Effects of pyrolysis conditions on gas separation properties of 6FDA/DETDA:DABA(3:2) derived carbon molecular sieve membranes

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Abstract

A previously reported polyimide, 6FDA/DETDA:DABA(3:2), was pyrolyzed under different protocols to produce carbon molecular sieve (CMS) dense film membranes for separation of important gas pairs, including pure gases CO₂/CH₄, O₂/N₂ and mixture gases 50% CO₂/50% CH₄ and 50% C₃H₆/50% C₃H₈. This study investigated the effects of pyrolysis temperature, O₂ doping, and precrosslinking on the separation performance of 6FDA/DETDA:DABA(3:2) CMS membranes. Comparing to the precursor membranes, separation performance of all 6FDA/DETDA:DABA(3:2) CMS membranes improves significantly with both higher permeability and selectivity. The CMS film pyrolyzed with a novel method, i.e., 800 °C with precrosslinking, shows very attractive separation performance with CO₂ and O₂ permeability of 4678 Barrer and 683 Barrer, CO₂/CH₄, O₂/N₂ selectivity of 71.5 and 8.0. Sorption measurements provide insight into the pore size distributions among these CMS membranes. The effects of these three parameters during pyrolysis on the CMS membranes gas separation performance are

summarized and compared, hypotheses regarding the structure changes brought about by changing these parameters are also provided.

1. Introduction

In this study, we extensively investigated the separation performance of carbon molecular sieves (CMS) membranes derived from 6FDA/DETDA:DABA(3:2) for gas pairs: O_2/N_2 , CO_2/CH_4 , and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$. Separation of O_2/N_2 is widely applied for multiple applications [1, 2]. Nitrogen-enriched air is used for inerting applications, chemicals, and fuel tanks and oxygen-enriched air is useful in processes including enhanced combustion efficiency or fluid catalytic cracking (FCC) catalyst regeneration in refineries [3, 4]. There are three main technologies used for the separation of O_2 and N_2 from air. While pressure-swing adsorption and cryogenic distillation dominate high purity production or where larger flowrates are required, membranes dominate relatively lower purity applications [2]. To further improve O_2/N_2 separation efficiency, membranes with both selectivity and high transmembrane fluxes are needed [3].

Natural gas is the fastest-growing fossil fuel throughout the world and by far, processing of natural gas is the largest industrial gas separation process [5, 6]. CO_2 , an abundant natural gas contaminant, may cause potential pipeline corrosion; therefore, CO_2/CH_4 separation is of great importance [5, 7-10]. For CO_2 removal, membrane technology competes with absorption, which is a relatively expensive, heavy, and high-maintenance approach, so higher performance membranes are especially attractive targets.

Propylene (C_3H_6) is one of the most important feedstocks for the petrochemical industry. Traditionally, C_3H_6 is separated from propane (C_3H_8) by fractional distillation under high pressure using many stages, making it an energy intensive process [11]. Membrane technology has been actively studied in academia and industry as an alternative technology to reduce energy

intensity [12-16]. A membrane with minimum permeability of 1 Barrer and selectivity of 35 has been suggested as adequate for this purpose [17].

This study is a significant extension of an earlier analysis of CMS membranes formed from pyrolysis of various polyimide precursors for gas separation applications [18, 19]. CMS membranes derived from the 6FDA/DETDA:DABA(3:2) polyimide precursor pyrolyzed at 550 °C has been shown to offer the greatest practical potential with the highest permeability, i.e., above 20,000 Barrer for CO₂ and above 4000 Barrer for O₂ at 35 °C; however, it only offers moderate separation selectivity for CO₂/CH₄, O₂/N₂ as 30 and 5. Consequently, the main focus of this work is to develop higher selective, free standing CMS dense film membranes derived from 6FDA/DETDA:DABA(3:2) and to characterize them for the above important applications.

To tailor the separation performance of CMS membranes, many tuning methods exist, but pyrolysis temperature is especially useful. Prior work showed that a higher pyrolysis temperature tends to give more compact and higher selective CMS membranes [8, 12, 20-22]. Pyrolysis atmosphere is another important variable. Geiszler and Koros studied separation performance of 6FDA/BPDA-DAM asymmetric hollow fiber CMS membranes pyrolyzed at different atmosphere: under vacuum (0.01-0.03 mtorr); under inert atmosphere of helium, argon, and carbon dioxide with gas flow rates of 20 and 200 sccm [23, 24]. They found CMS membranes produced by vacuum pyrolysis showed higher gas selectivity than those produced in any of the above inert atmospheres. Moreover, considering the uncertainty of the experimental data, little difference was observed among the membranes pyrolyzed under the three different inert purge gases: helium, argon, and carbon dioxide. Kiyono et al. [25, 26] developed a fine tuning method referred to as “oxygen doping”, in which trace amount of oxygen was introduced into the pyrolysis atmosphere. By studying the separation performance of 6FDA/BPDA-DAM CMS

membranes pyrolyzed in 4, 8, 30 and 50 ppm O₂ doped Argon at 1 atm, they found a strong correlation between the amount of oxygen available during pyrolysis and separation performance. Last but not the least, Qiu et al. developed a new decarboxylation-induced thermal crosslinking in DABA containing polymeric membranes at temperature below the material's T_g (glass transition temperature) [10, 27]. In this method, during pyrolysis, the polymeric membrane was thermally treated at 370 °C for an hour before raising the temperature to the final desired temperature. They demonstrated that the membrane was highly-crosslinked after being thermally annealed at 370 °C for an hour. What's more, this novel method not only stabilizes polymer membranes against swelling and plasticization in aggressive feed streams, it also induces a significant increase in membrane permeability with slight loss in selectivity. In this study we incorporated this method in the application of carbon membranes, and to the best of the authors' knowledge, no former publications have addressed these combined topics in a single systematic study.

This study uses the above tools to develop higher selective 6FDA/DETDA:DABA(3:2) CMS dense film membranes by adjusting the pyrolysis conditions, including pyrolysis temperature, atmosphere and temperature profile.

