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Experiments and Simulation of Transport and Separation of Gas Mixtures in Carbon Molecular Sieve Membranes†

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We report here the results of our recent studies describing the preparation of carbon molecular sieve membranes, their separation and transport characteristics with gas mixtures, and their molecular simulation. Poly(furfuryl alcohol) (PFFA) was used as the polymeric precursor for the preparation of the carbon films. The membranes were tested using single gases H_2, CO_2, CO, CH_4, and Ar, as well as binary mixtures of CO_2/CH_4 and a four-gas mixture consisting of $CO_2/CO/H_2/CH_4$. Separation factors for CO_2/CH_4 in the range of 34−37 were obtained for the binary and the four-gas mixtures. The membrane permeance decreased slowly during continuous testing with the four-gas mixture. This decline in performance was found, however, to be reversible. The initial membrane permeance was recovered by heating the membrane in an inert atmosphere of Ar. Modeling of the membrane's transport characteristics was carried out using a nonequilibrium molecular dynamics simulation. The modeling results agree qualitatively with the experimental data.

Introduction

Conventional separation systems are among the most energy demanding units in chemical process plants. The energy that is consumed in such operations not only increases the operating costs of the separation process itself but often has adverse environmental impacts that must be minimized. As a result, there has been a strong incentive in recent years for developing novel technologies to replace the more conventional separation techniques. A class of such technologies that are increasingly finding more widespread acceptance are membrane-based separations. A number of commercial gas-phase separations for the purification of a variety of gaseous mixtures are currently utilizing nonporous polymeric membranes.[1] These membranes often show good separation efficiency for molecules which are similar in size and shape, which present unique challenges for conventional separations. The good separation properties of nonporous polymeric membranes are due to their unique mechanism of transport, which involves solvation of the molecules into the polymeric film followed by solid-phase molecular diffusion. Differences in permeation characteristics among the various molecules can be attributed either to differences in solubility or to differences in the transport properties, or both. By choosing both the right polymer and preparation technique, a number of polymeric membranes have been obtained which show high separation factors for a variety of gaseous mixtures. These polymeric membranes, however, typically have low permeabilities making them impractical for several industrial gas separation applications. And though a number of glassy polymeric membranes with good thermal resistance exist, their safe operating temperatures are generally below the temperatures which would make them appropriate for use in "high-temperature" petrochemical applications. This restricts their application to the range of low to moderate temperatures.

The technical limitations of polymeric membranes have, in recent years, motivated the development of dense SiO_2 and metal membranes, as well as of porous inorganic membranes as alternative systems for use in high-temperature separations. Dense metal membranes (mostly Pd and Pd alloys but in recent years also a variety of other materials) are probably among the earliest membrane systems utilized for gas-phase separations. They are applicable to the separation of hydrogen from various gaseous mixtures, because hydrogen can transport through their metal lattice while other gases cannot. The problem with metal membranes, at least in the early years of development, was their high cost and relatively poor mechanical stability. Progress in both areas is being made in recent years. Dense SiO_2 membranes made by CVD techniques are more recent. Like the metal membranes they are capable of transporting hydrogen while excluding other gases. Existing SiO_2 membranes, however, have low hydrogen permeability and a reported sensitivity to H_2O vapor which seems to cause irreversible structure densification.

The earlier porous inorganic membranes (porous glass membranes notwithstanding) were mesoporous γ-alumina membranes prepared by sol−gel techniques.[2−4] The average pore size for these membranes is typically in the range of 25−100 Å. Gaseous molecules permeate through these membranes mainly by Knudsen diffusion (with some additional small contribution from surface diffusion at low temperatures). Though the permeability of these membranes is much higher than that of most polymeric membranes, their selectivity, for the majority of gaseous mixtures, is usually too low to make them appropriate for use in efficient gas-phase separation systems.

This has motivated the development of microporous inorganic membranes made from a variety of crystalline zeolitic materials by hydrothermal routes[5−8] and also amorphous silicas made via

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[†] This paper is written in celebration of the 80th birthday of Dr. Sidney Benson, a valuable friend and colleague for many years.

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sol−gel[9−13] and CVD techniques.[14−19] The resulting membranes have small mean pore diameters (typically <10 Å) comparable to the size of the molecules to be separated. As a result, they exhibit molecular sieving behavior. Separation of various molecules occurs as a combined outcome of their differing characteristics in terms of entering the pore structure and of the distinctly different transport and sorption behavior within the porous structure itself. The overall permeation process is generally activated and, as a result, exhibits a strong sensitivity to temperature. Increasing the temperature generally favors the permeation of the more mobile and less adsorbable species. At lower temperatures, microporous membranes often exhibit interesting behavior in which the more adsorbable species in a gaseous mixture adsorb and condense within the pore structure, preventing lighter and more mobile molecules from transporting through the membrane. The advantage of allowing the larger molecules, which are often impurities or the byproducts, to pass through the membrane to the permeate side, is that the smaller molecules remain in the high-pressure, retentate side.[20] No further need, therefore, exists for compressing the product stream to higher pressure for further processing. This is especially beneficial in the purification of hydrogen streams containing hydrocarbon impurities. It is also useful in the separation of methane from carbon dioxide in reforming units and in the upgrading of landfill gas. Inorganic membranes are quite stable at high temperatures and, therefore, better suited than polymeric membranes for moderate to high-temperature applications. It still remains a technical challenge, however, to prepare pinhole-free, large area zeolitic microporous membranes. And for amorphous silica-based membranes the irreversible loss of pore volume, when H_2O vapor is present, still remains an insurmountable challenge.

Carbon Molecular Sieve Membranes

Carbon molecular sieve membranes (CMSMs) prepared by the carbonization of polymeric precursors have been studied in the past few years as a promising alternative to both inorganic and polymeric membranes. They have, however, received relatively less attention than the competing zeolitic and amorphous silica systems. These membranes have been shown to have, for many commercially interesting separations, equal or higher permselectivity than polymeric membranes and a high enough permeability so as to be comparable with the microporous inorganic membranes. This makes them potentially attractive for a number of industrial applications. The CMSMs that have been reported so far have been prepared by pyrolysis, typically in an inert atmosphere, of either polymeric hollow fibers or thin polymeric films coated on porous substrates. The pyrolysis is generally carried out at temperatures between 500−1000 °C, depending on the polymer and the required final membrane structure. Depending on the conditions, the pyrolysis process removes most of the heteroatoms originally present in the polymeric macromolecules while leaving behind a cross-linked and stiff carbon matrix. It has been found possible to generate crack-free films by controlling the preparation and carbonization conditions. These include the concentration of the polymeric precursor solution, the carbonization temperature, and the heating rate. The CMSMs thus prepared have an amorphous porous structure created by the evolution of gases generated during the pyrolysis of the polymeric precursors. Though they are amorphous in nature one still finds in CMSMs subdomains where the structure of the polymeric precursors can still be recognized. This subdomain structure in part determines the differences that are found in the performance of CMSMs derived from various polymeric precursors. The extent of this subdomain structure also depends on the pyrolysis conditions. The higher the temperature and the longer the pyrolysis period is, the less similarity one finds between the final carbon matrix and the initial polymeric precursor structure. In some instances, for high carbonization temperatures, it has even been observed that the final carbon structure consists of graphite layers connected through a network of random pores created, as previously noted, by the gases generated during the pyrolysis process.

