that the activation energy for diffusion of CO is less than that for N_2. For all of the other gas pairs, the more permeable gas has the higher activation energy for diffusion.

Theory

Motion of a gas through a microporous barrier is generally accomplished with a pressure difference between each side of the microporous barrier. At minimum, there is a partial pressure difference* for at least one of the species. For barriers with holes fine enough to ignore forced convective flow, four separate mechanisms of transport can be envisioned: Knudsen diffusion, surface diffusion, capillary condensation, and molecular sieving (Fig. 2). We will not discuss capillary condensation because it is likely irrelevant at the temperatures of interest.

The Knudsen diffusion mechanism is well understood (*9*, *13*), and its primary result is that, when all other factors are equal, the ratio of the flow of species *i* to that of species *j* is given by the inverse of the square root of their molecular weight ratio. This result holds for multicomponent and single component systems. Because most gaseous species have a molecular weight between 10 and 100, selectivities are small, and it is rare to find a gas mixture wherein an efficient separation by Knudsen diffusion is possible. A key result of the Knudsen mechanism is that no chemical information is necessary to compute the flux. The molecules are treated

*The general case is a difference in chemical potential.

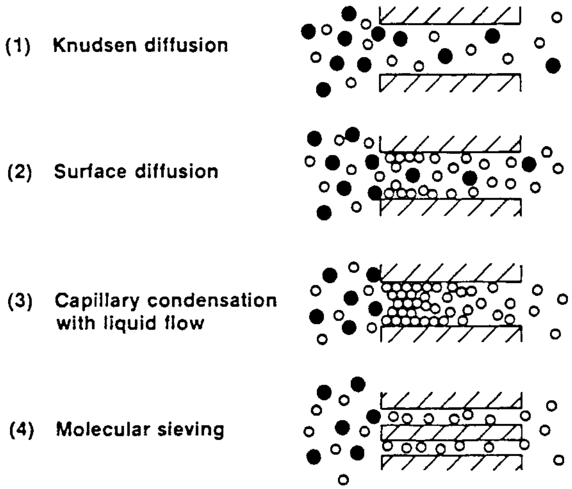

FIG. 2. Mechanisms of mass transfer through microporous membranes. The pore walls of rigid, inorganic membranes are stationary whereas those of polymer membranes exhibit thermal motion. Mechanisms are more clearly delineated for rigid membranes. Source: Fleming (*3*).

like billiard balls, and the pore walls are treated like billiard table edges with elastic collision properties.

The surface diffusion mechanism refers to the ability of molecules to reside on the surface and hop from point to point "along" the surface with no apparent residence time in the bulk gas phase above the surface. The surface chemistry of the microporous barrier plays a key role in this mechanism. Indeed, surface diffusion can be thought of as occurring when the energy state of the diffusing species is dominated by the interaction with the surface. Surface diffusion has largely been associated with the fields of catalysis, adsorption, and electronic device manufacturing (*1*, *2*, *18*, *20*). Nevertheless, it is recognized in the membrane literature (*10*, *11*). Until recently, however, no material other than Vycor glass appeared to exhibit this phenomenon.

The chemistry of the internal pore surface of the barrier and how the surface interacts with diffusing species can be studied by observation of the ability of the barrier to adsorb gases. Consequently, we can expect any theory of surface diffusion to incorporate some aspect of the thermodynamics of adsorbed phases (i.e., adsorption isotherms). Surface diffusion can occur regardless of the size of the pore but is negligible when transport through the bulk of the pore is dominating. Consequently, we can surmise that the distance from side to side of a pore must be much less than 10 atomic diameters before surface diffusion will be significant.

Molecular sieving refers, in its most absolute sense, to the complete blocking of transport of a certain size or shape of molecule and the free passage of smaller or differently shaped molecules. Molecular sieving is strongly and clearly exhibited by zeolites (*1*). Other materials (e.g., molecular sieve carbons) exhibit an element of this behavior in their ability to adsorb molecules of slight size differences at dramatically different rates. In molecular sieving, the diffusing molecule is in close and regular contact with both sides of the pore wall. In zeolites, this "pore wall" is the aperture to the inner zeolite cage. In a microporous barrier, a molecule will encounter a series of such "apertures" as it diffuses across the barrier, simply because the barrier is three-dimensional and nonuniform in its pore size distribution (Fig. 3). Indeed, in an irregular, heterogeneous array of interconnected pores, it is conceivable that a diffusing species would encounter a variety of constrictions wherein molecular sieving is dominant and would encounter other regions, intermediate to these restrictions, where surface diffusion or Knudsen diffusion is dominant (Fig. 4). In any

