Carbon molecular sieve structure development and membrane performance relationships

Meha Rungta[†], Graham B. Wenz[†], Chen Zhang, Liren Xu, Wulin Qiu, Jason S. Adams,

William J. Koros^{*}

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology,
311 Ferst Drive, Atlanta GA 30332, USA

Abstract

Characterization techniques beyond microscopy, scattering and spectroscopy approaches are needed to understand and improve sub-angstrom discrimination between penetrants in carbon molecular sieve (CMS) membranes. Here we use a method based on molecular scale gas diffusion probes to understand relevant membrane properties at the required level of detail. We further use this method to consider hypotheses about the evolution of structure responsible for fundamental properties of CMS materials derived from a high performance CMS precursor polymer, 6FDA:BPDA-DAM. While 6FDA:BPDA-DAM derived CMS membranes display a ~230 % improvement in CO₂ permeability when compared to Matrimid[®] derived CMS formed under the same conditions, the *diffusional selectivity* for these two materials are very similar at 35 and 38.5, respectively. These results indicate a non-trivial connection between CMS precursor material structure and resulting performance. Linking hypotheses about structural changes likely to occur during pyrolysis with the probe data provides insights regarding transformation of the random coil polyimide into ultra-rigid CMS, with exquisite size and shape diffusion selectivity. The results provide a framework for understanding and tuning properties of this special class of materials with important technological advantages in energy-intensive gas separations.

^{*}Corresponding author. Tel: +1 404 385 2845. Email: wjk@chbe.gatech.edu (W. J. Koros)

[†]M.R. and G.B.W contributed equally

1. Introduction and Background

Carbon molecular sieve (CMS) materials (1–6) surpass the permeability versus selectivity "upper bound" trade-off (7–10) of solution-processable polymers and provide a platform for creating advanced membranes. It is generally accepted that CMS transport properties rely upon a slit-like pore structure consisting of a distribution of larger ($\sim 7\text{--}20\text{ \AA}$) micropores connected by smaller ($< 7\text{ \AA}$) ultramicropore windows (3, 11–13). This fact notwithstanding, understanding the evolution of precursor semi-flexible polymers into final CMS structures is at an early stage. Figure 1a (i & ii) represent the CMS pore structure and bimodal distribution comprising micropores and ultramicropores. Figure 1b is a popular representation of a CMS material derived from a hydrocarbon precursor but it also provides a starting point for discussion of more complex CMS materials derived from polyimide precursors in our work, such as shown in Fig. 2.

Figure 1a. CMS (i) Ideal "slit-like" pore structure and (ii) Bimodal distribution of pores (1).

Figure 1b. Turbostratic carbon structure believed to represent some CMS materials (14).

Matrimid® (BTDA-DAPI)

BTDA: 3,3'-4,4'-benzophenone tetracarboxylic dianhydride

DAPI: 5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane

6FDA:BPDA-DAM (X=1, Y=1)

6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride

BPDA: 3,3'-4,4'-biphenyl tetracarboxylic dianhydride

DAM: 2,4,6-trimethyl-1,3-phenylene diamine

Figure 2. Chemical structure of semi-flexible precursor polyimides Matrimid® and 6FDA:BPDA-DAM(1:1).

Making a connection between the representations of the bimodal distribution of pores in Fig. 1a and a more chemically-relevant structure such as that in Fig. 1b is desirable—but challenging. It is reasonable to connect these two representations by attributing ultramicropores to defects *within the plates* shown in Fig. 1b, while attributing the micropores to the spaces *between the plates*. Of course, the details of the plate structure in such a picture will be different in a simpler hydrocarbon versus a polyimide derived CMS. Unlike oxygen-containing cellulosic and purely hydrocarbon precursors, the presence of fluorine and nitrogen in the polymer backbone introduces additional factors affecting the ultimate properties of the final CMS versus the case in Fig. 1b. Moreover, differences will exist even between CMS derived from different precursor polyimides (1, 15, 16); however, the general concepts and features should be similar, as is considered later in this discussion.

Previous work on CMS materials derived from Matrimid[®] and similar aromatic polyimide precursors noted the difficulties in using traditional characterization techniques, due to the amorphous nature of these materials (17–21). Recent work on more complex 6FDA-based polyimide precursors further highlighted the disconnect between precursor physical properties and the resulting CMS materials. This recent work documented the lack of direct physical connection between free volume and x-ray “d-spacings” of polymer precursors and corresponding properties of CMS (22). Considering these previous discussions, it is evident that this lack of a simple connection between the random coil precursor and the generally accepted slit-like structure of the final CMS, reminiscent to Fig. 1, needs to be addressed (1, 3). Establishing such a connection is critical to the advancement of the fundamental understanding of CMS materials. The current work aims to establish this important connection by discussing similarities and differences that arise from Matrimid[®] and 6FDA:BDPA-DAM derived CMS materials.

