CARBON MOLECULAR SIEVE GAS SEPARATION MEMBRANES-I. PREPARATION AND CHARACTERIZATION BASED ON POLYIMIDE PRECURSORS

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Abstract—Carbon molecular sieving membranes are new, high-performance materials for gas separations. The selectivities of these membranes are much higher than those typically found with polymeric materials, and the selectivities are achieved without sacrificing productivity. Ultramicroporous carbon membranes can be produced by pyrolyzing various thermosetting polymeric materials under a variety of pyrolysis conditions. The membranes described in this paper were produced from the pyrolysis of a hollow-fiber polyimide precursor under conditions found to yield membranes with good air separation properties. Membranes were produced by two different temperature protocols, and were evaluated with mixed gas feeds at pressures ranging up to 200 psig (1.48 MPa). The lower temperature protocol yielded membranes with O_2/N_2 selectivities ranging from 8.5 to 11.5, and a higher temperature pyrolysis yielded membranes with selectivities ranging from 11.0 to 14.0. These membranes were found to be quite stable over time periods of several days with high-purity, dry feeds. Limited studies also showed that these membranes were highly effective for the separation of other mixed gas pairs, including CO_2/N_2, CO_2/CH_4, and H_2/CH_4.

Key Words—Polyimide pyrolysis, carbon molecular sieve membranes, gas separation.

1. INTRODUCTION

As the field of membrane technology evolves, potential application areas are continually being identified and expanded. One limit to incorporating membranes into many separation processes, however, has been the nature of the membrane material itself. In many cases the economic feasibility of membrane operations will only be met as membrane performance improves. Thus, researchers in the field of membrane technology have focused their efforts on the development of new, high-performance materials. In addition to having good separation properties, the membranes must also be resistant to degradation in various process environments. Carbon molecular sieve (CMS) membranes have been identified as very promising candidates for gas separation, both in terms of separation properties and stability.

Carbon molecular sieves are porous solids that contain constrictions or apertures that approach the molecular dimensions of the diffusing gas molecules. At these constrictions the interaction energy between the molecule and the carbon is comprised of both dispersive and repulsive interactions. When the opening becomes sufficiently small relative to the size of the diffusing molecule, the repulsive forces dominate, and the molecule requires activation energy to pass through the constriction. In this region of activated diffusion, molecules with only slight differences in size can be effectively separated through molecular sieving[1]. Carbon molecular sieves produced from the pyrolysis of polymeric materials have proved very effective for gas separation in adsorption applications[2-5].

In recent years there has been a growing interest in developing carbon molecular sieving membranes. One

approach has been to construct membranes through compaction of microporous carbon materials[6-8], but it has proven difficult to obtain continuous, microporous films. The process of pyrolyzing thermosetting polymeric membranes has recently emerged as a very promising technique for producing carbon membranes[9-14]. The following study describes the gas separation properties obtained with carbon membranes produced from a polyimide precursor. The selectivities obtained with CMS membranes are much higher than those seen with conventional polymeric materials, and the selectivities are achieved without sacrificing productivity.

In addition to the excellent separation properties, CMS membranes also offer the advantage of operation in environments prohibitive to polymeric materials. P. L. Walker *et al.* have reported that some carbon molecular sieves are stable at temperatures up to 1400°C and also in strongly acidic solutions[1]. Thus, CMS membranes appear to be a highly promising advancement in the field of membrane technology.

2. EXPERIMENTAL

2.1 *Making carbon membranes*

Through a systematic study of both precursor materials and pyrolysis parameters, protocols were developed for producing carbon membranes with very good gas separation properties. Carbon membranes were produced from the pyrolysis of several different hollow-fiber polymeric materials, including cellulose acetate, polyaramides, and polyimides. Membranes were pyrolyzed on stainless steel supports in Thermcraft® tube furnaces with Omega temperature controllers. The

best carbon membranes, in terms of both separation and mechanical properties, were produced from the pyrolysis of aromatic polyimides. A number of different variables comprise the pyrolysis process, and small changes in pyrolysis parameters were found to have significant impact on final carbon membrane properties.