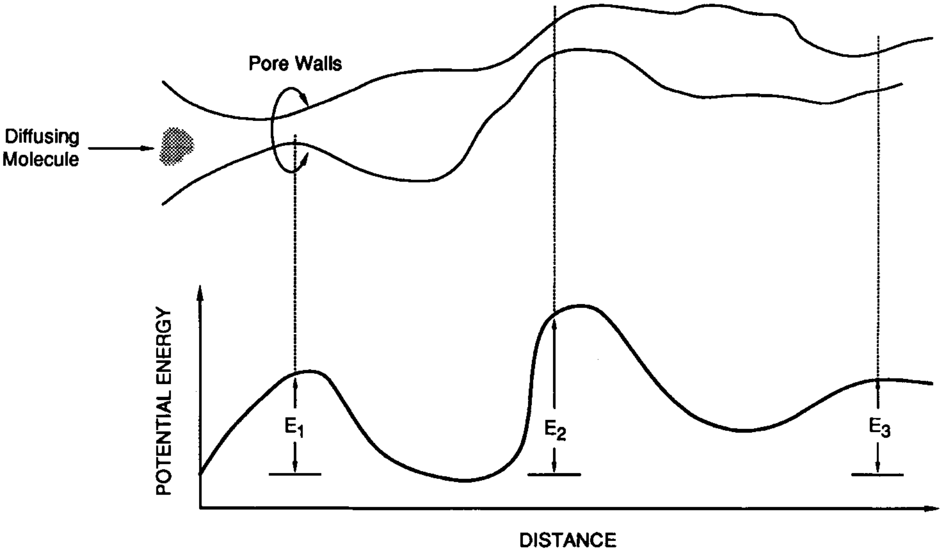

FIG. 3. Conceptual diagram of diffusion through molecular-sized holes (molecular sieve diffusion). Molecules pass through constrictions and experience energy fields as a result of their own size and the nature of the pore walls. The rate of diffusion is likely controlled by the largest activation energy barrier.

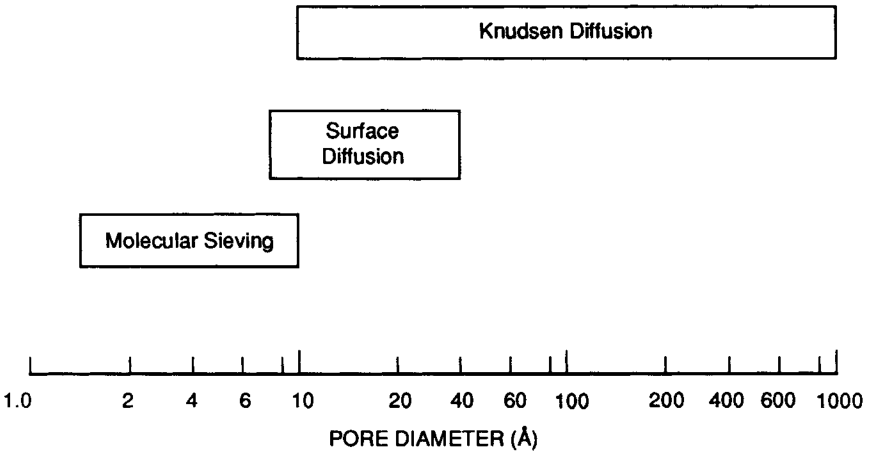

FIG. 4. Approximate operative pore size ranges for various mechanisms. We have assumed a typical penetrant diameter of 4 Å for placing the range for surface diffusion and molecular sieving.

case, when the pore size is on the order of 2 or 3 molecular diameters, molecular sieving will control the transport.

From consideration of transport through the internal pore gas phase and along the internal pore walls, an equation for the flux can be derived:

$$N_{i,\mathrm{pore}} = -D_i \frac{dC_i}{dx} - D_i^s \rho_s (1 - \epsilon) RT \sum_{j=1}^{N} \left(\frac{\partial n_i}{\partial P_j} \frac{dC_j}{dx} \right) \qquad (2)$$

Here, $N_{i,\mathrm{pore}}$ is the flux of species i (moles per unit pore area per unit time), D_i^s is the surface diffusion coefficient, ρ_s is the density of the native solid membrane material, ϵ is the void volume fraction in the microporous membrane, R is the gas constant, T is the absolute temperature, n_i is the moles of species i adsorbed on the internal pore surface per unit mass of adsorbent (membrane), D_i is the diffusion coefficient of species i in the internal pore gas phase, P_j is the partial pressure of any species j in the internal pore gas phase, C_i and C_j are the concentrations of species i and j in the internal pore gas phase, and N is the number of species in the multicomponent mixture. This equation explicitly makes clear that gradients in any species j will affect the flux of any species i on the surface. This result is intuitively reasonable since strongly adsorbed species will affect the surface concentration (and hence, surface concentration gradient) of all other species.*

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*When $\epsilon \to 0$, we have diffusion through the solid lattice only. A more general form of Eq. (2) is $\bar{N}_i = \epsilon N_{i,\mathrm{pore}} + (1 - \epsilon) N_{i,\mathrm{lattice}}$, where the last term is the solid lattice diffusion term and $\bar{N}_i$ is the flux on a total area basis. Generally, solid lattice diffusion is insignificant.