2. Transport Theory

Gas transport in CMS can be described using the sorption-diffusion model represented by Eq. 1, where, P_A is the permeability of component A, $\bar{D}_A$ and $\bar{S}_A$ are the average diffusion and sorption coefficients respectively. Permeability is measured in Barrer, where

$$1 \text{ Barrer} = 1 \times 10^{-10} [(\text{cc(STP) cm})/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})] = 3.34 \times 10^{-16} [(\text{mol})/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})].$$

$$P_A = \bar{D}_A \bar{S}_A \quad (1)$$

Gas molecules sorb into the CMS micropore sites and transport through the membrane by hopping from site to site, driven by a concentration gradient, which reflects the local chemical potential gradient of that penetrant. The critical ultramicropore windows restrict diffusion, allowing effective discrimination between similar sized gas molecules via a molecular sieving

effect (23, 24). These ultramicropore sites are the key to tailoring the gas separation performance of CMS produced under different conditions. Sorption in CMS can be characterized by a Langmuir isotherm (Eq. 2), where C'_{HA} is the Langmuir saturation constant, b_A is the Langmuir affinity constant, and p_A is the partial pressure of component A, respectively (25, 26).

$$C_A = C_{HA} = \frac{C'_{HA} b_A p_A}{1 + b_A p_A} \quad (2)$$

The sorption coefficient represents the concentration of gas (C_A) taken up by the membrane material at a given partial pressure (p_A) at equilibrium,

$$\bar{S}_A = \frac{C_A}{p_A} \quad (3)$$

The average transport diffusivity can then be obtained from Eq. 1 and Eq. 3 as $\bar{D}_A = P_A / \bar{S}_A$. Since the local transport (Fickian) diffusivity D_A tends to be concentration dependent, it is best to characterize molecular sieving behavior based on a thermodynamically corrected (Maxwell-Stefan) diffusivity $\mathfrak{D}_A$ by accounting for gas loading (25, 27) as follows:

$$D_A = \frac{\mathfrak{D}_A}{1 - \theta_A} \quad (4)$$

Here θ_A is the fractional site-saturation factor, represented by

$$\theta_A = \frac{C_A}{C'_{HA}} = \frac{b_A p_A}{1 + b_A p_A} \quad (5)$$

Thus, when the membrane downstream is at vacuum ($C_A = 0$), the average transport diffusivity ($\bar{D}_A$) can be correlated to the corrected diffusivity ($\mathfrak{D}_A$) and fractional site saturation (θ_A) as follows:

$$\bar{D}_A = \frac{\int_{C_A}^0 D_A dC_A}{\int_{C_A}^0 dC_A} = \frac{D_A}{\theta_A} \ln \left(\frac{1}{1 - \theta_A} \right) \quad (6)$$

A detailed derivation of the Equation 6 can be found in (25, 27, 28) .

The ideal selectivity of the membrane can be represented as

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{\bar{D}_A}{\bar{D}_B} \right) \left(\frac{\bar{S}_A}{\bar{S}_B} \right) \quad (7)$$

3. Experimental

3.1 Pyrolysis and Characterization Protocols

Earlier work involved pyrolysis of the commercial polyimide Matrimid[®], which lacks fluorine so no CF₃H or HF is evolved, but CO₂, CO, CH₄ and H₂ evolution still occurs (18, 29). Aromatized strands and plates resulting from Matrimid[®] pyrolysis, leading to an idealized CMS similar to that shown in Fig. 1b will be different in detail, but similar in overall strand-like nature. In our earlier study for the Matrimid[®] precursor, an attractive pyrolysis temperature in ultra high purity (UHP) Argon was found to be 675 °C (30). For comparison, besides the new results we report here for the 6FDA:BPDA-DAM derived CMS we also discuss the earlier Matrimid[®] derived CMS, results from pyrolysis at 675 °C in UHP Argon with the following heating protocol (30), viz.,

- 1) 50 °C → 250 °C at a ramp rate of 13.3 °C/min
- 2) 250 °C → (T_{max}-15) °C at a ramp rate of 3.85 °C/min
- 3) (T_{max}-15) °C → T_{max} °C at a ramp rate of 0.25 °C/min
- 4) Soak for 120 mins at T_{max}
- 5) Cool naturally to room temperature under flowing UHP Argon

where, T_{max} is the 675 °C final pyrolysis temperature noted above, unless otherwise specified.