2. Structure of CMS membranes

CMS materials are formed by thermal decomposition of a precursor polymer to produce a carbon rich material [28, 29]. Being heated in an inert atmosphere, polymers go through carbonization and residual materials of coke or char tend to be formed [30, 31]. During carbonization, if the precursor goes through a liquid phase, the polymer chains tend to form aromatic lamellae resulting in crystalline anisotropic coke; otherwise, isotropic char is formed. Most CMS membranes used for gas separation show a turbostratic nature with little long-range

order and can be viewed as amorphous and isotropic. Over the long range, this amorphous form contains lamellae arranged randomly, bent and twisted. Over the short range, the sp^2 -hybridized carbon sheets can align parallel to each other and form somewhat ordered structure, as shown in Figure 1.

Fig. 1: Structure of CMS membranes over a short range: the sp^2 -hybridized carbon sheets [30, 31].

A “slit-like” pore structure, as shown in Figure 2 (i), is believed to be formed from packing imperfection. A bimodal pore size distribution, as shown in Figure 2 (ii), is often used to describe the pore structure of CMS membranes [13, 19, 28, 32, 33]. Micropores ($\sim 7\text{-}20\text{ \AA}$) provide sorption sites and ultramicropores ($< 7\text{ \AA}$) enable molecular sieving. The combination of these two types of pore morphologies provides CMS materials with properties lying above the upper-bound limit of polymers [13, 34].

i)

ii)

Fig. 2: i) An idealized slit-like pore structures in CMS membranes. (a): 7-20 Å micropores (b): < 7 Å ultramicropores; ii) bimodal distribution of pores [19].

3. Experimental

3.1 Materials

In the authors' previous study [18], the synthesis, characterization, and pure gas separation performance of 6FDA/DETDA:DABA(3:2) CMS membranes pyrolyzed at 550 °C under UHP Argon have been discussed in detail. The repeating unit of the polyimide 6FDA/DETDA:DABA(3:2) is shown in Figure 3. The pure gases including CO₂, CH₄, O₂, and N₂ were purchased from Praxair, Inc. with purity higher than 99.97%. Mixture gases 50% CO₂/50% CH₄, 50% C₃H₆/50% C₃H₈, and “ppm” levels of O₂ (30ppm and 50 ppm) with balanced Argon were purchased from NexAir.

Fig. 3. Repeating unit of polyimide 6FDA/DETDA:DABA(3:2).

The molecular size of a penetrant is usually represented by kinetic diameters, which are based on the minimum equilibrium cross-sectional diameters, or the collision diameters calculated from Lennard-Jones potential. For light gases including CO₂, CH₄, O₂, and N₂, kinetic diameters are more often used and are listed in Table 1; however, for higher hydrocarbons like C₃H₆ and C₃H₈, the kinetic diameter may no longer provide a reasonable estimation. Through personal communication, Dr. Liren Xu in Dow Chemical Company kindly provided the molecular sizes of C₃H₆ and C₃H₈, as listed in Table 1, estimated from CPK models and model slit shaped pores typical of CMS materials. The critical temperatures of these gases are also shown in Table 1 [35-37].

Table 1. Molecular sizes and critical temperatures of gases studied.		
Gases	Kinetic diameter (Å)	Critical temperature (K)
CO ₂	3.30	304
CH ₄	3.80	191
O ₂	3.46	155
N ₂	3.64	126
C ₃ H ₆	3.82	365
C ₃ H ₈	3.95	370

3.2 Formation of 6FDA/DETDA:DABA(3:2) polymeric and CMS dense films

The formation of 6FDA/DETDA:DABA(3:2) polymeric dense films using a solution casting method has been described in detail in previous studies [18, 38].

6FDA/DETDA:DABA(3:2) CMS dense films were formed by pyrolyzing the precursor polymeric films under specified conditions. The pyrolysis setup is shown in Figure 4 [21].

Fig.4. Schematic representation of the pyrolysis system used in this study [21].

In this study, CMS dense films were formed from the following different pyrolysis protocols:

a) Formation of different temperature pyrolyzed CMS dense films

6FDA/DETDA:DABA(3:2) dense films were pyrolyzed under UHP Argon at three different final pyrolysis temperatures of 550 °C, 675 °C, and 800 °C, following the temperature protocols listed below:

Protocol 1: for 550 °C-pyrolyzed CMS membranes:

- 1) 50-250 °C with a ramp rate of 13.3 °C /min.
- 2) 250 °C-535 °C ($T_{\max} - 15$) with a ramp rate of 3.85 °C /min.
- 3) 535 °C-550 °C with a ramp rate of 0.25 °C /min.
- 4) Soak for 2 hours at 550 °C.

5) Naturally cooling back to 30 °C under UHP Argon.

Protocol 2: for 675 °C- and 800 °C-pyrolyzed CMS membranes:

1) 50-250 °C with a ramp rate of 13.3 °C /min.

2) 250 °C-535 °C with a ramp rate of 3.85 °C /min.

3) 535 °C-550 °C with a ramp rate of 0.25 °C /min.

4) 550 °C-($T_{\max}$ -15) °C with a ramp rate of 3.85 °C /min.

5) ($T_{\max}$ -15) °C- $T_{\max}$ °C with a ramp rate of 0.25 °C /min.

6) Soak for 2 hours at $T_{\max}$ °C.

7) Naturally cooling back to 30 °C under UHP Argon.

b) Formation of different amount of O₂-doped CMS dense films

All O₂-doped CMS membranes were pyrolyzed with a final temperature of 550 °C following the temperature protocol 1 listed above. Instead of using continuous pure Argon as a purge gas, mixtures of Argon and various controlled amounts of Oxygen in ppm levels were used during pyrolysis and post pyrolysis cooling back to 30 °C. The whole system was purged with the mixture at a flow rate of 200 scc/min for at least 12 hours before each pyrolysis experiment. An oxygen analyzer was used in the downstream to monitor the oxygen concentration levels ($\pm$ 0.1 ppm).

c) Formation of precrosslinked CMS dense films

All precrosslinked CMS membranes were pyrolyzed with a final temperature of 800 °C under UHP Argon following a temperature protocol 3 listed below:

Protocol 3: for 800 °C-pyrolyzed and precrosslinked CMS membranes:

1) 50-250 °C with a ramp rate of 13.3 °C /min.