The physical meaning of the partial derivative $\partial n_i/\partial P_j$ is the change in the moles of species i on the internal pore surface for a given change in the partial pressure of species j in the internal gas phase above the internal pore surface (all other partial pressures held constant). For a single component gas, this term is the slope of the pure component isotherm, derived from experimental data. For a multicomponent gas, this term could also, in principle, be determined from multicomponent adsorption data. In practice, multicomponent data are very difficult to obtain. Since the number of data points one needs to take is nearly infinite to map the range of compositions one may encounter in a given application, there is a *strong* incentive to relate multicomponent isotherms (e.g., represented by $\partial n_i/\partial P_j$) to pure component isotherms. This relationship can be accomplished with ideal adsorbed solution (IAS) theory (*16*) and will be the subject of a future paper.

The internal pore gas phase diffusion coefficient D_i is given by the Knudsen mechanism or the molecular sieving mechanism, depending on the pore size. Hence we have

$$D_{i,Kn} = G_i\left(\frac{RT}{2\pi m_i}\right)^{1/2} \tag{3}$$

and

$$D_{i,ms} = D^o_{i,ms}\exp\left(-\frac{E_i}{RT}\right) \tag{4}$$

In Eqs. (3) and (4), G_i is a "geometric factor" (equal to $8r/3$ for right angle cylinders of radius r), m_i is the molecular weight of species i, and E_i is the controlling activation energy barrier for species i. The activation energy barrier E_i is related to the pore size and penetrant size. A quantitative relationship is presently lacking in the literature.

We expect the surface diffusion term will be negligible at temperatures above 500 K and that Knudsen diffusion or molecular sieving will dominate. Indeed, since the pores of this material are generally smaller than 20 Å, we expect molecular sieving to control the transport. This expectation is largely substantiated by our present data as discussed below.

DISCUSSION

According to kinetic theory, the lighter gases should diffuse faster in a Knudsen diffusion regime. However, the trend of the permeability data in Table 3 indicate that He permeates faster than H_2 even though He is the

TABLE 3
Role of Molecular Weight and Kinetic Diameter

Gas molecule	Kinetic diameter (Å)	Permeability at 343 K (Barrer)	Molecular weight (g/mol)
He	2.6	568	4.0
H_2	2.89	285	2.0
CO_2	3.3	53.2	44.0
N_2	3.64	1.75	28.0
CO	3.76	4.56	28.0

heavier molecule. The CO_2 permeability is higher than both N_2 and CO, which have a much lower molecular weight.

The inability of Knudsen diffusion to explain the experimental results is underscored by the ideal separation factors. For example, Eq. (3) predicts that the CO_2/N_2 separation factor would be 0.8, indicating that the membrane would be selective for N_2. The experimentally determined ideal CO_2/N_2 selectivity from Table 2 is 30.4 at 343 K. With the exception of the H_2/CO_2 separation factor, all of the separation factors in Table 2 greatly exceed the values that would be expected from a Knudsen diffusion mechanism. Also, the hollow fibers are selective for CO over N_2. Because N_2 and CO have the same molecular weight, no separation would be expected from a Knudsen diffusion mechanism. Therefore, based on the experimental permeability data in Table 3 and the ideal separation factors in Table 2, mass transfer in the silica hollow fibers is not controlled by Knudsen diffusion.

The remaining possible transport mechanisms from Fig. 2 to explain the experimental data for these silica hollow fiber membranes are surface diffusion and molecular sieving. As shown in Fig. 5, the permeability of gases through these membranes appears to be strongly related to kinetic diameter supporting a molecular sieving mechanism. The smallest molecule, He, is the most permeable, while the largest molecules, N_2 and CO, are the least permeable. A molecular sieve mechanism has been reported by Koresh and Sofer (*14*, *15*) for gas separation with carbon membranes. Our size correlation is not perfect, however, because carbon monoxide is over twice as permeable as N_2 even though CO is slightly larger. The higher CO permeability may be a result of an interaction between CO and the surface of the silica membrane. The polar CO molecule may be attracted to the polar hydroxylated silica surface which would increase the surface coverage and the permeability of CO relative to N_2 or another noninteracting gas. The interaction between the CO and the silica membrane surface should