3.2. Gas Probes

CMS dense films were characterized using pure gas permeation and equilibrium sorption measurements. Details of CMS fabrication, permeation and sorption experiments for feed pressures up to 100 psia have been reported previously (28). Sorption coefficients were obtained from direct sorption measurements using Eqs. 2 and 3 and average transport diffusivities were back-calculated using permeability and sorption coefficients with Eq. 1. Further, Maxwell-Stefan corrected diffusivities were calculated using Eq. 6. An extensive array of gases (Table 1), were used to gain insight into CMS performance and properties.

Table 1: Size (σ) and critical temperature (T_c) for common gases (H_2 , CO_2 , O_2 , N_2 , CH_4) adopted from (26), noble gases (He, Ne, Ar, Kr, Xe) from (31, 32), for SF_6 from (26, 31), with size of C_2H_4 and C_2H_6 defined based on slit-like pores using space-filling CPK models and calibrated "slits" (17, 33).													
Gas	He	Ne	H_2	CO_2	O_2	Ar	N_2	Kr	C_2H_4	CH_4	C_2H_6	Xe	SF_6
σ (Å)	2.6	2.8	2.89	3.3	3.46	3.5	3.64	3.7	3.75	3.8	3.85	4.1	5.5
T_c (K)	5.3	44.5	33.2	304	155	151	126	209	283	191	306	290	319

4. Results and Discussion

4.1 Evolution of the CMS structure

Although CMS materials formed from various polyimide precursors will exhibit differences in final structure and performance, the general features and concepts presented here should be relevant to all such precursors. For the specific case of the 6FDA:BPDA-DAM precursor of interest here, we will focus on the evolution from the random coil precursor during transformation into a disrupted plate structure with slit-like ultramicropores related to Fig. 1b in a typical pyrolysis protocol. Such a general protocol, noted in the experimental section, is represented in Fig. 3 with three distinct periods: ramp, soak, and cool. During these periods, the

random polymer coil (Fig. 4-(i)) is transformed to a dramatically different CMS material. Elemental analysis of the CMS and consideration of evolved gases during the “ramp” phase of pyrolysis under UHP argon indicate that CF_3H , HF as well as CO_2 , CO and H_2 are important components leaving during pyrolysis of such a precursor (29). During the temperature ramping process, further aromatization occurs, with considerable nitrogen maintained in the carbon until rather high temperatures (Table S-1), consistent with other studies (34–38). On the other hand, CO and CO_2 evolution occurs even at relatively low temperatures to remove most, but not all, of the originally present oxygen atoms. For the precursor in Fig. 2, considering pathways consistent with the loss of the components mentioned above leads to a possible rigid, highly aromatic strand represented in Fig. 4-(ii), which will be used in discussion of the CMS formation. Details of the suggested strand structure are not crucial for high level considerations that are the main interest here, and this representative example strand will be discussed later.

Figure 3. Typical time versus temperature profile used for CMS formation in this study.

Pyrolysis of a typical $\sim 150,000$ g/mol semi-flexible random coil polyimide, which loses only $\sim 40\%$ of its weight upon pyrolysis, to produce a high molecular weight rigid structure presents a *solid state packing problem*. A similar problem is encountered in transforming a high

molecular weight cellulosic precursor to the type of structure in Fig. 1b or 4-(vi). In either case, the entangled semi-flexible precursor undergoing aromatization and extreme linearization will tend to experience sufficient localized stresses to cause periodic scissions along its backbone, illustrated in Fig. 4-(i), (ii). Such backbone scissions are envisioned to occur during the temperature ramp to the final pyrolysis temperature (cf. Fig. 3 – “ramp”) allowing aromatization to proceed while producing shorter, more mobile structural strands; however, *a packing issue still exists* for such rigid strand oligomers.

We envision that the rigid strands “solve the packing problem” in the way a rigid liquid crystalline polymer responds to the presence of high concentrations of rigid strands—by organizing into more packable entities such as plates(39). While counterintuitive, the aligned plates comprised of strands (Fig. 4-(iii)) are in an overall higher entropy state. Alignment of these strands during the temperature ramp phase of the pyrolysis is preferred as it reduces the excluded volume present within a “random” phase packing of strands (Fig. 4-(ii), allowing for an increased number of possible packing states of lateral entities. Some lateral linkages due to consolidation of lateral strands may occur, evolving molecular H₂ in the process. Nevertheless, an amorphous nature results, since kinetic restrictions hinder perfect organization within the plates themselves and with imperfect long range stacking of plates during the limited time at high temperature during the “soak” phase in Fig. 3, when mobility is high. A typical idealized micropore “cell” with imperfectly packed sides comprised of imperfectly organized strands, reminiscent of Fig. 1b, is illustrated in Fig. 4-(iv). Ongoing evolution to the many neighboring cells in the idealized CMS structure is envisioned to occur during the final thermal soak and cooling after pyrolysis, as illustrated in Fig. 4-(iv) through Fig. 4-(vi). During the soak and cooling phases (cf. Fig. 3), adjacent micropore “cells” (Fig. 4-(iv)) will coalesce, wherein