- 2) 250 °C-370 °C with a ramp rate of 3.85 °C /min.
- 3) Soak for 90 min at 370 °C.
- 4) 370 °C-785 °C ($T_{\max} - 15$) °C with a ramp rate of 3.85 °C /min.
- 5) 785 °C- 800 °C with a ramp rate of 0.25 °C /min.
- 6) Soak for 2 hours at 800 °C.
- 7) Naturally cooling back to 30 °C under UHP Argon.

3.3 CMS dense film permeation and sorption measurements

The systems and testing procedures for permeation and sorption measurements have been outlined previously [24, 39, 40]. All pure gas permeabilities were measured at 35 °C and 30 psia, and mixture gas permeabilities were measured at 35 °C and 60 psia. *Permeation results reported in this study represent the average of at least 3 samples with variance within 15%.* All sorption isotherms were measured at 35 °C with pressures range from 10 psia to 160 psia.

4. Results and discussion

4.1 Effect of final pyrolysis temperature on CMS membrane separation performance

4.1.1 Permeation

6FDA/DETDA:DABA(3:2) CMS dense films were formed from pyrolysis of precursor films under UHP Argon at three final pyrolysis temperatures: 550 °C, 675 °C, and 800 °C using the applicable pyrolysis protocol 1 or protocol 2 listed above. The CMS dense films obtained were tested on 6 gases, including 4 pure gases: CO₂, CH₄, O₂, and N₂ at 35 °C and 30 psia, and 2

mixture gases: 50% CO₂/50% CH₄ and 50% C₃H₆/50% C₃H₈ at 35 °C and 60 psia. As noted earlier, *Permeation results reported represent the average of at least 3 samples with variance within 15%.*

The steady state gas separation performance of these three different final temperature pyrolyzed CMS membranes are listed in Table 2. The pure gas CO₂, O₂ permeability and CO₂/CH₄, O₂/N₂ selectivity results are plotted in Fig. 5. As seen from Fig. 5, both permeabilities and selectivities of CMS membranes are significantly higher than those of the precursor membranes and surpass the polymeric upper bound. As pyrolysis temperature increases, permeability drops dramatically, while corresponding selectivity increases. It is also interesting to see from Table 2 that CO₂ permeability is lower and CO₂/CH₄ selectivity is higher in the case of mixture gas separation in comparison to the case of pure gas feeds. These observations may reflect the so-called dual mode competition effects between CO₂ and CH₄ molecules [38, 41]. The competition between both molecules reduces sorption and hinders diffusion of both gases, resulting in somewhat lower permeabilities. On the other hand, CO₂ sorption is favored over CH₄ sorption during the competition due to its higher critical temperature, with a resultant increase in mixed gas selectivity.

Table 2: Pure and mixture gases permeation results of three different final temperature pyrolyzed CMS membranes as well as polymeric membranes derived from 6FDA/DETDA:DABA(3:2). Pure gas permeations were measured at 35 °C and 30 psia, mixture gas permeations were measured at 35 °C and 60 psia. Results represent the average of at least 3 samples with variance within 15%.

Membranes	Pure gases			
	P_{CO_2} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	P_{O_2} (Barrer)	$\alpha_{\text{O}_2/\text{N}_2}$
Polymeric-	238	22.0	54	3.5
550 °C-CMS	21740	30.1	4293	4.9
675 °C-CMS	5569	55.0	928	7.5
800 °C-CMS	1812	88.3	300	7.6
Membranes	Mixture gases			
	50% CO ₂ /50% CH ₄		50% C ₃ H ₆ /50% C ₃ H ₈	
	P_{CO_2} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	$P_{\text{C}_3\text{H}_6}$ (Barrer)	$\alpha_{\text{C}_3\text{H}_6/\text{C}_3\text{H}_8}$
Polymeric-	-	-	-	-
550 °C-CMS	20073	37.6	2444	12.7
675 °C-CMS	4107	66.4	401	30.2
800 °C-CMS	1397	102.7	71	63.7

$$\text{Barrer} = 10^{-10} \frac{\text{cc(STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

Fig. 5. (a) Pure CO₂ permeability and CO₂/CH₄ selectivity; (b) pure O₂ permeability and O₂/N₂ selectivity of 6FDA/DETDA:DABA(3:2) precursor and CMS dense films pyrolyzed at 550 °C, 675 °C, and 800 °C. Robeson's CO₂/CH₄ and O₂/N₂ upper bound lines are shown for reference [42].

Fig. 6 represents the bimodal pore distribution in CMS membranes with larger micropores connected with smaller ultramicropores. We envision that as pyrolysis temperature increases, CMS structure becomes more tightly packed, and both micropores and ultramicropores distributions shift to smaller sizes. As a result for all gases and gas pairs, permeabilities decrease and selectivities increase.

Fig. 6. Hypothetical pore structure evolution in CMS membranes as pyrolysis temperature increases: (a): micropores with sizes of 7-20 Å; (b): ultramicropores with sizes < 7 Å.

4.1.2 Sorption

To further probe changes in micropores, pure gas CO₂, CH₄, O₂, and N₂ sorption capacities at 35 °C of 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense films were measured and are shown in Fig. 7. In carbon materials, with a finite number of sorption sites and rigid saturable capacity, the sorption coefficient is described by Langmuir isotherm, viz.,

$$S_i = \frac{C_i}{p_i} = \frac{C'_{Hi} b_i}{1 + b_i p_i} \quad (1)$$

where C'_{Hi} is the Langmuir hole filling capacity and b_i is the Langmuir affinity constant.