The membranes described in this study were produced from the pyrolysis of an asymmetric hollow-fiber polyimide precursor. The precursor is typical of asymmetric membranes used in membrane-based gas separations with a selective skin layer on a porous substrate[15]. The polyimide is derived from a reaction of 2,4,6-trimethyl-1,3-phenylene diamine, 5,5-[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene]-1,3-isobenzo-furandione and 3,3′,4,4′-biphenyl tetra carboxylic acid dianhydride (Fig. 1).

Pyrolysis is carried out under vacuum (<1 torr), at temperatures of 500° and 550°C. The final pyrolysis temperature is reached in several steps, with heating rates starting at 13.3°C/min and slowing to 0.25°C/min as the final temperature is approached. The final pyrolysis temperature is held for 2 hours, and then the membranes are allowed to cool to room temperature in the furnace tube. As will be shown below, the resulting membranes have very good gas separation properties.

The degree of carbonization of the polyimide precursor increases with increasing pyrolysis temperature, and a temperature of 500°C was found to be sufficient to produce a highly carbonized membrane under the pyrolysis conditions described above. Initial electron spectroscopy for chemical analysis (ESCA) of a 500°C membrane revealed the presence of 95.0 atomic % carbon and 5.0 atomic % oxygen. Tens of angstroms of

fiber surface and surface-sorbed O_2 were next etched away by Argon ablation, and the sample was re-analyzed. The repeat analysis showed 98.7 atomic % carbon, 1.3 atomic % oxygen, and a barely detectable N_2 peak. These results confirm that the membranes are indeed primarily carbon.

Membranes produced from pyrolysis under vacuum were found to have better separation properties than those produced from pyrolysis with inert purge gases. The nature of the pyrolysis system, with numerous glass-to-metal seals and connections, makes very small air leaks inevitable. The resulting trace levels of O_2 present during pyrolysis become critical factors in determining final membrane properties.

The asymmetry of the precursor is carried through the pyrolysis process, and the resulting carbon membranes show a distinct transition in porosity through the film thickness. Not surprisingly, scanning electron micrographs (SEMs) of these two membrane types also show that the higher pyrolysis temperature membranes have a denser macropore structure (Fig. 2). The
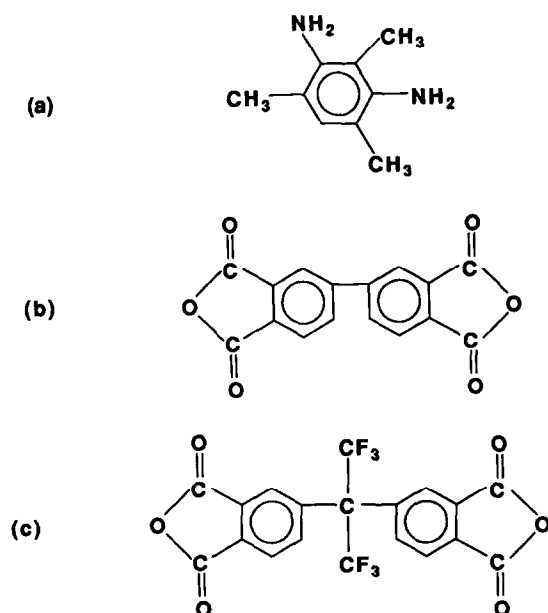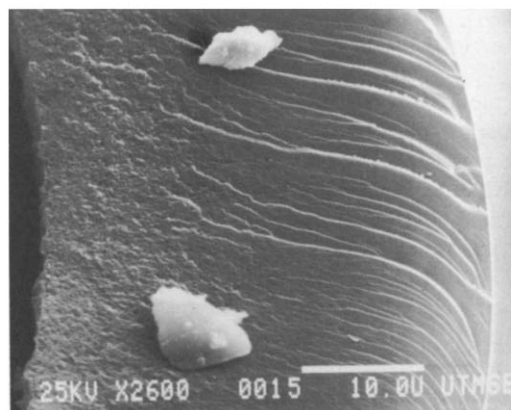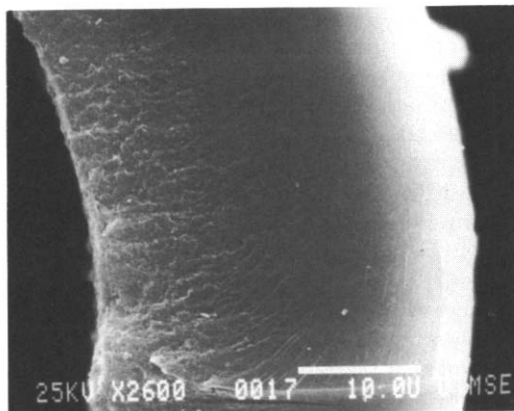