ultramicropore “walls” will be shared between “cells”, resulting in a cellular structure envisioned to have a form similar to Fig. 4-(vi), where the front ultramicropore “walls” have been removed to highlight the resulting structure. The amorphous CMS, with micropores separated by ultramicropores in the micropore plate walls, will, however, have molecular sieving properties. The hypothetical evolution path and structures illustrated in Fig. 4 is useful not only to envision the formation of the polyimide-derived CMS, but also to understand how controlling pyrolysis atmosphere and post-processing of CMS materials affect resulting membrane performance.

Figure 4. Envisioned initial steps in transformation from random coil precursor polyimide to organized amorphous CMS material with bimodal distribution of micropores with ultramicropores.

Post-synthesis, CMS materials are subject to a physical aging phenomenon, where partial densification of the imperfectly stacked plates may occur, with reduction in the average distance between the plates, i.e. the *micropore size* or the molecular jump length (λ in Fig. 5a) (40–42). Such minor changes in organization of the aromatic strands *within the various plates* result in minor diffusion selectivity changes associated with the slits (d_{um} in Fig.5a) *between* the imperfectly organized strands, but with significant reductions in diffusion and sorption coefficients (40). The conceptual model presented in Figs. 4 & 5 helps clarify how processing and structure can be related to resultant membrane performance in a consistent manner.

Figure 5a. Aging or annealing of CMS structure results in micropore settling with only minor ultramicropore slit tightening.

Figure 5b. Oxygen doping of CMS structure results in tightening of size-selective ultramicropores with no changes in micropore distribution.

During CMS formation, addition of parts per million of molecular oxygen into the pyrolysis atmosphere leads to selective functionalization of the edges of the imperfectly organized strands, illustrated by the idealized aromatic structure in Fig. 4-(ii) (43, 44). This doping can selectively narrow accessible points, and tighten the ultramicropore distribution as shown in Fig. 5b, resulting in an increase in membrane selectivity with a moderate reduction in productivity. Oxygen doping has been shown to only modify the size selective ultramicropores in Matrimid[®] derived CMS materials, *not the micropores believed to be responsible for sorption coefficients in Eqs. 1 and 7* (45). Another study demonstrated that for different 6FDA-based polyimide precursors the same effect applies, and presumably is general to all CMS materials (46). While determination of the exact state of the oxygen is outside the scope of this current discussion, spectroscopic evidence of carbonyls has been previously reported (43); however one can envision a multitude of oxygen chemisorption pathways during the complex pyrolysis process. In fact, as noted later, CMS formed under UHP Argon contains residual oxygen (Table S-1), which may be present in various states. For example, oxygen resulting in an alcohol

functionality, whether remaining from precursor materials or due to oxygen doping, may undergo tautomerization to the previously observed carbonyl form (47, 48). Detailed identification of the array of oxygen functionalities in the CMS materials will clearly benefit from additional work in the future.

Finally, Figs. 4 & 5 also provide a framework to discuss changes in precursor structure and the impact on CMS separation properties. The biphenyl link in the BPDA unit in Fig. 2 provides a potential weak point in the precursor backbone, which actually offers a tool to control strand structure. Increasing the 6FDA:BPDA monomer ratio from (1:1) to (2:1) may impact the complex process of aromatization, fragmentation and organization envisioned in Fig. 4, along with and the ultimate CMS properties. The above conceptual framework will be used to discuss such issues in a self-consistent manner in the following sections.

4.2 Impacts of Precursor Structure.

Sorption Isotherms and Pore Distribution Analysis from CO₂ Sorption

Gas sorption measurements for the extensive array of gases in Table 1 were carried out on CMS derived from 6FDA:BPDA-DAM at 675 °C. Newly measured sorption isotherms for 6FDA:BPDA-DAM at 35 °C are shown along with earlier reported results for Matrimid[®] derived CMS in Fig. 6 (17).