Only one sorption measurement was carried out for each sample without replicate considering the large amount of time the sorption tests consumed. Moreover, we believe after

comparing with permeation and diffusion, sorption is a parameter of secondary importance. The experimental data were fitted to Langmuir isotherms and the fitted parameters are listed in Table 3. Assuming that the majority of gas molecules are sorbed in micropores, sorption isotherms offer a useful probe of the CMS micropore structures. This assumption is justified by the preponderance of volume associated with micropores and the relatively lower energy state available in micropores vs. ultramicropores with dimensions approaching those of the penetrants themselves. Fig. 7 shows as final pyrolysis temperature increases, the sorption capacity for all gases of the corresponding CMS membrane decreases. From Table 3, it can be seen the loss of sorption capacity mainly results from the decrease of C_H' , which implies a reduction of Langmuir sorption sites and tightened micropore structures. The relatively constancy of the affinity coefficient (b) with increasing temperature, however, suggests relatively small changes in the micropore distribution, with primarily a reduction in overall number of microvoids.

Fig. 7. Pure gas CO_2 , CH_4 , O_2 , and N_2 sorption isotherms at 35 °C of 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense film.

Table 3. Pure gas CO₂, CH₄, O₂, and N₂ Langmuir isotherm parameters at 35 °C of 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense films.

		550 °C-CMS		675 °C-CMS		800 °C-CMS	
		CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C'_H	[cm ³ (STP)/cm ³]	172.2	114.3	160.7	111.3	140.1	94.7
b	[1/psia]	0.039	0.014	0.035	0.013	0.031	0.013
		O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
C'_H	[cm ³ (STP)/cm ³]	108.3	65.2	104.2	61.7	99.7	57.0
b	[1/psia]	0.007	0.009	0.007	0.008	0.006	0.007

The sorption coefficients for penetrants A and B in a binary mixture case can be defined as below:

$$S_A = \frac{C'_{HA} b_A}{1 + b_A p_A + b_B p_B} \quad (2)$$

$$S_B = \frac{C'_{HB} b_B}{1 + b_A p_A + b_B p_B} \quad (3)$$

where C'_{Hi} is the Langmuir hole filling capacity and b_i is the Langmuir affinity constant of the pure component i from the pure gas sorption test, all of which are listed in Table 3. The competitive sorption uptakes of penetrants CO₂ vs. CH₄ in a binary mixture of 50% CO₂/50% CH₄ are calculated according to Eqs. (2) and (3) and are shown in Table 4. As has been discussed in Section 4.1.1, both CO₂ and CH₄ permeabilities decreased in the mixed gas environment compared to the pure gas permeabilities, along with an increase in the CO₂/CH₄ selectivity. When both gases are present simultaneously, CO₂ and CH₄ compete for the limited Langmuir sorption sites in the membrane, which brings down the sorption coefficients of both

gases as shown in Table 4. As a result, the permeabilities of both decrease as well. The increase in the mixture gas sorption selectivity might be due to the favorable CO₂ sorption over CH₄.

Table 4. The sorption coefficient S_A and sorption selectivity S_A/S_B of gas pairs CO₂/CH₄ for 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense films of: 1) pure gas at 35 °C and 30 psia; 2) mixture gas at 35 °C and 60 psia.

	Pure gas			Mixture gas		
	S_{CO_2}	S_{CH_4}	S_{CO_2}/S_{CH_4}	S_{CO_2}	S_{CH_4}	S_{CO_2}/S_{CH_4}
	cc(STP)/cm ³ /psia			cc(STP)/cm ³ /psia		
550 °C-CMS	3.1	1.1	2.8	2.6	0.6	4.3
675 °C-CMS	2.7	1.0	2.6	2.3	0.6	3.8
800 °C-CMS	2.3	0.9	2.5	1.9	0.5	3.8

Table 5 below summarizes the CO₂, O₂ permeabilities, sorption coefficients, diffusion coefficients and the corresponding CO₂/CH₄, O₂/N₂ selectivities of 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia. The permeability P_A , overall membrane selectivity $\alpha_{A/B}$, sorption coefficient S_A and sorption selectivity S_A/S_B are determined directly from permeation and sorption measurements. The sorption coefficient, $S = C/P$, is determined to be the secant slope of the isotherm at a given pressure, and for consistency, the sorption coefficients reported here correspond to a sorption pressure of 30 psia, equal to the permeation feed pressure. The diffusion coefficient D_A and diffusion selectivity D_A/D_B are calculated according to Eq. (4)

$$P_i = D_i * S_i \quad (4)$$

Both sorption and diffusion coefficients follow a similar trend as permeability, decreasing with an increase in pyrolysis temperature. Diffusion coefficients in CMS reflect the packing of a material matrix and a decreased diffusion coefficient represents an overall tightened matrix, which is in consistent with our hypothesis regarding the structure evolution as shown in Fig. 6. On the other hand, sorption selectivity and diffusion selectivity show different responses in comparison to the overall selectivity for gas pairs CO₂/CH₄ vs. O₂/N₂. For CO₂/CH₄ separation, the great enhancement in overall selectivity mainly results from the increase in diffusion selectivity (from ~12 to ~35) while sorption selectivity remains in the range of 2.8-2.5. Nevertheless for O₂/N₂ separation, the contribution from sorption selectivity and diffusion selectivity is similar. More pronounced O₂/N₂ diffusion selectivity enhancement might be achieved if higher pyrolysis temperature, 900 °C for instance, were explored; however, this was beyond the scope of this study.

Table 5. The permeability P_A , overall membrane selectivity $\alpha_{A/B}$, sorption coefficient S_A , sorption selectivity S_A/S_B , diffusion coefficient D_A , and diffusion selectivity D_A / D_B of gas pairs CO_2/CH_4 and O_2/N_2 for 550 °C-, 675 °C-, and 800 °C- pyrolyzed 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia. Permeation results represent the average with variance within 15%.