Fig. 1. Monomers used in polyimide synthesis. (a) 2,4,6-trimethyl-1,3-phenylene diamine (b) 3,3′,4,4′-biphenyl tetra carboxylic acid dianhydride (c) 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzofurandione.

wall thickness = 35μ

pyrolyzed at 500°C

wall thickness = 30μ

pyrolyzed at 550°C

Fig. 2. Effects of pyrolysis temperature on membrane porosity.

carbon membranes have outer diameters of 170 to 180 μm, with wall thicknesses of 30 to 35 μm.

2.2 Single fiber module construction

Characterization work has been done with single-fiber test modules constructed from $\frac{1}{4}''$ stainless steel tubing and Swagelok® $\frac{1}{4}''$ tees. A small length of tubing is attached to each arm of the tee to form a housing, as shown in Fig. 3. The hollow-fiber carbon membrane is threaded through the housing so that a length of carbon fiber extends on each end. Five-minute epoxy is used to plug the ends of the tubing, and the ends of the carbon membrane are snapped off after the epoxy hardens.

2.3 Membrane test system

A diagram of the membrane test system is shown in Fig. 4. The membrane module is attached in a bore feed method of operation, and the feeds are high-purity gases supplied from compressed gas cylinders. Feed pressures range up to 200 psig (1.48 MPa), and the system is run at ambient temperature. Also shown is a stainless steel canister used as a gas saturation vessel for the studies described in part 2.

Vacuum is maintained on the shell side of the hollow-fiber membrane, and the permeate is pulled through a calibrated sample volume connected to an MKS Instruments, Inc., Baratron pressure transducer (0–10 torr). By closing the sample volume valve to vacuum, the permeate pressure increase over a small period of time can be measured, and the flux calculated from the ideal gas law. Composition of the permeate is determined by gas chromatography using a Hewlett-Packard 5890 gas chromatograph with a thermal conductivity detector (TCD). The flux of each individual species is calculated and reported in gas permeation units (GPU).
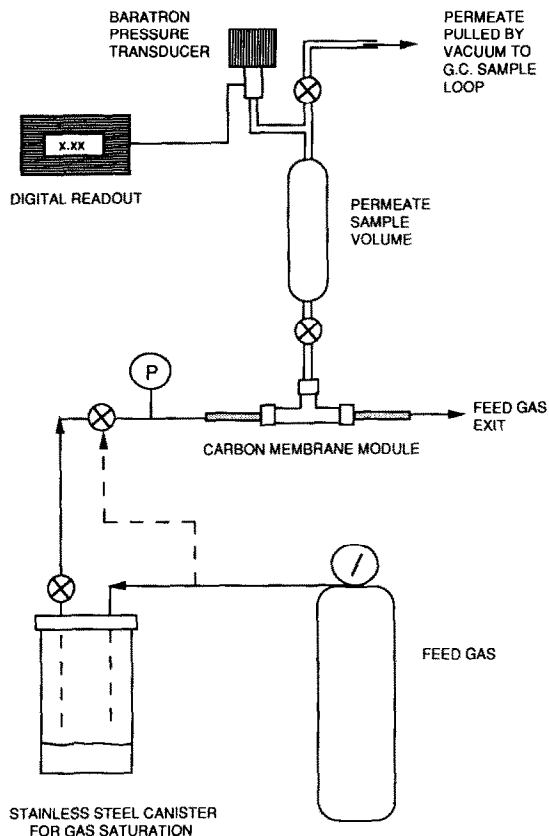