As described earlier, gas molecules sorb into micropore sites of the CMS and transport through the membrane by making diffusive jumps from one sorption site to the next through size selective ultramicropore slits. Gas sorption generally increases with condensability (e.g. critical temperature, T_c) but may also be augmented by other factors like dipoles and quadrupoles (49). Since micropore sorption sites communicate by narrower ultramicropore windows, exclusion of

the larger penetrant in a gas pair can occur; however, the distribution of ultramicropore sizes makes complete exclusion unlikely. As expected, sorption isotherms in Fig. 6 show a general trend of increasing sorption uptake with increasing penetrant critical temperature (Table 1). Helium can sample most of the pores, but its sorption uptake is very small owing to its low critical temperature. On the other hand, SF₆ with a high critical temperature and condensability shows low sorption uptake, presumably due to substantial molecular sieving because of its large size. For all gases, higher sorption is seen in 6FDA:BPDA-DAM derived CMS, compared to the corresponding Matrimid[®] derived CMS reported earlier at 675 °C, reflecting larger 6FDA:BPDA-DAM CMS micropore volume compared to Matrimid[®] (17).

Figure 6. Sorption isotherms of different gases for CMS derived from UHP Ar pyrolysis of Matrimid® and 6FDA:BPDA-DAM at 675 °C.

Figure 7. Pore size distribution from CO₂ uptakes for CMS derived from UHP Ar pyrolysis of Matrimid[®] (- - -) and 6FDA:BPDA-DAM (—) at 675 °C. Data generated by Micromeritics for samples supplied from this work. Details in (1).

A similar trend was also reported by Kiyono et al. for CMS derived from Matrimid[®] and 6FDA:BPDA-DAM pyrolysis at 550 °C (43). A pore size distribution (Fig. 7), obtained from analysis of CO₂ uptake measurements at 0 °C, complement the above conventional sorption findings (1). Consistent with trends observed in the sorption data for the wide range of gases in Fig. 6, the 6FDA:BPDA-DAM CMS has a larger overall micropore volume compared to Matrimid[®] CMS reported earlier (1). The higher sorption uptakes of the 6FDA:BPDA-DAM derived CMS compared to the Matrimid[®] derived CMS reflect higher saturation capacities, consistent with larger micropore volume when compared to Matrimid[®] noted in Fig. 7 and reported in Table S-2. The increased micropore volume is due to presence of the bulky –CF₃ groups in the 6FDA unit of the 6FDA:BPDA-DAM precursor, which are evolved during the pyrolysis process as HF and HCF₃, disrupting polymer chain packing. Loss of these bulky fluorinated groups leads to a more open CMS structure with higher porosity when compared to Matrimid[®] which lacks any bulky fluorinated groups, and is reflected in the measurements

above. Although useful for characterizing micropores, small ultramicropores with sizes $< 4 \text{ \AA}$ cannot be probed via CO_2 or N_2 sorption pore characterizations.

Gas Diffusion as Ultramicropore Probes

Permeability of the penetrant gases listed in Table 1 for CMS derived from the pyrolysis of Matrimid[®] and 6FDA:BPDA-DAM at 675 °C are reported in Fig. 8. Permeability trends cannot be conclusively understood using pore size distributions obtained from sorption measurements; however diffusivity trends allow investigation of *ultramicropore dimensions* responsible for molecular sieving. The strong dependence of diffusivity upon molecular size is the basis for an effective “molecular ruler” to characterize the amorphous CMS materials, complementing traditional characterization methods (17). Examining diffusion coefficients and diffusion selectivities for various penetrant gas pairs can provide insight into CMS materials not captured in permeability and sorption measurements. Corresponding sorption and average transport diffusion coefficients (determined from $P/\bar{S}_A$ using Eq. (1)) are reported in supplemental figures S-1 & S-2, respectively.

For all gases, the 6FDA:BPDA-DAM-derived CMS shows higher permeabilities than Matrimid[®] derived CMS. The higher permeabilities and free volume of the 6FDA:BPDA-DAM versus Matrimid[®] polymer precursor correlates with higher permeabilities in the final CMS; however, as shown by Fu et. al. (22), such a correlation is not always seen. Given the complex events during the CMS formation, this lack of a simple correlation should not be surprising.

Figure 8. Permeabilities of different gases for CMS derived from Matrimid[®] and 6FDA:BPDA-DAM at 675 °C under UHP Argon. Permeability measurements were made at 35 °C using 50 psia feed pressure.