An area of current interest, motivating the development of CMSMs (and of microporous membranes in general), is the separation of CO_2 from gaseous mixtures. Applications here involve the processing of reformate mixtures, the upgrading of biogas and landfill gas, and the treatment of flue gas. CMSMs are thought to potentially have an important role to play in this area. Preparation of CMSMs has followed two distinct routes: (1) either through the carbonization of preexisting polymeric substrates (e.g., hollow fibers, self-supporting thin polymeric films) or (2) through the carbonization of films deposited on underlying macro- and mesoporous supports. Carbonization of polymeric hollow fiber precursors was the technique utilized by Koresh and Sofer,[21] in their pioneering studies on the preparation of CMSMs. They prepared CMSMs by carbonization of a polymeric hollow fiber whose composition was not disclosed. They studied the effect of carbonization temperature by preparing membranes at 800 and 950 °C, as well as the effect of different activation methods (e.g., oxidation and outgassing at different conditions). For the He/N_2 gas pair, they have reported a separation factor of 2.0 and for the CO_2/N_2 gas pair a separation factor of 9.0, based on single-gas permeation tests. A number of studies have since followed. Jones and Koros,[22] for example, have prepared CMSMs by the carbonization of commercially available asymmetric hollow fiber polyimide membranes. Carbonization was carried out at two different temperatures, 500 and 550 °C. They reported an O_2/N_2 separation factor in the range of 11.0−14.0 and a CO_2/N_2 separation factor of about 55. Exposure of these membranes to volatile organic compounds (VOCs) at ambient temperatures resulted in losses in both permeance and selectivity.[23] For applications with “real” feeds this still remains a problem with all microporous membranes; the presence of VOCs in such feeds is, of course, also known to be detrimental to polymeric membranes. They have also studied the effect of humidified feeds on O_2/N_2 selectivity and permeability using feeds with relative humidity between 23 and 85%.[24] Some performance losses occurred at all humidity levels, with the losses increasing with increasing humidity level. This sensitivity to humidity at ambient conditions was reduced by rendering the membrane surface hydrophobic by coating it with a thin layer of Teflon.[25] It was also shown, in addition, that membranes carbonized at higher temperatures show smaller losses in performance in the presence of water vapor. In subsequent studies by the same group the effect of different pyrolysis conditions (in particular, the effect of the type and flow rate of the inert gas used) on the properties of CMSMs were studied.[26]

Haraya et al.[27] also prepared a CMSM by carbonization of a Kapton hollow fiber membrane at 950 °C. These membranes were, in some instances, further treated by coating them with a thin layer of polydimethyl siloxane (PDMS) to prevent gas flow through defects in the structure. The separation factors for the H_2/N_2 and He/N_2 gas pairs (based on single gas permeation tests) were reported to be 10 and 12.7, respectively, at 0 °C. The separation factors increased to 194 and 270.6 at 200 °C, but decreased to 151 and 173 at the higher temperature of 250 °C. Mixed-gas permeation tests were also performed with the PDMS-coated membrane for the H_2/CO and H_2/CO_2 binary mixtures in the temperature range of 0−150 °C with the best separation factors (51 and 39, respectively) obtained at 30 °C.

Shusen et al.[28] also reported the preparation of asymmetric CMSMs from the pyrolysis of thin self-supporting films of a thermosetting phenol−formaldehyde resin (50−100 μm average thickness) followed by controlled oxidation of only one side of the film. Separation factors of 23.6 and 10.6 (based on single-gas permeation studies) for the H_2/N_2 and O_2/N_2 gas pairs were reported at ambient temperatures.

A number of groups have reported the preparation of carbon membranes by the carbonization of polymeric films previously deposited on porous inorganic and metal substrates. Rao and Sircar,[29] for example, have prepared CMSMs by carbonization at 1000 °C (under a N_2 atmosphere) of a thin, uniform layer of poly (vinylidene chloride)acrylate terpolymer latex film deposited on a macroporous graphite or alumina support from an aqueous suspension. They have measured pure gas permeabilities of He and H_2 as well as mixed gas permeabilities of H_2−hydrocarbon mixtures. For a ternary mixture of CO_2, CH_4, and H_2 a CO_2/CH_4 separation factor of 18 was observed.[30] The membranes have also recently been tested in a pilot plant-scale unit.[31] These membranes work the best at ambient and subambient temperatures, where the membranes preferentially allow the permeation of hydrocarbons and carbon dioxide over hydrogen.

Hayashi et al.[32] prepared CMSMs by the carbonization of thin polyimide films deposited on the outer surface of α-alumina tubular supports (mean pore diameter ∼1400 Å) at various temperatures between 500−900 °C. The resulting membranes showed a CO_2/CH_4 separation factor of about 100 (for a carbonization temperature of 800 °C) at 30 °C. They studied the effect of carbonization temperature on permselectivity and permeance of the membrane. They showed that for the CO_2/N_2, and CO_2/CH_4 binary mixtures the higher the carbonization temperature the greater the selectivity and the lower the permeance of the resulting membranes. They have also studied the permeation and selectivity of the C_2H_6/C_2H_4 and C_3H_6/C_3H_8 binary mixtures in a membrane that was carbonized at 700 °C.[33] The membrane showed separation factors of 7 and 56 for the C_2H_4/C_2H_6 and C_3H_6/C_3H_8 binary mixtures, respectively. The same group has also studied the feasibility of modifying the pore size of carbon membranes by pyrolysis of propylene within the membrane's pores.[34]

Foley et al.[35] prepared a CMSM by pyrolysis of PFFA (poly(furfuryl alcohol)) films deposited on a macroporous sintered stainless steel flat plate. They measured the permeation of single gases (H_2, He, Ar, O_2, N_2, and SF_6) to determine the permselectivity of the membrane. Separation factors of 2−3 for the O_2/N_2 and up to 30 for the H_2/N_2 gas pairs were obtained from single-gas permeation experiments at 20 °C.

As seen from the above discussion, almost all of the early studies focused on the transport of single gases and binary mixtures with little work being done with more complicated mixtures. Little fundamental theoretical understanding exists, furthermore, of the phenomena that determine the permselectivity characteristics and permeance of such membranes.[36] Similar to amorphous carbon adsorbents, CMSMs have a high surface area and adsorptive capacity toward many molecules, mostly through van der Waals type forces. Thus differences in the adsorptive capacity between various species in a mixture play a significant role in determining the separation efficiency. Pore filling and condensation, hindered and surface diffusion, are the additional main factors in determining the permeation and molecular sieving characteristics at lower temperatures. At higher temperatures, the permeation mechanism changes to activated diffusion and, as a result, the membrane allows the smaller molecules to permeate through more efficiently.