	P_{CO_2} Barrer	$\alpha_{\text{CO}_2/\text{CH}_4}$	S_{CO_2} cc(STP)/cm ³ /psia	$S_{\text{CO}_2}/S_{\text{CH}_4}$	D_{CO_2} 10 ⁻⁷ cm ² /s	$D_{\text{CO}_2} / D_{\text{CH}_4}$
550 °C-CMS	21740	30.1	3.1	2.8	36.3	10.8
675 °C-CMS	5569	55.0	2.7	2.6	10.7	21.2
800 °C-CMS	1812	88.3	2.3	2.5	4.1	35.3
	P_{O_2} Barrer	$\alpha_{\text{O}_2/\text{N}_2}$	S_{O_2} cc(STP)/cm ³ /psia	$S_{\text{O}_2}/S_{\text{N}_2}$	D_{O_2} 10 ⁻⁷ cm ² /s	$D_{\text{O}_2} / D_{\text{N}_2}$
550 °C-CMS	4293	4.9	0.6	1.4	37.0	3.5
675 °C-CMS	928	7.5	0.6	1.5	8.0	5.0
800 °C-CMS	300	7.6	0.5	1.7	3.1	4.5

4.2 Effect of O_2 doping on 6FDA/DETDA:DABA(3:2) CMS membrane separation performance

As noted earlier, Kiyono et al. [25, 26] developed a fine tuning method referred to as “oxygen doping”, in which a trace amount of oxygen was introduced into the pyrolysis atmosphere. They found a strong correlation between the amount of oxygen available during pyrolysis and separation performance. In this study, 6FDA/DETDA:DABA(3:2) precursor dense films were pyrolyzed at 550 °C using protocol 1 listed above except that instead of purging pure Argon, a mixture of Argon and 30 ppm or 50 ppm Oxygen was used.

4.2.1 Permeation

The gas separation performance for pure and mixture gases of these two O₂ doped samples, along with the original 550 °C-undoped CMS membranes are listed in Table 6. The pure gas CO₂, O₂ permeability and CO₂/CH₄, O₂/N₂ selectivity results are plotted in Fig. 8. It is clear that as the doping amount of O₂ increases, gas selectivity increases with a moderate reduction in permeability. It is noteworthy that comparing to pyrolysis temperature, O₂ doping for the ranges explored, exerts smaller effects on the gas transport property in CMS membranes, i.e., smaller permeability and selectivity changes are witnessed. This finding supports the claim by Kiyono that O₂ doping is a fine tuning method in adjusting the separation performance of CMS membranes [43].

Table 6: Pure and mixture gases permeation results of 550 °C-, 550 °C-30 ppm O₂ doped and 550 °C-50 ppm O₂ doped CMS membranes as well as polymeric membranes derived from 6FDA/DETDA:DABA(3:2). Pure gas permeations were measured at 35 °C and 30 psia, mixture gas permeations were measured at 35 °C and 60 psia. Results represent the average of at least 3 samples with variance within 15%.

Membranes	Pure gases			
	P _{CO₂} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	P _{O₂} (Barrer)	$\alpha_{\text{O}_2/\text{N}_2}$
Polymeric-	238	22.0	54	3.5
550 °C-CMS	21740	30.1	4293	4.9
550 °C-30 ppm O ₂ doped-CMS	9679	41.8	1908	6.7
550 °C-50 ppm O ₂ doped -CMS	3213	60.9	450	6.3

Membranes	Mixture gases			
	50% CO ₂ /50% CH ₄		50% C ₃ H ₆ /50% C ₃ H ₈	
	P _{CO₂} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	P _{C₃H₆} (Barrer)	$\alpha_{\text{C}_3\text{H}_6/\text{C}_3\text{H}_8}$
Polymeric-	-	-	-	-
550 °C-CMS	20073	37.6	2444	12.7
550 °C-30 ppm O ₂ doped-CMS	7972	48.5	941	23.1
550 °C-50 ppm O ₂ doped -CMS	2163	70.3	101	50.7

Fig. 8. (a) Pure CO₂ permeability and CO₂/CH₄ selectivity; (b) pure O₂ permeability and O₂/N₂ selectivity of 6FDA/DETDA:DABA(3:2) precursor and CMS dense films pyrolyzed at 550 °C, 550 °C-30 ppm O₂ doped, and 550 °C-50 ppm O₂ doped. Robeson's CO₂/CH₄ and O₂/N₂ upper bound lines are shown for reference [42].

Fig. 9 represents a hypothetical schematic illustrating the oxygen doping process during pyrolysis based on $\sim 17X$ higher reactivity of micropore edges vs. basal planes [44-46]. As a result for all gases, permeabilities decrease and selectivities increase upon moderate oxygen doping [26]. This process narrows the ultramicropore windows, and as a result, lowers the membrane permeability and enhances the selectivity. Nevertheless in Kiyono's study [26], they demonstrated the existence of an optimum. If exceedingly amount of oxygen molecules is available in the pyrolysis environment, both lower permeability and lower selectivity can occur. In this work, we have not reached such a point, since selectivity was not found to decrease at any of the O_2 doping levels that showed "over-doping" in Kiyono's work with intrinsically less packing resistance precursors such as Matrimid[®] and 6FDA:BPDA/DAM [43].

Fig. 9. A hypothetical schematic of oxygen doping process during pyrolysis. ● represents chemisorbed O_2 molecule.

4.2.2 Sorption

Consistent with the schematic in Figure 9, O_2 doping has negligible impact on sorption. The sorption isotherms of pure gas CO_2 , CH_4 , O_2 , and N_2 at 35 °C of 550 °C-, 550 °C-30 ppm O_2 doped, and 550 °C-50 ppm O_2 doped 6FDA/DETDA:DABA(3:2) CMS dense films are shown in Fig. 10. The fitted Langmuir isotherms parameters are listed in Table 7. The almost unchanged sorption capacity and C'_H for all gases leads us to the conclusion that the oxygen doping process

has little influence on the micropore structure. The O₂ doping is, as in Kiyono's case, associated with the diffusion-moderating ultramicropores with sizes similar to the penetrants.