While permeability and sorption coefficients have practical utility; the special capability of CMS to execute penetrant size and shape selectivity is seen best by extracting and analyzing diffusion coefficients from permeability and solubility coefficients. The more meaningful thermodynamically corrected diffusivities in CMS derived from 6FDA:BPDA-DAM are shown in Fig. 9, along with values for previously studied Matrimid[®] derived CMS created at 675 °C under UHP Argon (17). These thermodynamically corrected coefficients are preferred here, since they avoid complications with concentration dependence of diffusion for highly condensable

gases, and depend exclusively on penetrant shape and size. As expected, the corrected diffusion coefficients decrease by orders of magnitude with small differences in penetrant size. The diffusivities for all gases are much larger for the 6FDA:BPDA-DAM derived CMS compared to the Matrimid[®] derived CMS. Although ultramicropore windows are the diffusion limiting pores in CMS, the squared jump length in Eq. (8) also enters into the effective diffusion coefficient:

$$D_A = f_A \lambda_A^2 / 6 \quad (8)$$

where f_A and λ_A are the random walk jumping frequency, and jump length, respectively (50). For a given CMS type, an *average* jump, $\lambda \sim d_\lambda$ in Fig. 1a, applies. In the context of the idealized models in Fig. 1 and 4, d_λ corresponds to the average distance *between the walls* in an average micropore, such as shown in Fig. 4-(iv). The larger pore volumes at each effective size in 6FDA:BPDA-DAM-derived CMS compared to Matrimid[®] derived CMS in Fig. 6 suggests larger average values of $\lambda \sim d_\lambda$ (cf. Fig. 1a) in 6FDA:BPDA-DAM derived CMS. This is due to presence of the bulky $-\text{CF}_3$ groups in the 6FDA unit of 6FDA:BPDA-DAM precursor, which disrupt polymer chain packing leading to a more open CMS structure after pyrolysis. This feature contributes to higher diffusion and sorption coefficients—and hence much higher permeabilities. The ratio of thermodynamically-corrected diffusivities, measures the *relative jump frequency* for members of a gas pair in each of the two CMS types. In all cases, these data show higher selectivities when considering a given gas pair in Matrimid[®] derived CMS, reflecting a more compact organization of the corresponding ultramicropores comprising the walls of the respective micropores. While these trends hold in general, understanding subtle differences in ultramicropore distributions of CMS membranes derived from different polymer precursors is essential to engineering CMS for specific gas separations. Two of the most

important cases, CO₂/CH₄ and C₂H₄/C₂H₆ will be considered further to illustrate some principles and the utility of the framework provided by Figs. 1, 4 and 5.

Figure 9. Corrected diffusivities of different gases at 35 °C for CMS derived from UHP Argon Pyrolysis of Matrimid[®] and 6FDA:BPDA-DAM to 675 °C.

Considering the CO₂/CH₄ separation, the CO₂ permeability of the 6FDA:BPDA-DAM derived CMS is approximately 230% higher than that of the Matrimid[®] derived CMS (due to combined higher CO₂ diffusion and sorption effects). Despite this large productivity advantage for the 6FDA:BPDA-DAM CMS over the Matrimid[®] CMS, the CO₂/CH₄ *diffusion selectivity* (shown in Table 2) is quite similar for both materials. From this perspective, considering 6FDA:BPDA-DAM CMS over Matrimid[®] CMS for CO₂/CH₄ separations is more desirable. In

addition, this allows the 6FDA:BPDA-DAM CMS to be tuned to improve its CO₂/CH₄ selectivity even further while maintaining attractive permeability.

The technologically important C₂H₄/C₂H₆ pair is even more challenging to separate than the CO₂/CH₄ pair. Due to similarity in critical temperatures and size of these gases (Table 1), both sorption selectivity and diffusion selectivity of the C₂H₄/C₂H₆ pair tend to be low, thereby suppressing permselectivity (51–53). This pair is also particularly interesting, since it allows insights related to two relatively large penetrants with sizes *at the higher size tail end of the ultramicropore pore size distribution* illustrated in Fig. 4. Considering CMS formed at 675 °C under UHP Argon, the C₂H₄ permeability of the 6FDA:BPDA-DAM CMS is approximately 320% higher than that of the Matrimid[®] CMS; however, the diffusion selectivity is 54% lower for the 6FDA:BPDA-DAM vs. Matrimid[®] derived CMS (shown in Table 2). This permeability-selectivity trade-off is especially apparent when considering the C₂H₄/C₂H₆ pair, and additional tools for tuning the selectivity without considerable permeability reductions become even more important.

Table 2. Corrected diffusion coefficients and diffusional selectivity properties of key gas pairs for Matrimid[®] and 6FDA:BPDA-DAM(1:1) CMS pyrolyzed to 675 °C under UHP Argon.