In this paper we report results of our ongoing investigation of the preparation and transport characteristics of carbon molecular sieve membranes. Our study has three primary goals: (i) to develop cost-efficient preparation techniques for membranes with acceptable permeances and separation factors, (ii) to apply such membranes to the separation of gaseous mixtures with an immediate industrial potential, and (iii) to develop a fundamental understanding of the transport phenomena occurring in such membranes through the development of effective nonequilibrium molecular dynamics models.

In the paper attention will be mostly focused on the first two aspects of our work with only a brief discussion at the end of the paper devoted to the modeling aspects of the research. The membranes, whose preparation and transport characteristics are reported here, were prepared by the carbonization of PFFA films. Our work is, however, different from the research of Foley and co-workers[35] in two important regards: (i) our membranes are tubular in shape, and (ii) we utilize ceramic rather than porous metal substrates.

Transport investigations are reported with two gaseous mixtures. These are the binary CO_2/CH_4 mixture, of interest in the upgrading of biogas and landfill gas (which mainly consist of CO_2 and CH_4, after the trace amounts of organic impurities are removed), and the quartenary (e.g., four-gas) mixture of CH_4, H_2, CO, and CO_2, which is of interest in the processing of reformate mixtures. With the exception of the studies of Sircar, Rao, and co-workers, this is the only study we know that reports transport experiments with a multicomponent mixture using a CMSM. The study of Sircar and co-workers[29−31] utilized a different membrane and was carried out in a different region of experimental conditions (i.e., ambient and subambient).

The paper is organized as follows: First we describe the preparation techniques. Following that, we discuss the transport investigations. We conclude with a discussion on the modeling of transport using nonequilibrium molecular dynamic (NEMD) techniques.

Membrane Preparation

Poly(furfuryl alcohol) (PFFA) resin was chosen as the polymeric precursor for the preparation of the membranes. PFFA is produced by the acid catalyzed polymerization of furfuryl alcohol, a member of the furan family, and is among the rare examples of synthetic polymers not derived from petroleum. Their origin instead is biomass (e.g., agricultural waste). The resinification of furfuryl alcohol has been studied by spectroscopic and NMR techniques. It involves in the initial phase the polycondensation of a methylol group and the furan ring to give predominantly linear chains, followed by branching and ultimately cross-linking due to the condensation between methylene and methylol groups among neighboring chains.[37] PFFA is a thermosetting resin. It is potentially a good material for the preparation of CMSMs, because of its high carbon yield and the fact that it is a nongraphitizing polymer, which means that its carbonization, even at elevated temperatures (up to 1400 °C), is known not to result in a graphitic structure.[38] This behavior is attributed to the lack of proper (i.e., low activation energy) "pathways" from the initial (e.g., polymeric) to a potentially graphitic final structure because of the high cross-linking density in the precarbonized film. As a result of this high cross-linking density, graphitization requires a relatively higher temperature and time.[39]

To prepare the carbon membranes, thin films of PFFA were first deposited on porous substrates intended to provide the membrane with the required mechanical strength for applications. In our studies tubular rather than flat substrates were used as the carbon membrane supports. Tubular membranes might present advantages for the large-scale applications we envision because of the flexibility they provide when packed together in honeycomblike modules. Ceramic rather than metal supports were selected, furthermore, to avoid the potential (during high-temperature applications) of undesirable interactions between the carbon film and the underlying metal support. The support substrates, supplied by U.S. Filter (Membralox), were cylindrical alumina tubes (7 mm i.d., 10 mm o.d.) consisting of four layers. As reported by the manufacturer, the innermost layer is made of a γ-alumina film about 5 μm thick containing pores with an average diameter of 40 Å. The second and third layers of the membrane consisted of α-alumina layers with average pore diameters of 2000 and 8000 Å and thickness of 30 and 50 μm, respectively. The outermost layer of the support membrane was about 1.5 mm thick and consisted of macroporous α-alumina containing pores with an average diameter of 15 μm. The tubes were purchased in 25 or 75 cm long sizes. For the experiments reported here they were cut in 5.5 cm long pieces, the ends glazed with a Duncan GL 611 Ultra clear glaze. Creating a dense, impermeable glaze along the support ends involves heat treatment for 2 h at 850 °C. During this procedure some pore widening occurs to a mean pore diameter ~100−120 Å.

One of the advantages of CMSMs over other microporous membranes is their relative ease in preparation and repair of pinholes and other defects that might invariably develop during use, especially under high-temperature conditions. Repair of damaged membranes (or those in which preparation has failed to produce good permselective layers) involves burning the carbon layer off the porous support. This procedure generates heat, which can raise the surface temperature and is likely to result in damage to the underlying γ-alumina support membrane layer. We have adopted the following procedure in preparing the supports (after the carbon film had been burned off) for further film deposition. The supports were first cleaned with isopropyl alcohol in an ultrasonic bath for 1 h. They were subsequently dip coated by a boehmite solution. The sol was prepared according to Yoldas.[40] The preparation procedure involved first dissolving 9 g of aluminum-*sec*-butoxide in 30 mL of *sec*-butyl alcohol. The resulting solution was then diluted with 180 mL of deionized water. Upon addition of water, a boehmite precipitate was formed by hydrolysis. This precipitate was subsequently peptized by addition of an 8 N HCl solution at 85 °C under refluxing conditions. To the peptized boehmite solution was added 3 mL of polyvinyl alcohol (PVA) solution. This solution was prepared by adding 0.5 g of PVA to 5 mL of a 1 M HCl solution in 50 mL of water. The addition of the PVA solution is to help prevent crack formation during the calcination of films.[41] The substrates were subsequently dried in air for 48 h. The dried membrane was then calcined in air. The calcination procedure involved raising the temperature at a rate of 0.2 °C/min until it reached 100 °C, where it was held constant for 4 h. Subsequently the temperature was raised under the same heating rate to 500 °C and was held constant there for 6 h. The membrane was then cooled very slowly down to room temperature. This procedure was repeated each time a new coating was added. To determine whether the support is ready for the next step (i.e., the coating by the polymeric film) we measure the permeance of Ar through the membrane at a fixed temperature and transmembrane pressure gradient after each calcination step. Supports, whose permeance was lower than a given value, were deemed ready for use in the carbon film deposition procedure. Those with permeances above this value were subjected to further dip coating and calcination steps. Although this simple test cannot guarantee the exact same porous structure for the supports it has been shown to be an effective, nondestructive means for choosing a reliable support for subsequent polymer coating.