Fig. 10. Pure gas CO₂, CH₄, O₂, and N₂ sorption isotherms at 35 °C of 550 °C-, 550 °C-30 ppm O₂ doped, and 550 °C-50 ppm O₂ doped 6FDA/DETDA:DABA(3:2) CMS dense films.

Table 7. Pure gas CO₂, CH₄, O₂, and N₂ Langmuir isotherm parameters at 35 °C of 550 °C-, 550 °C-30 ppm O₂ doped, and 550 °C-50 ppm O₂ doped 6FDA/DETDA:DABA(3:2) CMS dense films.

		550 °C-		550 °C- 30 ppm O ₂ doped		550 °C- 50 ppm O ₂ doped	
		CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C'_H	[cm ³ (STP)/cm ³]	172.2	114.3	168.4	109.9	174.8	112.4
b	[1/psia]	0.039	0.014	0.040	0.015	0.039	0.014
		O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
C'_H	[cm ³ (STP)/cm ³]	108.3	65.2	109.0	66.4	108.1	66.4
b	[1/psia]	0.007	0.009	0.007	0.009	0.007	0.008

Table 8 below summarizes the CO₂, O₂ permeabilities, sorption coefficients, diffusion coefficients and the corresponding CO₂/CH₄, O₂/ N₂ selectivities of 550 °C-, 550 °C-30 ppm O₂ doped, and 550 °C-50 ppm O₂ doped 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia. Sorption coefficient remains almost unchanged while diffusion coefficients drop as the amount of oxygen doping increases, which is the main reason for permeability drop. On the other hand, the gain in overall selectivity also mainly stems from the increase in diffusion selectivity, which is in agreement with what have been found in the study on different temperature pyrolyzed CMS membranes.

Table 8. The permeability P_A , overall membrane selectivity $\alpha_{A/B}$, sorption coefficient S_A , sorption selectivity S_A/S_B , diffusion coefficient D_A , and diffusion selectivity D_A/D_B of gas pairs CO₂/CH₄ and O₂/N₂ for 550 °C-, 550 °C-30 ppm O₂ doped, and 550 °C-50 ppm O₂ doped 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia. Permeation results represent the average with variance within 15%.

Membranes	P_{CO_2} Barrer	α_{CO_2/CH_4}	S_{CO_2} cc(STP)/cm ³ /psia	S_{CO_2}/S_{CH_4}	D_{CO_2} 10 ⁻⁷ cm ² /s	D_{CO_2}/D_{CH_4}
550 °C-CMS	21740	30.1	3.1	2.8	36.3	10.8
550 °C-30 ppm O ₂ doped-CMS	9679	41.8	3.1	2.7	16.2	15.5
550 °C-50 ppm O ₂ doped -CMS	3213	60.9	3.1	2.9	5.4	21.0
Membranes	P_{O_2} Barrer	α_{O_2/N_2}	S_{O_2} cc(STP)/cm ³ /psia	S_{O_2}/S_{N_2}	D_{O_2} 10 ⁻⁷ cm ² /s	D_{O_2}/D_{N_2}
550 °C-CMS	4293	4.9	0.6	1.4	37.0	3.5
550 °C-30 ppm O ₂ doped-CMS	1908	6.7	0.6	1.3	16.5	5.2
550 °C-50 ppm O ₂ doped -CMS	450	6.3	0.6	1.4	3.8	4.5

4.3 Effect of precrosslinking on CMS membrane separation performance

4.3.1 Permeation

Since as discussed above, crosslinking tends to open up the membrane structure, a final pyrolysis temperature of 800 °C, which has been proven to offer compact CMS membrane, was selected. An adjusted pyrolysis protocol listed earlier as “protocol 3” was followed. More specifically, 6FDA/DETDA:DABA(3:2) polymer membrane was precrosslinked by soaking in 370 °C for 90 minutes before being heated to 800 °C. The proposed mechanism of decarboxylation-induced crosslinking is illustrated in Fig. 11.

Fig. 11. Chemical structure of 6FDA/DETDA:DABA (3:2) and crosslinking mechanism of decarboxylation-induced crosslinking. Possible crosslinking sites are noted with an arrow [18].

The precrosslinked membranes were tested for their solubility to serve as an indirect proof of whether crosslinking happened. Polymeric 6FDA/DETDA:DABA (3:2) membranes were thermally treated in the pyrolysis system at 370 °C for 90 mins and soaked in NMP. The original 6FDA/DETDA:DABA (3:2) polymeric dense film were easily dissolved in NMP at room temperature; however, the thermally treated membranes were insoluble in NMP either at room temperature or elevated temperature, indicating the membranes were highly crosslinked.

The same 4 pure gases and 2 mixture gases were used to examine the separation performance of this novel 800 °C-precrosslinked CMS, and results are shown in Table 9. The earlier-illustrated separation performance of 550 °C- and 800 °C- pyrolyzed CMS membranes are also listed for comparison purpose. The pure gas CO₂, O₂ permeability and CO₂/CH₄, O₂/N₂ selectivity results are plotted in Figure 12. It can be observed that compared with 800 °C-pyrolyzed CMS, the permeabilities for both pure and mixture gases of 800 °C-precrosslinked CMS were significantly higher. It is believed that the higher permeabilities results from the DABA moiety in the precursor polymer. As decarboxylation occurs, microvoids and packing disruptions are created and the polymer chains are locked in. Such a crosslinked structure might thereby be maintained in the subsequent pyrolysis process. As will be shown in the later sorption section, this permeability increase mostly is due to the increase of available sorption sites. What accompany these huge permeability enhancements are slight selectivities losses. Detailed analysis of diffusion selectivity and sorption selectivity in the following section will provide further explanation of the overall selectivity losses.

Table 9: Pure and mixture gases permeation results of 550 °C-, 800 °C- and 800 °C-precrosslinked-6FDA/DETDA:DABA(3:2) CMS membranes. Pure gas permeations were measured at 35 °C and 30 psia, mixture gas permeations were measured at 35 °C and 60 psia. Results represent the average of at least 3 samples with variance within 15%.