Gas	σ (Å)	Matrimid [®]		6FDA:BPDA-DAM(1:1)	
		$\bar{D}$ (cm ² /s)	α_D	$\bar{D}$ (cm ² /s)	α_D
CO ₂	3.30	7.7 E-08	CO ₂ /CH ₄ = 38.5	13.5 E-08	CO ₂ /CH ₄ = 35.0
C ₂ H ₄	3.75	2.5 E-09	C ₂ H ₄ /C ₂ H ₆ = 12.3	4.5 E-09	C ₂ H ₄ /C ₂ H ₆ = 5.7

An additional topic on the impacts of precursor polymer structure relates to the 6FDA:BPDA-DAM(1:1) precursor shown in Fig. 2 with awareness that the BPDA component provides a potential weak point in the precursor backbone. In this regard, increasing the

6FDA:BPDA monomer ratio from (1:1) to (2:1) tends to reduce backbone scissions in the stressed structure during aromatization. Larger, less mobile strands may suppress packing arrangement and lead to larger micropore volume and longer jump lengths in the (2:1) CMS variant. At the same time, after losing the CF_3H groups, a more linear strand structure in the 6FDA:BPDA (2:1) case will have less degrees of freedom of movement due to fewer biphenyl bonds in the aromatized strand. This second factor could provide an intrinsically tighter, more selective ultramicropore size distribution. For instance, when considering the CO_2/CH_4 pair, our preliminary work is consistent with these two aforementioned effects and interpretable in terms of higher micropore volume and longer jump lengths with tighter and a more size and shape selective ultramicropore distribution for the 2:1 variant. Specifically, the 675 °C pyrolyzed CMS 6FDA:BPDA-DAM(1:1) derived CMS gives 1100 Barrers CO_2 permeability and permselectivity $\text{CO}_2/\text{CH}_4 = 66$, while the CMS from the precursor 6FDA:BPDA-DAM(2:1) gave 2800 Barrers CO_2 permeability with selectivity $\text{CO}_2/\text{CH}_4 = 77$.

4.3 Additional Pore Size Tuning Tools.

Oxygen Doping

As described in the previous section, the similar diffusion selectivity between CMS derived from Matrimid[®] and 6FDA:BPDA-DAM (cf. Table 2) provides a major opportunity for tuning for the later material. Specifically, the productivity advantage of the 6FDA:BPDA-DAM derived CMS can be leveraged by further controlled tightening of the ultramicropores to sacrifice some permeability to create a more selective membrane. This strategy, illustrated in Fig. 10 by careful ultramicropore tuning via oxygen doping, results in moderate reductions in CO_2 permeability with significant selectivity increases (43). Consistent with the representation in Fig.

5b, oxygen doping of the ultramicropore edges improves diffusion selectivity while maintaining large $\lambda \sim d_\lambda$ that results in high diffusivity, and high micropore sorption capacity, so permeability also remains high. In the context of Fig. 5, oxygen doping primarily affects size selective ultramicropores rather than affecting the sorption coefficients in Eqs. 1 and 7. These oxygen doping results support the idea that modification of only the size selective ultramicropores can lead to a membrane material with both attractive selectivity and permeability. Although Fig. 10 relates to 550 °C pyrolysis, the same approach could clearly be applied for the 675 °C pyrolysis conditions to further augment performance of the 6FDA:BPDA-DAM(2:1) CMS even beyond the appealing preliminary results noted for this case.

This ultrafine pore size engineering can also be extended to even more challenging gas pairs, for instance the C₂H₄/C₂H₆ pair which differ only by 0.1 Å in effective size (Table 1). Preliminary oxygen doping shows a remarkable effect for 6FDA:BPDA-DAM(1:1) for pyrolysis, with an optimum of 10 ppm O₂ in Argon at 675 °C, versus UHP Argon at 675 °C. Specifically, the permselectivity was raised more than 30% from 7.3 in Fig. 8 to 9.6, with only moderate reduction of 30% in the attractive permeability under the 10 ppm O₂ in Argon versus UHP Argon at 675 °C. Additional detailed studies of oxygen doping for this and other challenging gas pairs are currently underway.

Figure 10. Separation performance of oxygen-doped 6FDA:BPDA-DAM(1:1) CMS films, pyrolyzed to 550 °C. Reprinted with permission from reference (43). Copyright 2010 Elsevier.