TABLE 1: Results of GPC Analysis for PFFA Resins Used for Membrane Preparation[a]

	M_n	M_p	M_w	polydispersity
March 17, 1997				
resin B1	1333	3356	3924	2.94
resin B2	1136	2073	2333	2.05
July 2, 1997				
resin B1	1194	2794	4089	3.43
resin B2	942	2132	2713	2.88

[a] $M_w = \Sigma n_i M_i^2/\Sigma n_i M_i$; $M_n = \Sigma n_i M_i/\Sigma n_i$.

Our studies have shown that the state of the PFFA resin plays an important role in one's ability to prepare good quality membranes. The state of the resin, furthermore, seems to be dependent on environmental factors such as the storage conditions. Table 1, for example, shows the analysis results, using gel permeation chromatography (GPC), of two samples (hereinafter referred to as samples B1 and B2) from lot 9-31-23 purchased from Monomer Polymer and Dajac Laboratories, Inc., PA, several months apart analyzed on the same day in our laboratories. Sample B1 up to that point had been stored under "dark conditions" in a hood. The results show that both PFFA resin samples had relatively low average molecular weight ~1100−1400. There are clear differences between the samples, however. As it can be seen in Table 1, resin B2 has a smaller average molecular weight than resin B1. Additionally, the average molecular weight of both resins, when analyzed 3.5 months later, had dropped even further (see Table 1). Though the main reason for the change in average molecular weight is, probably, slow degradation[37] of the resin, increases in the polydispersity and in M_w are indicative that some polymerization also takes place.

We are not exactly sure why (further investigations are currently in progress) but, upon receiving the resin B2, we found it impossible to prepare good microporous membranes (the resulting membranes were either essentially impermeable or had very low permeability) using a procedure that was previously established by our group with resin B1. This procedure involves dissolving the resin in toluene, while stirring rigorously at 20 °C for 16−20 h. When the solution is prepared, it is used in the making of the membranes by dip coating. This involves immersing the substrate (its exterior surface covered with Teflon tape) in the solution for 3−5 min and then withdrawing it out of the solution at a rate of 4 cm/min. The coated substrates were then allowed to dry for 48 h at room temperature in a clean box prior to carbonization. The carbonization was performed in the presence of flowing argon in a cylindrical furnace heated externally. For the carbonization the temperature was raised slowly (1 °C/min) and then held constant at temperatures of 100, 200, 350, and 450 °C for periods of 1 h each and then at 600 °C for a period of 4 h. The coating/carbonization procedure was repeated for as many layers as desired (see Discussion below). We found that the following procedure worked in resolving the problem we encountered in preparing membranes using the as received resin B2. During preparation the resin solution was heated at 65 °C under continuous solvent reflux for 24 h. During this heating treatment a gellike phase formed. The solution was then decanted to separate the gellike phase and the remaining solution was used to prepare membranes following the dip-coating procedure described above.

Transport Investigations

After the membranes were prepared, their separation characteristics were tested. The focus of the study was on applications involving landfill gas, biogas, and reformate mixtures. We have, therefore, investigated the transport of the single gases CH_4, CO, H_2, and CO_2 of relevance to such mixtures, and of Ar, which is the inert gas used in the membrane preparation. We have also investigated the transport characteristics of the binary mixture CO_2/CH_4 consisting of the two main components of biogas and the four-gas mixture $CH_4/CO/H_2/CO_2$.

The experimental apparatus utilized has been described in detail elsewhere.[42] Argon, methane, hydrogen, carbon dioxide, and carbon monoxide were all supplied from high-pressure gas cylinders equipped with regulators. The flow rates were controlled with Tylan FC-260 mass flow controllers. All gases used were 99.95% pure or better. They were, in addition, purified by passing them through drierite in order to capture any water vapor impurity that might be present and heated in a preheater (a stainless steel coil equipped with a pair of semihemispherical heaters controlled by an Omega CN2000 controller), which operated at the testing module temperature. They were then fed into the testing module containing the CMSM, a detailed description of which has also been provided elsewhere.[42] The membrane was sealed in the module using compressible graphite tape and compression fittings. The testing module was made of 316 SS and supplied with inlet and outlet ports for both its tube and permeate sides. Temperature control of the module was accomplished with a pair of semihemispherical heaters controlled by an Omega CN2000 temperature controller. The permeate- and tube-side effluents (for the mixed gas studies) were measured on stream using a Varian 3400 gas chromatograph. Pressure in the system was measured with an accuracy of 0.1 psia by Omega DP2000 pressure transducers. The tube side pressure was controlled by a needle valve placed in the outlet. The permeate side was maintained at atmospheric pressure. Measurement of the outlet gas flow rates was accomplished using a soap bubble rotameter. Membrane permeances were calculated by the following relationship:

$$P_j = \frac{VP_mT_0}{T_mP_02\pi RL(\Delta P)} \tag{1}$$

In the above relationship, P_j is the species permeance in cm^3(STP)/(cm^2 min psi), V is the volumetric flow of gas across the membrane in cm^3/min, P_m is the flow rate measurement pressure in psia, T_m is the flow rate measurement temperature in K, L is the membrane length in cm, R is the membrane radius in cm, $P_0 = 14.696$ psia, and $T_0 = 273.15$ K. ΔP is log−mean pressure difference between the tube and permeate sides defined as

$$\Delta P = \frac{(P_{t_1} - P_{p_1}) - (P_{t_2} - P_{p_2})}{\log\frac{P_{t_1} - P_{p_1}}{P_{t_2} - P_{p_2}}} \tag{2}$$

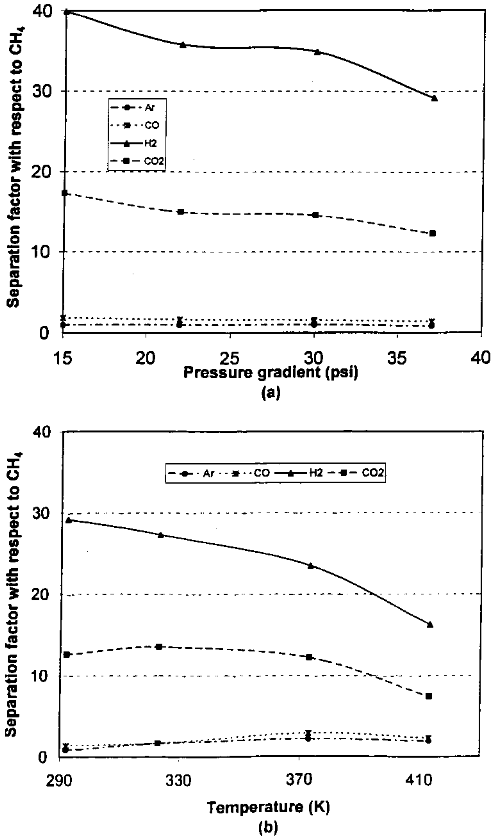

Figure 1. Separation factor with respect to CH_4 based on single gas permeation tests. (a) The effect of the pressure gradient under constant temperature ($T = 293$ K) conditions, and (b) the effect of temperature under a constant pressure gradient ($\Delta P = 40$ psi).