Fig. 4. Permeation system.

$$GPU = 10^{-6} \frac{cc(STP)}{sec\text{-}cm^2\text{-}cmHg}$$

$$= 3.35 \times 10^{-7} \frac{gmol}{m^2\text{-}sec\text{-}KPa}$$

3. RESULTS AND DISCUSSION

3.1 Air separation

The primary focus of the work to date has been the development of membranes that are highly effective for air separation applications, and the pyrolysis protocols described above were optimized for this separation process. The O_2/N_2 selectivities achieved with these membranes are quite high relative to polymeric materials, and these selectivities are achieved without sacrificing productivities. For each of the two protocols, samples from more than 20 different pyrolysis batches were evaluated with dry air feeds. The 500°C pyrolysis protocol typically produces membranes with O_2/N_2 selectivities ranging from 8.5 to 11.5, with O_2 fluxes of 20 to 50 GPU. The 550°C protocol produces membranes with O_2/N_2 selectivities ranging from 11.0 to 14.0, with O_2 fluxes of 15 to 40 GPU. The variations in membrane properties for a given protocol reflect the difficulty in maintaining identical conditions for each pyrolysis run. As a point of comparison, a

Fig. 3. Construction of carbon membrane modules for bore side feed.

very good asymmetric polysulfone membrane has an O_2/N_2 selectivity ranging from 5.5 to 6.2, with an O_2 flux of 20–30 GPU[16]. Thus, the molecular sieve carbon membranes offer exceptional gas separation properties, as compared to traditional polymeric materials.

The effect of feed pressure on membrane performance was evaluated with representative samples from each protocol, and results are shown in Figs. 5 and 6. Selectivity and productivity were measured as the feed pressure was incrementally increased up to 200 psig (1.48 MPa), and again as the pressure was incrementally decreased. The O_2 flux appears to be strongly influenced by the feed pressure at lower pressures in both membranes, but does not appear to be signifi-
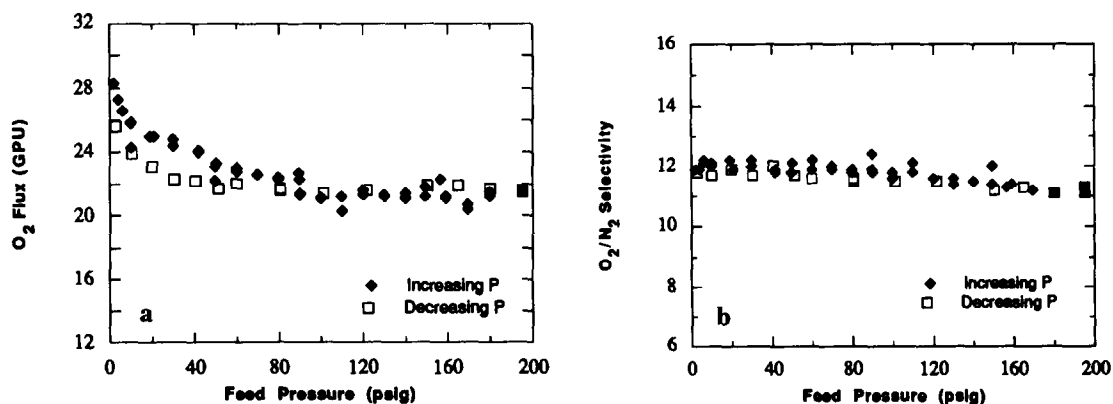