Amine Doping

The upper end of the CMS ultramicropore size distribution and the lower end of the micropore distribution (cf. Figs. 4 & 5) reflect morphological features that control separation of larger penetrants in the upper size range of Table 1. This terrain ideally allows diffusion jumps by more compact large penetrants without losing size and shape selectivity relative to slightly less compact large penetrants. Pore tuning in this range, therefore, provides additional insight into the complex domain in Fig. 1, 4, and 5 comprising large ultramicropores and small micropores as morphologically distinct entities, which is considered next. A small number of poorly packed strands within intercommunicating micropore walls should comprise the upper range of the ultramicropore distribution. On the other hand, local regions with more “settled” plates having small values of $\lambda \sim d_\lambda$ in Eq. (8) will comprise the lower range of the micropore

distribution. In fact, the largest ultramicropores may effectively comprise defects in packing associated with the chaotic drive towards ordered plates, which may not be so neatly organized as the idealized representation in Fig. 4. Indeed, the actual CMS composition (Table S-1), while envisioned to comprise mostly C, H, and N, with structures illustrated in Fig. 4, also includes some oxygen *even when formed under UHP Argon*. Although speculative, we envision naturally occurring, residual oxygen-containing sites to be associated with such regions of less perfection created during the chaotic scission and organization process.

These residual oxygen-containing sites may provide a route for selective functionalization of the CMS membranes with carefully selected “dopants”, sharpening the upper ultramicropore and lower micropore size distributions illustrated in Fig. 4. This observation motivated recent work (41), exploiting this fact as an extension of the more conventional oxygen doping concept, noted earlier in Fig. 5b. As shown in Fig. 11a, addition of small molecule dopants are envisioned to functionalize the larger slits resulting from imperfect packing of strands in the CMS structure. In the context of Fig. 11, treatment of conventionally-produced CMS was doped with trace amounts (1000 - 10 ppm) of paraphenylene diamine (PPDA) in tetrahydrofuran (THF) (41). While a wide array of molecular dopants can be envisioned, utilization of diamines in this preliminary study was based on the fact that small amine penetrants introduced to the CMS are tenaciously, even covalently retained (54). This preliminary work was done on identical asymmetric CMS membranes with the same thin dense layer formed at 550 °C, so productivity is reported in GPU ($1 \text{ GPU} = 10^{-6} \text{ cc(STP)/cm}^2 \text{ cmHg}$).

Figure 11. (a) Comparison of oxygen and “amine doping” techniques. (b) Performance of amine doped 6FDA:BPDA-DAM CMS membranes for CO₂/CH₄ separation. Reprinted with permission from reference (41). Copyright 2016 Wiley.

The lower pyrolysis temperature, compared to 675 °C, was chosen to maintain larger micropore dimensions (cf. Fig 5a) to provide high sorption capacity (C'_H) and diffusion jump lengths (d_λ in Fig. 1a-i). The provocative trends in Fig. 11b suggest that amines may be suited to sharpen the large end of the ultramicropore range to complement oxygen doping for the small and mid-range ultramicropores. Combining these two ultramicropore engineering tools will provide abilities to refine CMS for such larger penetrants such as the olefin-paraffin pairs, as well as smaller ones in Fig. 5 and Table 1.

5. Conclusions

Differences in CMS structure and performance resulting from the use of different polymer precursors, while keeping other pyrolysis conditions fixed, were discussed. Sorption uptake measurements were used to characterize the CMS micropore distribution. A gas probe method

provided insight into changes in CMS transport properties in terms of differences in ultramicropore distributions, leading to changes in CMS performance. As with other studies, the relationship between precursor and ultimate CMS properties was shown to be more complex than one related only to precursor fractional free volume. The 6FDA:BPDA-DAM 675 °C CMS shows a higher C₂H₄ permeability but lower C₂H₄/C₂H₆ selectivity compared to the Matrimid[®] CMS. This general permeability-selectivity trade-off however may not always be obvious since in the case of CO₂/CH₄ separation, the 6FDA:BPDA-DAM CMS shows a comparable selectivity as the Matrimid[®] CMS, but with much higher permeability. This is especially important when the effects due to multiple pyrolysis parameters are coupled. For example, simply increasing the pyrolysis temperature may result in a CMS with higher selectivity but lower permeability as seen in going from pyrolysis of Matrimid[®] at 500 °C vs. 675 °C (17). On the other hand changing the polymer precursor to 6FDA:BPDA-DAM while increasing the pyrolysis temperature at the same time may produce a more optimal CMS avoiding this unwanted trade-off, as was demonstrated for CO₂/CH₄ separation. Careful consideration of the CMS micropore and ultramicropore distributions is thus important for engineering CMS for a given gas separation application.

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