In the above equation, P_{p_1} is the test pressure at the permeate side inlet, P_{p_2} the pressure at the permeate side outlet, P_{t_1} the pressure at the tube side inlet, and P_{t_2} the pressure at the tube side outlet, all in psia. The separation factor, S_i of a given species i, is defined as the ratio of its measured permeance to the CH_4 permeance:

$$S_i = P_i/P_{CH_4} \tag{3}$$

Single-Gas Permeation Tests. The separation factors (with respect to methane) of four different gases (Ar, CO, H_2, and CO_2) measured by single-gas permeation tests are shown in Figure 1. In the tests whose results are shown in the top part of Figure 1, the temperature was kept constant at 292 K and the pressure gradient across the membrane was varied. The membrane in this figure was prepared using the resin B2, following the modified preparation procedure previously described. The permeances of CH_4, CO, and Ar are significantly lower than those of H_2 and CO_2, indicating that this membrane exhibits molecular sieving properties. The most permeable of all gases is hydrogen followed by CO_2. Much less permeable are CO, Ar, and CH_4. In Figure 1, as the pressure gradient increases the H_2 and CO_2 separation factors decrease by about 20%. This change is more a reflection of an increase in the permeance of CH_4, because the permeance of H_2 and CO_2 remain relatively unchanged. In fact, the permeance of hydrogen first slightly increases and then levels off. Sharper decreases in the separation factors are observed as a function of temperature (see bottom part of Figure 1). They are again the outcome of large gains in CH_4 permeance. The behavior in Figure 1 is attributable to the complex interaction of transport and sorption

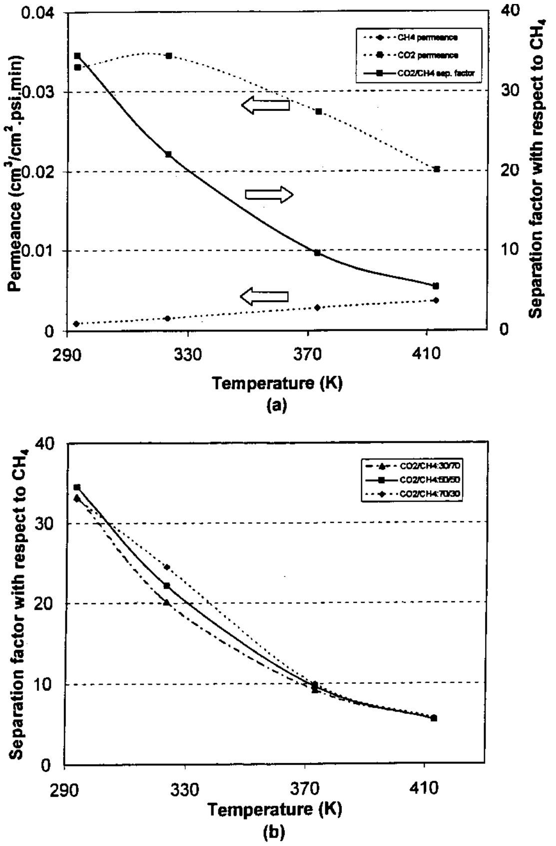

Figure 2. Permeance and separation factor with respect to CH_4 of binary mixtures of CO_2/CH_4 as a function of temperature ($\Delta P = 30$ psi). (a) Permeance and separation factor for an equimolar mixture and (b) separation factor for different gas compositions.

within the microporous membrane structure itself. Results of a detailed statistical/molecular dynamics model of these phenomena consistent with the experimental observations will be briefly described later in this paper.

Binary Mixture Tests. Binary mixtures of CO_2 and CH_4 of varying compositions were generated in order to allow us to study the separation behavior of CMSMs toward landfill gas and biogas. The permeances of CO_2 and CH_4 and the CO_2/CH_4 separation factor for an equimolar mixture as a function of temperature, at a constant transmembrane pressure gradient of 30 psi, are shown in the top part of Figure 2. The permeation behavior of both gases is very similar to the behavior observed during the single-gas permeation studies. While CH_4 permeation increases with temperature, showing an activated diffusion mechanism, CO_2 permeation passes through a maximum around 323 K and then decreases. The separation factor for this case decreases sharply as temperature increases, the final value being close to the single-gas permeation case. The bottom part of Figure 2 shows the CO_2 separation factor as a function of temperature for three mixture compositions. It appears that there is a slight increase in the separation factor with increasing content of CO_2 in the mixture. The differences are, however, not significant. The effect of temperature and composition on the separation factor of the binary mixture is nicely predicted by the molecular dynamics calculations of transport of the same gas mixture through slitlike graphite pores (see discussion to follow), indicative of the fact that the qualitative characteristics of transport are sorption dominated.

Four-Gas Mixture Tests. Experiments with two different membranes using an equimolar mixture consisting of four gases $CO_2/CO/CH_4/H_2$ are shown in Figure 3. The figure shows the effect of temperature on the permeance and separation factors for the gases in the mixture. One of the membranes in the figure was prepared with a fresh US Filter substrate utilizing resin B1 about 11 months after receiving the resin. The other membrane was prepared utilizing resin B2, using a substrate on which we had previously deposited a number of carbon layers which subsequently we burned away to reclaim the underlying substrate. There are, of course, differences both in the permeances and separation factors of both membranes. Given, however, that these membranes were more likely undergoing a "conditioning process" at least during part of the transport tests (see discussion to follow) and the fact that two different resins were used for their preparation, the reproducibility of the membrane preparation technique is, in our opinion, satisfactory.

Of interest in Figure 3 is the separation factor of different gases with respect to CH_4 over the temperature range tested. CO_2/CH_4 separation factors of 36.8 and 36.7 were obtained, at room temperature, indicating the potential of such membranes in the processing of reformate mixtures. One should also note that there is a difference between the H_2/CH_4 separation factor obtained in single gas tests and the same separation factor obtained in experiments with a four-gas mixture. During single-gas tests, H_2 is the most permeable among the four gases of the reformate mixture, while in the mixed gas permeability tests it is the CO_2 that is the most permeable species. The transport behavior of the individual components of the four-gas mixture is a strong function of the manner these species accommodate themselves within the pore structure. CO_2, as the molecular dynamics calculations indicate, is the most "adsorbable" of the four molecules in the mixture and, therefore, occupies most of the pore space. The permeability of the other three gaseous components reflects their ability to accommodate themselves within a CO_2 rich adsorbed phase.