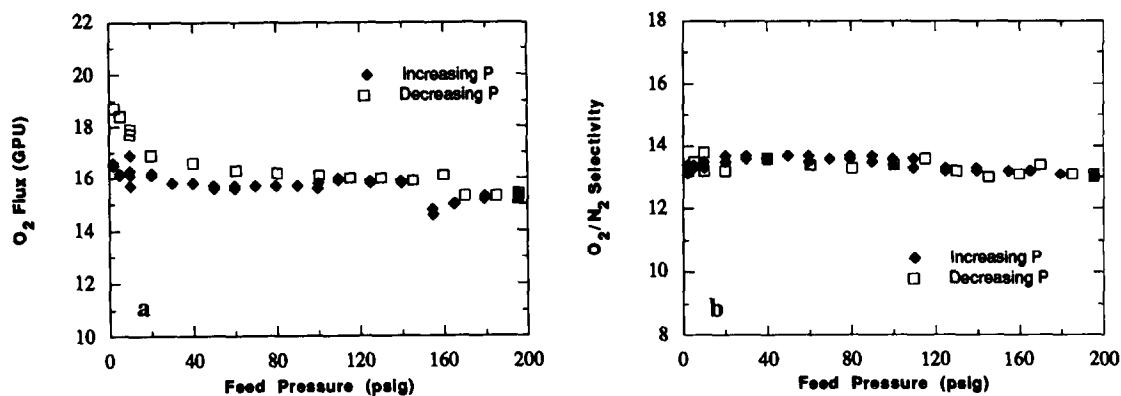Fig. 5. Pressure effects in 500°C membrane on (a) O_2 flux; (b) selectivity.

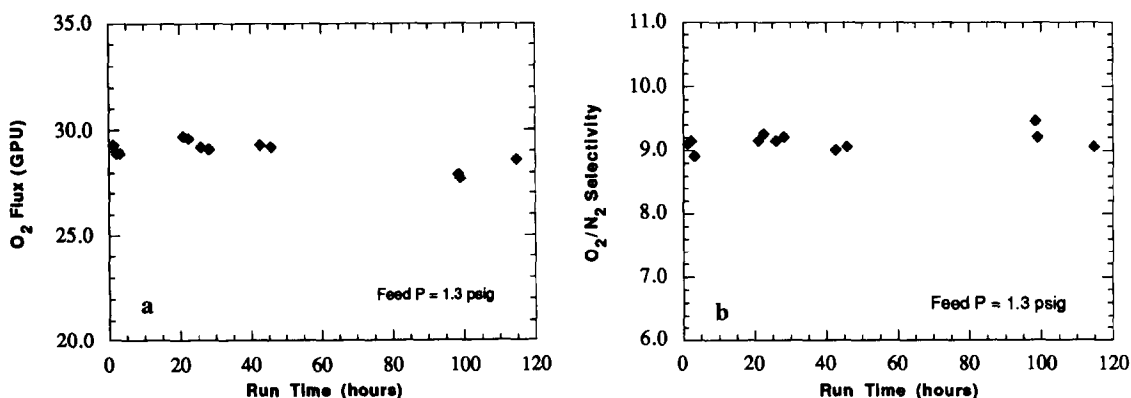Fig. 6. Pressure effects in 550°C membrane on (a) O_2 flux; (b) selectivity.

Fig. 7. (a) O_2 flux stability with dry air feed (500°C membrane); (b) O_2/N_2 selectivity stability with dry air feed (500°C membrane).

cantly affected by changes in pressure above 60–70 psig (515–584 KPa). Very little, if any, change is observed in the membrane selectivity over the 200 psig pressure range.

3.2 Membrane stability

Results of a run with another 500°C membrane are shown in Fig. 7, and demonstrate that the carbon membranes are quite stable with high-purity, dry feeds over time periods of several days. As these membranes are stored over longer periods of time, however, small changes in membrane properties are observed.

Membranes are stored in a very low-humidity, air environment. Over a period of months, the membrane selectivities tend to increase gradually as productivities decrease. This may be the result of gradual oxygen and/or H_2O sorption near the molecular sieving constriction points in the carbon matrix. The changes may also result from some slow rearrangements of the carbon matrix itself.

3.3 Other mixed gas separations

Limited studies have shown that these membranes are also highly effective for the separation of several other mixed gas pairs. Runs with CO_2/N_2, CO_2/CH_4, and H_2/CH_4 feed mixtures have demonstrated selectivities much higher than those typically observed with polymeric materials[17].