Membranes	Pure gases			
	P_{CO_2} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	P_{O_2} (Barrer)	$\alpha_{\text{O}_2/\text{N}_2}$
Polymeric-	238	22.0	54	3.5
550 °C-CMS	21740	30.1	4293	4.9
800 °C-CMS	1812	88.3	300	7.6
800 °C- precrosslinked- CMS	4678	71.5	683	8.0

Membranes	Mixture gases			
	50% CO ₂ /50% CH ₄		50% C ₃ H ₆ /50% C ₃ H ₈	
	P_{CO_2} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	$P_{\text{C}_3\text{H}_6}$ (Barrer)	$\alpha_{\text{C}_3\text{H}_6/\text{C}_3\text{H}_8}$
Polymeric-	-	-	-	-
550 °C-CMS	20073	37.6	2444	12.7
800 °C-CMS	1397	102.7	71	63.7
800 °C- precrosslinked- CMS	2690	59.8	200	52.0

Fig. 12. (a) Pure CO₂ permeability and CO₂/CH₄ selectivity; (b) pure O₂ permeability and O₂/N₂ selectivity of 6FDA/DETDA:DABA(3:2) precursor and CMS dense films pyrolyzed at 550 °C, 800 °C, and 800 °C-precrosslinked. Robeson's CO₂/CH₄ and O₂/N₂ upper bound lines are shown for reference [42].

4.3.2 Sorption

The sorption isotherms of pure gas CO₂, CH₄, O₂, and N₂ at 35 °C of 800 °C- and 800 °C-precrosslinked 6FDA/DETDA:DABA(3:2) CMS dense films are shown in Fig. 13. The fitted Langmuir isotherms parameters are listed in Table 10. After precrosslinking, the sorption capacity for all gases increases. The increase in C_H suggests a somewhat more open micropore structure with more Langmuir sorption sites.

Fig. 13. Pure gas CO₂, CH₄, O₂, and N₂ sorption isotherms at 35 °C of 800 °C, and 800 °C-precrosslinked 6FDA/DETDA:DABA(3:2) CMS dense films.

Table 10. Pure gas CO₂, CH₄, O₂, and N₂ Langmuir isotherm parameters at 35 °C of 800 °C- and 800 °C-precrosslinked- 6FDA/DETDA:DABA(3:2) CMS dense films.

		800 °C		800 °C with precrosslinking	
		CO ₂	CH ₄	CO ₂	CH ₄
C'_H	[cm ³ (STP)/cm ³]	140.1	95.2	155.4	110.7
b	[1/psia]	0.031	0.013	0.039	0.014
		O ₂	N ₂	O ₂	N ₂
C'_H	[cm ³ (STP)/cm ³]	99.7	57.0	110.3	88.9
b	[1/psia]	0.006	0.007	0.007	0.006

The CO₂, O₂ permeabilities, sorption coefficients, diffusion coefficients and the corresponding CO₂/CH₄, O₂/ N₂ selectivities of 800 °C- and 800 °C-precrosslinked 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia are listed in Table 11. It can be seen that the increase in permeability results from the increase in both sorption and diffusion coefficient. On the other hand, again sorption selectivity and diffusion selectivity have different contributions to the overall selectivity for different gas pairs CO₂/CH₄ vs. O₂/N₂. For CO₂/CH₄, the overall selectivity decreases after precrosslinking, which is solely due to the drop in diffusion selectivity from ~35 to ~28. Nevertheless O₂/N₂ overall selectivity increases slightly after precrosslinking, which is a combined result from opposing effects from sorption selectivity and diffusion selectivity. Since the diffusion selectivity increase is more prominent than sorption selectivity decrease, overall O₂/N₂ selectivity increases. The higher diffusion selectivity maybe due to the more complex and tortuous pore structures in precrosslinked CMS membranes, but this topic will need more investigation.

Table 11: The permeability P_A , overall membrane selectivity $\alpha_{A/B}$, sorption coefficient S_A , sorption selectivity S_A/S_B , diffusion coefficient D_A , and diffusion selectivity D_A / D_B of gas pairs CO_2/CH_4 and O_2/N_2 for 800 °C-, and 800 °C-precrosslinked- 6FDA/DETDA:DABA(3:2) CMS dense films at 35 °C and 30 psia. Permeation results represent the average with variance within 15%.

Membranes	P_{CO_2} Barrer	$\alpha_{\text{CO}_2/\text{CH}_4}$	S_{CO_2} cc(STP)/cm ³ /psia	$S_{\text{CO}_2}/S_{\text{CH}_4}$	D_{CO_2} 10 ⁻⁷ cm ² /s	$D_{\text{CO}_2} / D_{\text{CH}_4}$
550 °C-CMS	21740	30.1	3.1	2.8	36.3	10.8
800 °C-CMS	1812	88.3	2.3	2.5	4.1	35.3
800 °C- precrosslinked -CMS	4678	71.5	2.8	2.5	8.6	28.1
Membranes	P_{O_2} Barrer	$\alpha_{\text{O}_2/\text{N}_2}$	S_{O_2} cc(STP)/cm ³ /psia	$S_{\text{O}_2}/S_{\text{N}_2}$	D_{O_2} 10 ⁻⁷ cm ² /s	$D_{\text{O}_2} / D_{\text{N}_2}$
550 °C-CMS	4293	4.9	0.6	1.4	37.0	3.5
800 °C-CMS	300	7.6	0.5	1.7	3.1	4.5
800 °C- precrosslinked -CMS	683	8.0	0.6	1.3	5.8	6.2

4.4 Comparison of effects of pyrolysis temperature, O₂-doping, and precrosslinking during pyrolysis on 6FDA/DETDA:DABA(3:2) CMS membrane separation performance

Section 4.1, 4.2 and 4.3 investigated the effects of pyrolysis temperature; O₂ doping; and precrosslinking, respectively, on the separation performance of 6FDA/DETDA:DABA(3:2) CMS membranes. In this section, the effects of these three pyrolyzing parameters are summarized and compared. Moreover, some speculative hypotheses regarding the structure changes brought about by changing these parameters are also provided.