The effect of preparation conditions on membrane permeance and separation factor is shown in Figure 4. In this figure the membrane was prepared with an initially fresh substrate, on which we deposited a number of successive carbon layers. After the deposition of each single polymeric film, the film was carbonized and the resulting membrane was subjected to permeation test with the equimolar reformate mixture, referred to above, for a region of experimental conditions. Upon the completion of the permeation tests, the membrane would be removed from the permeation apparatus and another PFFA film would then be placed on it, and then carbonized again. The results of tests with several successive film depositions/carbonizations are shown in Figure 4, plotted in terms of the separation factors of H_2 and CO_2 in the four-gas mixture as a function of the membrane's CH_4 permeance. The separation factors for both CO_2 and H_2 have been improved after adding each additional carbon layer. This improvement in separation factor is mainly due to the reduction in the number of pinholes and cracks of the carbon membrane's structure. However, the reduction in the CO_2 permeance observed after adding each new layer also suggests that the thickening of the carbon film as well as some pore narrowing may have also contributed to the separation performance enhancement, which is accompanied unfortunately by a reduction in the value of permeance.

Membrane Stability Tests. Our studies are of fundamental nature aiming at a better understanding of sorption and transport phenomena in microporous membranes. As such we have utilized UHP gases throughout the investigation and have in addition utilized adsorbents to remove any traces of humidity. As a result we have not observed any of the dramatic and sudden changes in permeance and separation factor that have previously

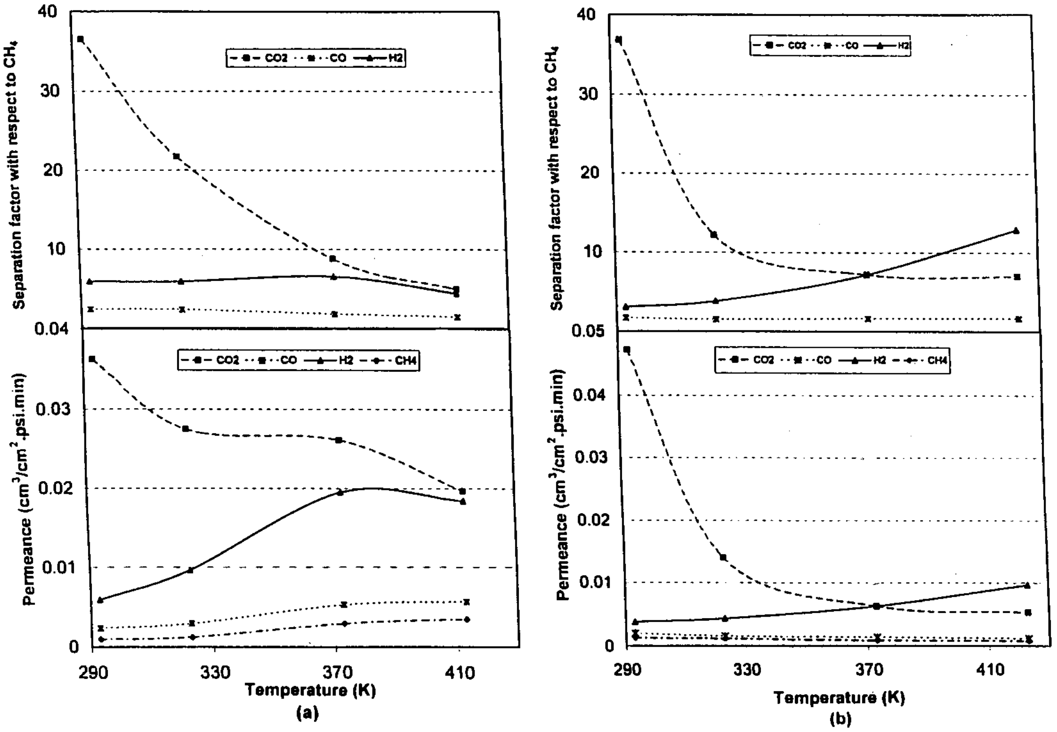

Figure 3. Permeances and separation factors with respect to CH_4 for an equimolar mixture of CO_2/CO/H_2/CH_4 as a function of temperature. (a) Membrane prepared from resin B2 ($\Delta P = 30$ psi) and (b) membrane prepared from resin B1 ($\Delta P = 30-40$ psi).

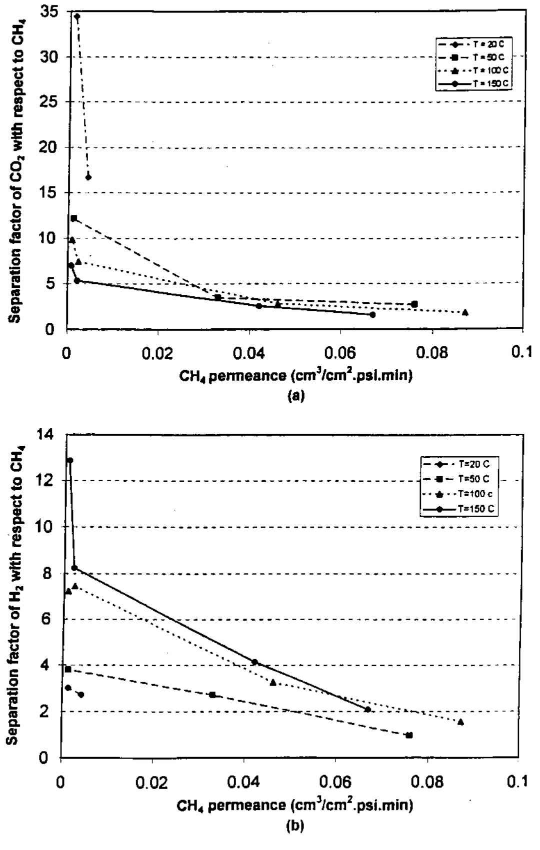

Figure 4. Separation factors with respect to CH_4 as a function of the corresponding CH_4 permeance at different temperatures. (a) CO_2 separation factor and (b) H_2 separation factor.

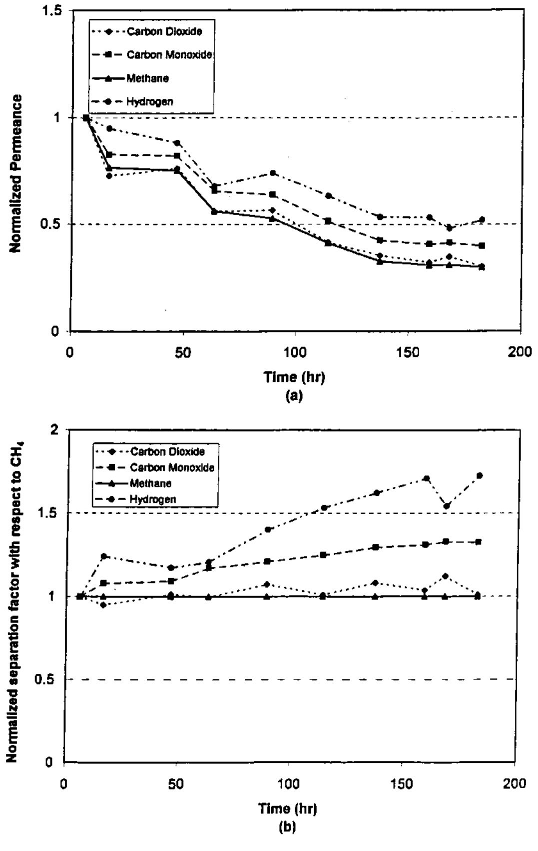

Figure 5. Normalized permeances and separation factors with respect to CH_4 for an equimolar mixture of CO_2/CO/H_2/CH_4 as a function of testing time ($T = 293$ K, $\Delta P = 30$ psi). (a) Normalized permeance and (b) normalized separation factor.

been reported by other investigators. Even though we are using UHP gases (99.95% or better), we have still on occasion observed noticeable changes in membrane performance. These changes are more significant during the low temperature runs.