3.3.1 CO_2/N_2. One potential application area for the use of carbon membranes is the removal of CO_2 from flue gas. A typical flue gas might contain about 15% CO_2, with much of the balance being nitrogen introduced in the air for combustion. Accordingly, a feed gas mixture of 15% CO_2/85% N_2 was used for this study, and membrane performance was evaluated at feed pressures up to 195 psig (1.45 MPa). The membrane tested was produced by the 500°C protocol, and had an O_2/N_2 selectivity of 10.8, and an O_2 flux of 35.5 GPU.

As shown in Fig. 8 the CO_2 and N_2 fluxes decreased with increasing feed pressure at about the same rate. As a result, the membrane selectivity remained constant over the pressure range tested. The CO_2/N_2 selectivity of 55–56 measured for this membrane is very good relative to most polymeric materials, which have CO_2/N_2 selectivities typically ranging from 15–25. The CO_2 concentration in the permeate with this particular membrane was about 90%, and the permeate CO_2 concentration should be even higher in the membranes with higher O_2/N_2 selectivities. Thus, preliminary results indicate that these membranes would be very useful for removing CO_2 from flue gases.

3.3.2 CO_2/CH_4. The membrane used for this study was produced from the 550°C protocol, and proved highly effective for separating CO_2 and CH_4. The feed was a 50% CO_2/50% CH_4 mixture, and membrane performance was evaluated at pressures up to 150 psig (1.13 MPa). Several readings were made at each pressure step, and the values were averaged. Results from this run are shown in Fig. 9.
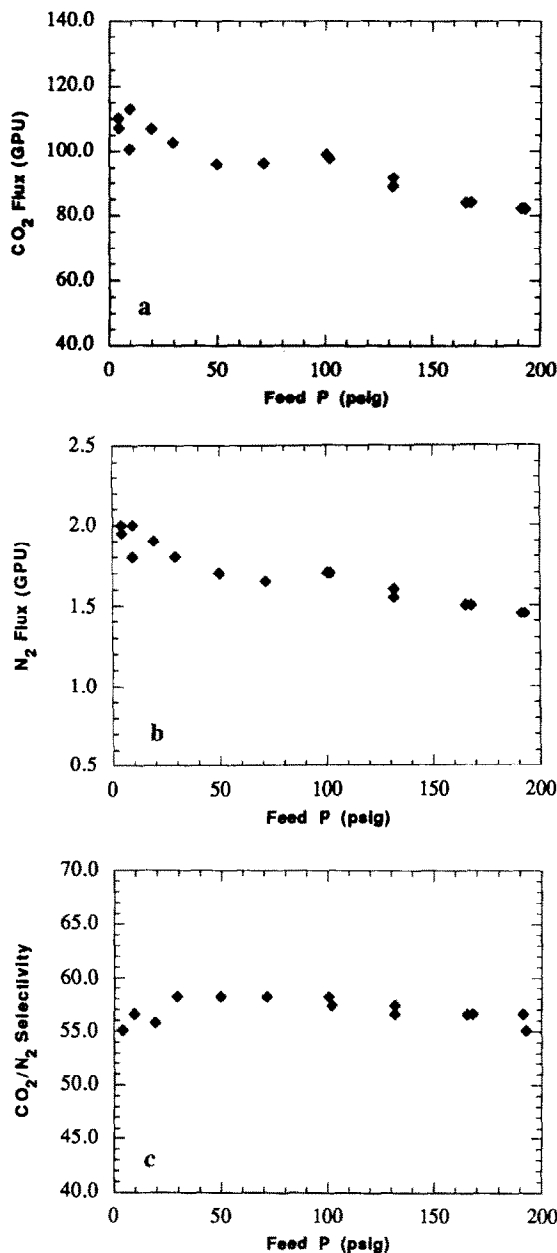

Fig. 8. Pressure effect with CO_2/N_2 feed on (a) CO_2 flux; (b) N_2 flux; (c) selectivity.

Although both CO_2 and CH_4 fluxes decline with increasing pressure, the decline is more pronounced with the CO_2. As a result, the membrane selectivity decreases as feed pressure increases. Even at higher pressures, however, the membrane selectivity is very good, compared to polymeric membranes. Whereas conventional polymeric membranes show typical CO_2/CH_4 selectivities of 15 to 40, a selectivity as high as 190 was achieved with the carbon membrane.