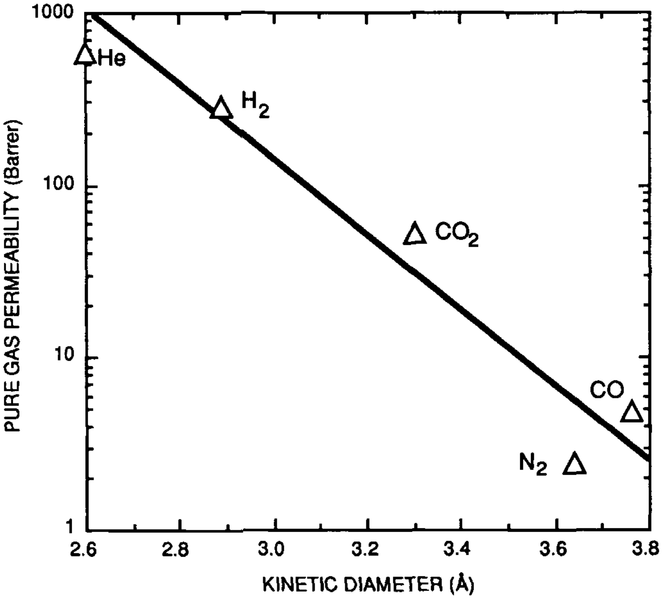

FIG. 5. The effect of molecular size on pure gas permeability. Permeability measurements were performed at 21.4 atm and 343 K. The equation of the exponential fit is $Q = (5.02 \times 10^8)10^{-2.18D}$.

decrease at higher temperatures, which would decrease the ideal separation factor. This trend is exactly what is observed; the CO/N_2 separation factor decreases from 4.06 at 298 K to 2.61 at 343 K.

A similar mechanism may explain the H_2/CO_2 ideal selectivity. Although there is a large size difference between CO_2 and H_2 of 0.41 Å, the separation factor is somewhat small (approximately 5). This result may be caused by an interaction of CO_2 with the silica membrane surface which increases the surface concentration and the permeability. On this basis, we expect the selectivity for H_2 to increase with increasing temperature because the surface coverage of CO_2 should decrease at higher temperatures; this trend is what is observed.

Surface diffusion has been observed previously during gas permeability measurements with microporous alumina membranes. Van Vuren et al. (*19*) studied the transport of H_2, N_2, and CO_2 through γ-alumina membranes at ambient pressure and moderate temperatures. Transport of H_2 and N_2 was described by Knudsen diffusion theory, and CO_2 permeabilities were 30% higher than predicted on the basis of molecular weight differences. The authors attributed the difference to surface diffusion of weakly adsorbed CO_2. The effect of surface diffusion decreased at constant pressure as the temperature was increased to 373 K. In Van Vuren's study, transport of CO_2 was probably a result of both surface diffusion and Knudsen diffusion.

Analogously, both surface diffusion and molecular sieving appear to be contributing to the permeability of the silica hollow fibers. Without knowledge of the pore size distribution, it is difficult to quantitatively assign the importance of each mechanism. However, a qualitative explanation could be that the smallest pores provide the selectivity of the separation, and the larger pores provide much of the permeability at the cost of selectivity. As discussed above, the gas permeability appears to depend on molecular size and the degree that the gas molecules interact with the surface. Molecules with a larger surface interaction will have higher permeabilities than those of a noninteracting gas of similar size.

CONCLUSIONS

We have reported that microporous silica hollow fibers can be used as gas separation membranes. Single component permeabilities were measured for several noncondensible permanent gases including He, H_2, CO_2, N_2, and CO at 298, 313, and 343 K. High ideal separation factors (permeability ratios) of 163 and 62 are observed at 343 K for H_2/N_2 and H_2/CO, respectively. The transport mechanism cannot be explained by solution-diffusion or Knudsen diffusion mechanisms. Proposed mass transfer mechanisms are surface diffusion and molecular sieving. Molecular sieving appears to be the dominant mechanism. Surface diffusion depends on the degree that the gas molecules interact with the silica surface and makes possible the observed ability of CO to permeate faster than N_2, even though N_2 has a smaller kinetic diameter. Further fundamental research is needed to understand the microstructure and mass transfer mechanism in these novel materials.

Acknowledgments

The authors gratefully acknowledge financial support from the Department of Energy Morgantown Energy Technology Center (Contract DE-AC21-88MC25204) and PPG Industries for donation of the silica hollow fibers used in this study. The COTRs at METC were Mr. Daniel C. Cicero and Ms. Lisa A. Jarr. The authors would also like to thank Dr. Joseph J. Hammel, Mr. Walter J. Robertson, and Dr. Yaw Yang at PPG Industries for helpful discussions.

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Received by editor February 26, 1990