For example, Figure 5 indicates the results of a transport investigation, in which the membrane was exposed continuously to the reformate mixture of gases for about 8 days at room-temperature conditions. Every day or so the membrane permeation characteristics were tested. In this figure we plot (top part) the normalized permeance (i.e., the ratio of the permeance at any time during the test to the permeance of the fresh membrane) in order to have a better basis for comparison in behavior observed among the various gaseous components. The normalized permeance of CO_2 and CH_4 dropped to about 0.4 after about 140 h of testing. After this period the rate in permeance reduction became very slow. CO_2 and CH_4 experienced larger drops in permeance than H_2 and CO did. The separation factor for CO_2 did not change over time (bottom part of Figure 5). The separation factor of H_2 and CO increased by about 60% and 30%, respectively. One of the possible reasons for the permeation loss could be the adsorption within the membrane of water vapor and other impurities, which may still be present even in the UHP feed stream, which would then result in slow transient changes in the state of the carbon surface. This explanation would also be consistent with the observed increase in the separation factor for H_2 and CO, which is probably due to the pore narrowing which makes the pores more selective in favor of molecules with smaller kinetic diameters. Whatever the reason causing the decline in permeation, the phenomenon is completely reversible. We could easily reverse the loss in permeation, for example, by treatment in an Ar atmosphere at 400 °C.

Modeling of Transport

In a parallel effort we are also modeling transport and sorption phenomena in microporous carbon membranes. In our studies we use novel nonequilibrium molecular dynamics techniques. Molecular models, which are based on either equilibrium or nonequilibrium molecular dynamics (NEMD) simulations, can provide a deeper understanding of the mechanisms of adsorption and transport in porous materials. In particular, NEMD is ideally suited for the practical situation in which an external driving force (e.g., a chemical potential gradient) is imposed on the system. Among such methods the grand-canonical molecular dynamics (GCMD) method,[43−45] in which Monte Carlo (MC) and MD simulations are combined in a dual control volume, has been used for calculating the diffusivity of a single gas through a slit pore. However, their extension to the technologically important problem of transport of a gas mixture through a porous medium is highly nontrivial, and the few attempts that have been made[46−49] in this direction suffer from several shortcomings and do not correspond to realistic experimental conditions.

In this paper we only discuss the study of transport and adsorption of a binary gas mixture in a slitlike carbon nanopore. Studies with multicomponent mixtures and more complex porous structures, which are currently in progress, will be discussed in future publications. We simulate transport of a binary mixture of CH_4 (component 1) and CO_2 (component 2) in a slit pore with periodic boundary conditions applied only in one direction. We utilized both smooth and structured pore walls. For the smooth walls, the classical 10-4-3 potential of Steele was used to calculate the interaction between a fluid atom and the wall.[50] The structured walls were composed of individual carbon atoms at fixed positions, consistent with the graphite structure. The two ends of the pore are exposed to bulk fluid at fixed gas concentration at high and low chemical potentials, respectively. In our simulation we combine MD moves and grand-canonical MC (GCMC) steps. The high and low chemical potentials are maintained constant by carrying out a sufficient number of GCMC particle (molecule) insertions and deletions. The ratio of the number of GCMC insertions and deletions to the number of MD steps between successive GCMC steps, which must be selected in such a way so that the correct density and chemical potentials in the bulk regions are maintained, and also reasonable transport rates at the boundaries between the bulk regions and the pore, are calculated, varied from 50:1 (for large pores) to 400:1 (for small pores). Details of the simulation method are discussed elsewhere.[36]

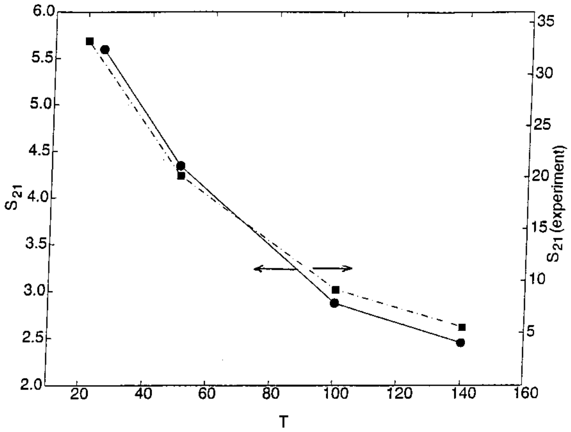

Figure 6. Comparison between experimental (square) and simulation (circle) results for the CO_2 separation factor with respect to CH_4 in a binary mixture of CO_2/CH_4 as a function of temperature (70% CH_4, 30% CO_2, $\Delta P_t = 2$ atm, $H_p = 2.2\ \sigma_{CH_4}$).

The simulation box in the direction x of the applied chemical potential gradient was divided into grids of size equal to σ_{CH_4}, the kinetic diameter of methane. For each MD step the density profiles $\rho_i(x)$ were obtained by averaging the number of particles of type i over a distance σ_{CH_4}. The flux J_i of component i was obtained by measuring the net number of particles crossing a given yz plane of area A_{yz}.

$$J_i = \frac{(N_i^{LR} - N_i^{RL})}{(n_s \Delta t A_{yz})} \tag{4}$$

In the above equation N_i^{LR} and N_i^{RL} are the numbers of gas molecules moving from left to right and from right to left, respectively. Δt is the MD time step (in the results reported in Figure 6, we used $\Delta t \approx 0.0137$ ps) and n_s is the number of MD steps over which the average was taken (we used $n_s = 5000$). The system was considered to have reached steady state when the fluxes calculated at various yz planes were within 5% from the averaged values. The permeability K_i of species i was then calculated from

$$K_i = \frac{J_i}{(\Delta P_i / L_p)} = \frac{L_p J_i}{\Delta P_i} \tag{5}$$

In the above equation ΔP_i is the partial pressure difference for species i across the pore. The most important properties of interest are the dynamic separation factor $S_{21}=K_2/K_1$ and its equilibrium counterpart for each bulk region defined as $S_{eq,j} = (\rho_{2j}/\rho_{1j})/(y_{2j}/y_{1j})$, where ρ_{1j} and ρ_{2j} are the average densities in the bulk region j ($j = 1$ and 2 correspond to the high and low bulk chemical potentials regions, respectively), obtained from the equilibrium GCMC calculations, and y_{1j} and y_{2j} are the corresponding bulk-phase mole fractions. In the calculations in Figure 6, we used total pressures of 3 and 1 atm in the high and low chemical potential bulk phase (consistent with the experimental transport measurements presented above). The dimensions of the pore were $W_p = 40\sigma_{CH_4}$, $L_p = 20\sigma_{CH_4}$. H_p, the slit height in the *z*-direction, was varied in the range of narrow pore sizes for which the membrane exhibits molecular sieving properties.