3.3.3 H_2/CH_4. Results from a run with a membrane produced by the 550°C protocol indicate that these membranes would also be highly effective in hydrogen recovery applications. The feed for this run
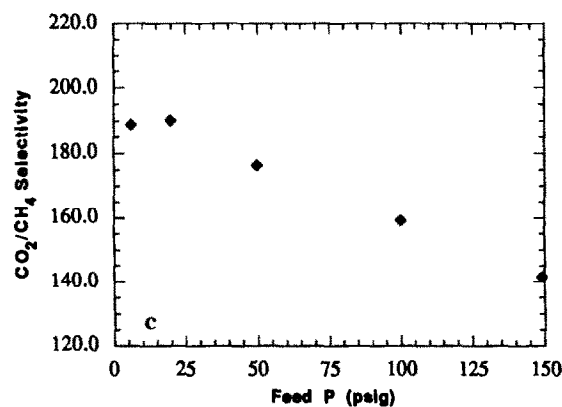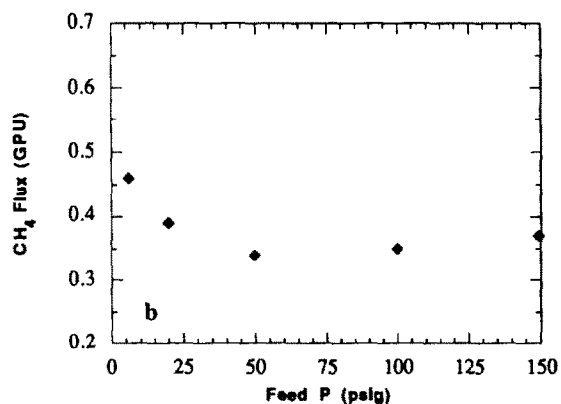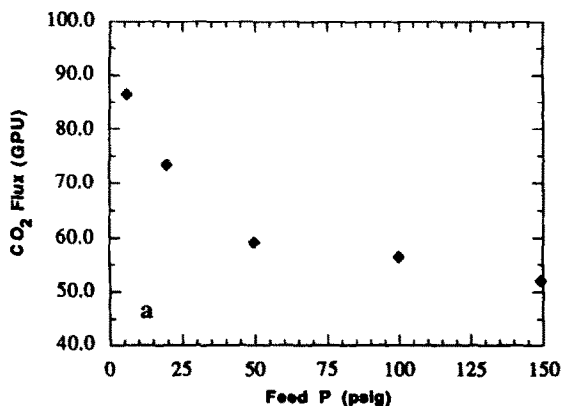
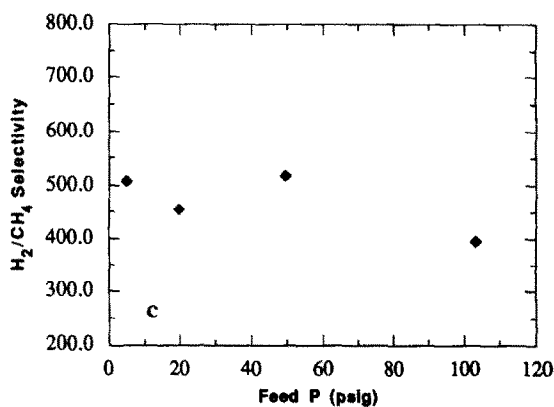Fig. 9. Pressure effect with CO_2/CH_4 feed on (a) CO_2 flux; (b) CH_4 flux; (c) selectivity.
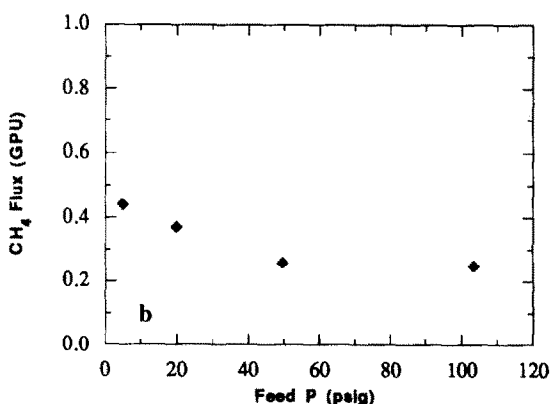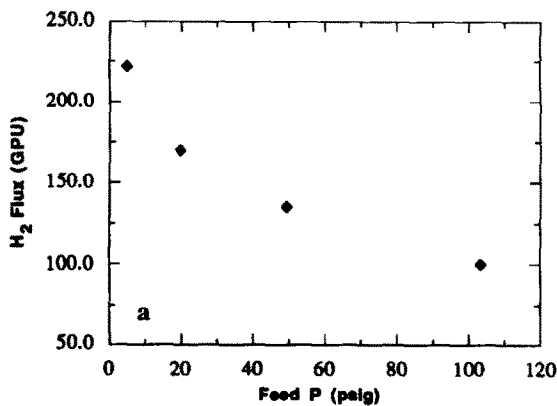
Fig. 10. Pressure effect with H_2/CH_4 feed on (a) H_2 flux; (b) CH_4 flux; (c) selectivity.