Our simulations indicate that CO_2 is adsorbed much more than CH_4 on the pore walls, with the adsorbed amount increasing with decreasing pore size H_p. Decreasing H_p, as a result, improves separation of the two gases (S_{21} increases). $S_{eq,j}$ the equilibrium separation factor corresponding to the high-pressure bulk region, is always larger than the dynamic separation factor S_{21}. This is because S_{21} involves diffusional mixing, which in the case of the CO_2/CH_4 binary mixture lowers separation of the two gases. We also find that there is very little difference between the results with the smooth and structured pore walls, and S_{21} is a strongly decreasing function of T. This is demonstrated in Figure 6, where we also compare the results with our experimental data which exhibit precisely the same qualitative behavior as the simulation results. Given all the simplifications that were made in our simulations, the close qualitative agreement between the simulation results and the data is very encouraging; Our current modeling investigations aim at improving the agreement between data and experiments by utilizing (1) more realistic descriptions of the pore structure (e.g., a network of interconnected pores), rather than a single pore, (2) more realistic molecular representation of the gas molecules (accounting, for example, for the electrical charges on the CO_2 molecule), (3) using more confined pore sizes that resemble more closely the membrane pore structure, and (4) accounting for entrance effects, which are present in the experiments and may hinder motion of one of the components into the membrane more strongly than the other.

Conclusions

We have described here the preparation of CMSMs by the carbonization of thin PFFA films deposited on tubular alumina substrates. These membranes show promise for application in the upgrading of the heating value of biogas and landfill gas, and for the processing of reformate mixtures. We have presented here transport investigations with single gases and mixtures of gases, which are of direct relevance to these applications. These membranes, during single gas experiments, show preferential permeation to hydrogen indicative of the fact that they are mostly crack-free, and that they exhibit molecular sieving properties. In studies with reformate-type mixtures, at lower temperatures, these membranes show preferential permeation toward CO_2, which is mostly due to its enhanced sorption affinity within the membrane structure.

The transport experiments with the binary gas mixture of CH_4 and CO_2 have shown a separation efficiency, which is significantly higher than its counterpart, based on single-gas tests. It was observed during our studies that increasing the concentration of CO_2 had a slight but generally beneficial effect on separation efficiency. These observations are consistent with theoretical investigations of the same mixtures in slitlike graphitic pores. A concise description of these simulation techniques has been presented. The experimentally observed permeances and separation factors and the results of the modeling investigations indicate that these membranes are potentially promising for application to the separation of CO_2 from landfill gas and biogas in order to upgrade their heating value. These membranes also show promise for application in the processing of reformate mixtures, which contain (in addition to H_2O) four gases, namely, CH_4, CO_2, CO, and H_2. Though concerns about the effect of humidity remain, techniques have been proposed by other groups that would make such membranes less susceptible to the presence of water vapor.[25]

As with all microporous and dense membrane systems, concerns always exist about the effect of impurities in the feed streams. The emphasis in this study was on fundamental issues, so we studiously avoided the presence of impurities in our test gas mixtures. Nevertheless, we still observed noticeable, but reversible changes in the membrane's permeation characteristics. One cannot, of course, never completely exclude the presence of an impurity, which can come even from the most unlikely of sources. Another equally plausible explanation of the "conditioning period" in the membrane performance that we observed is that it represents a kinetically controlled, transient period, during which time the membrane surface slowly equilibrates with the fluid phase. That the membrane permeation properties eventually reach a steady state value and the loss in permeation appears to be easily reversible are certainly consistent with such a view.

PFFA is an advantageous precursor for membrane preparation due to the ease in its handling and in the preparation of the precursor solutions. We were pleasantly surprised, however, by the fact that we were able to obtain continuous and pinhole-free PFFA polymeric films, which we were able subsequently to carbonize into promising membranes. We were expecting PFFA, as a low molecular weight polymer, to be difficult to prepare thin polymeric films with, which would be appropriate precursors for CMSMs for the selective separation of CO_2 from its mixture with other gases. We are also currently investigating a variety of other polymeric precursors to optimize the preparation techniques so that we can obtain a more CO_2 selective CMSM with reasonable permeance.

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List of Symbols

ρ_{1j}	molecular density of species 1 in the high ($j = 1$) or low ($j = 2$) chemical potential region (no. of molecules/Å^3)
ρ_{2j}	molecular density of species 2 in the high ($j = 1$) or low ($j = 2$) chemical potential region (no. of molecules/Å^3)
σ_{CH_4}	kinetic diameter of CH_4, angstroms
ΔP	log-mean pressure difference between the tube and permeate side
ΔP_i	partial pressure gradient of species i (atm)
ΔP_t	total pressure gradient (atm)
Δt	the MD time step, 0.0137 ps
A_{yz}	plane perpendicular to flow in simulation box (Å^2)
H_p	pore height (Å)
J_i	flux of species i (no. of molecules/Å^2.ps)
K_i	permeability of species i (no. of molecules Å/(Å^2 atm ps))
L	membrane length (cm)
L_p	pore length (Å)
N_i^{LR}	number of gas molecules moving from the left to the right
N_i^{RL}	number of gas molecules moving from the right to the left
n_s	the number of MD step used for averaging, 5000
P_0	reference pressure, 14.696 psia
P_j	species permeance (cm^3(STP)/(cm^2 min psi))
P_{p_1}	test pressure at permeate side inlet (psia)
P_{p_2}	test pressure at permeate side outlet (psia)
P_m	flow rate measurement pressure (psia)
P_{t_1}	test pressure at tube side inlet (psia)
P_{t_2}	test pressure at tube side outlet (psia)

R	membrane radius (cm)
S_{21}	dynamic separation factor of CO_2 with respect to CH_4
$S_{eq,j}$	equilibrium separation factor of CO_2 with respect to CH_4 in the high ($j = 1$) or low ($j = 2$) chemical potential region
S_i	separation factor of species i with respect to methane
T_0	reference temperature, 273.15 K
T_m	flow rate measurement temperature (K)
V	volumetric flow across the membrane (cm^3/min)
W_p	pore width (Å)
Y_{1j}	bulk mole fraction of species 1 in the high ($j = 1$) or low ($j = 2$) chemical potential region
Y_{2j}	bulk mole fraction of species 2 in the high ($j = 1$) or low ($j = 2$) chemical potential region

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