was a 50% H_2/50% CH_4 mixture, and performance was evaluated at pressures up to 105 psig (825 KPa). Several readings were taken at each pressure step, and the average values reported. Results from this run are shown in Fig. 10.

Both H_2 and CH_4 fluxes decline with increasing pressure, with the H_2 flux decline continuing over the pressure range studied. The CH_4 flux decline appears to level out at 50 psig (446 KPa), resulting in a gradual decline in the membrane selectivity at higher pressures. Again, the membrane selectivity for the H_2/CH_4

pair is very high, compared to values for polymeric membranes, which typically fall below 200.

4. CONCLUSIONS

Carbon molecular sieving membranes produced from the pyrolysis of a hollow-fiber polyimide precursor demonstrate exceptional gas separation capabilities. The selectivities obtained with these membranes are much higher than those found with conventional polymeric materials, and the selectivities are achieved

without sacrificing membrane productivity. Although the membranes described in this study were developed and optimized for air separation applications, limited studies show that they are also highly effective for other gas pair separations, including CO_2/N_2, CO_2/CH_4, and H_2/CH_4.

REFERENCES

1. P. L. Walker, Jr., L. G. Austin, and S. P. Nandi, In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 2, p. 257. Marcel Dekker, New York (1966).
2. J. Koresh and A. Soffer, *J.C.S. Faraday I* **76**, 2457 (1980).
3. J. Koresh and A. Soffer, *J.C.S. Faraday I* **76**, 2472 (1980).
4. J. Koresh and A. Soffer, *J.C.S. Faraday I* **77**, 3005 (1981).
5. A. Kapoor and R. T. Yang, *Chemical Engineering Science* **44**, 1723 (1989).
6. R. Ash, R. W. Baker, and R. M. Barrer, *Proc. Roy. Soc. A* **299**, 434 (1967).
7. R. Ash, R. W. Baker, and R. M. Barrer, *Proc. Roy. Soc. A* **304**, 407 (1968).
8. A. J. Bird and D. L. Trimm, *Carbon* **21**, 177 (1983).
9. J. Koresh and A. Soffer, *Sep. Sci. and Tech.* **18**, 723 (1983).
10. A. Soffer, J. Koresh, and S. Saggy, U.S. Patent 4,685,940 (1987).
11. M. Inagaki, S. Harada, T. Sato, T. Nakajima, Y. Horino, and K. Morita, *Carbon* **27**, 253 (1989).
12. H. Yoneyama and Y. Nishihara, U.S. Patent 5,089,135 (1992).
13. H. Hatori, Y. Yamada, and M. Shiraishi, *Carbon* **30**, 303 (1992).
14. H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, and S. Yoshitomi, *Carbon* **30**, 719 (1992).
15. O. M. Ekiner and G. Vassilatos, *J. Membr. Sci.* **53**, 259 (1990).
16. I. Pinnau, Ph.D. Dissertation, The University of Texas at Austin (1991).
17. W. J. Koros, M. R. Coleman, and D. R. B. Walker, *Annu. Rev. Mater. Sci.* **22**, 47 (1992).