Table 12 tabulates the permeabilities, sorption coefficients, Langmuir hole filling capacities C'_H and Langmuir affinity constants b of gas CO₂ as well as the CO₂/CH₄ selectivity of polymeric-; 550 °C-CMS; 800 °C-CMS; 550 °C-50 ppm O₂ doped -CMS membranes, and 800 °C-precrosslinked-CMS derived from 6FDA/DETDA:DABA(3:2). Figure 14 summarizes the fitted Langmuir sorption isotherms of pure gas CO₂ at 35 °C of these membrane materials. As can be seen compared to the 550 °C-CMS membrane: 1) with increased pyrolysis temperature, the 800 °C-CMS membrane presents lower CO₂ permeability, sorption coefficient, C'_H and b and higher CO₂/CH₄ selectivity; 2) with O₂ doping, the 550 °C-50 ppm O₂ doped -CMS membrane presents lower CO₂ permeability, higher CO₂/CH₄ selectivity, but almost the same sorption coefficient, C'_H and b ; compared to the 800 °C-CMS membrane, with precrosslinking, the 800 °C-precrosslinked-CMS membrane presents higher CO₂ permeability, sorption coefficient, C'_H and b and lower CO₂/CH₄ selectivity. These trends provide information of the membrane pore morphologies. Figure 15 is a speculative scheme showing the comparison of the effects of final pyrolysis temperature, oxygen doping and precrosslinking on the CMS structures.

Table 12: Permeabilities, sorption coefficients, Langmuir hole filling capacities and Langmuir affinity constants of gas CO₂ as well as the CO₂/CH₄ selectivity of polymeric-; 550 °C-CMS; 800 °C-CMS; 550 °C-50 ppm O₂ doped -CMS membranes, and 800 °C-precrosslinked-CMS derived from 6FDA/DETDA:DABA(3:2). Permeation results represent the average with variance within 15%.

	P _{CO₂} (Barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$	S _{CO₂} cc(STP)/cm ³ /psia	C _H (CO ₂) [cm ³ (STP)/cm ³]	b (CO ₂) [1/psia]
Polymeric-	238	22.0	-	-	-
550 °C-CMS	21740	30.1	3.1	172.2	0.039
800 °C-CMS	1812	88.3	2.3	140.1	0.031
550 °C-50 ppm O ₂ doped - CMS	3213	60.9	3.1	174.8	0.039
800 °C- precrosslinked- CMS	4678	71.5	2.8	155.4	0.039

Fig. 14. Pure gas CO₂ sorption isotherms at 35 °C of 550 °C-CMS; 800 °C-CMS; 550 °C-50 ppm O₂ doped-CMS; and 800 °C-precrosslinked-CMS membranes derived from 6FDA/DETDA:DABA(3:2).

Fig. 15: Speculative cartoon representation of the effects of the final pyrolysis temperature, oxygen doping, and precrosslinking on CMS structures: (i) 550 °C-CMS; (ii) 800 °C-CMS; (iii) 550 °C-50 ppm O₂ doped -CMS; and (iv) 800 °C-precrosslinked-CMS. (a): micropores with sizes of 7-20 Å; (b): ultramicropores with sizes < 7 Å.

As has been discussed above and shown in Figure 1, CMS membranes can be described as amorphous over the long range with turbostratic structures, and over the short range, the sp^2 -hybridized carbon sheets may align parallel to each other and form somewhat ordered structure. It is hypothesized that the micropores between the turbostratic structures, resulting from the packing imperfection, provides sorption sites; while the ultramicropores between the ordered carbon sheets enable molecular sieving. The hypothesized location of micropores and ultramicropores are highlighted in Figure 15. Pyrolysis at a relatively lower temperature of 550 °C appears to result in an open intrinsic CMS framework with both large micropores and ultramicropores as can be seen in Figure 15 (i). During pyrolysis at a higher temperature of 800 °C, the CMS framework is condensed with both tightened micropores and ultramicropores as shown in Figure 15 (ii). The condensed micropore structures result in lowered permeability and sorption while the tightened ultramicropore enhances gas selectivity. For oxygen doping during 550 °C, shown in Figure 15 (iii), the intrinsic open framework is not condensed with unchanged micropore structure and thus sorption capacity, however, ultramicropores are tuned by selective chemisorption of oxygen and results in higher gas selectivity. Figure 15 (iv) illustrates the pore morphology of 800 °C-precrosslinked-CMS membrane, the precrosslinking step appears to opens up the micropores and gives higher permeability and sorption capacity; however in the same time, it disturbs the ordered carbon sheets, and the less anisotropic ultramicropores lose some molecular sieving ability.

It is critical to understand the difference between tuning CMS membrane performance by O_2 doping and by pyrolysis temperature since it will help drive the development path. These two methods yield essentially identical permeability and selectivity performance yet the underlying reason to the performance is different. A higher pyrolysis temperature tends to provide CMS membranes with both condensed micropores and ultramicropores, which might be a potential solution to suppress physical aging in CMS membranes. On the other hand, O_2 doping mainly

affects the ultramicropore morphologies and fine tunes the separation performance of CMS membranes.

5. Summary and Conclusions

The effects of pyrolysis conditions including pyrolysis temperature, O₂ doping, and precrosslinking were studied based on 6FDA/DETDA:DABA(3:2) derived CMS dense film membranes for separation of important gas pairs including pure gases CO₂/CH₄, O₂/N₂ and mixture gases 50% CO₂/50% CH₄ and 50% C₃H₆/50% C₃H₈. As expected, the increased pyrolysis temperature tends to give lower permeable but more selective membranes. The O₂ doping provides a fine tuning method for altering the separation performance of CMS membranes. Finally, CMS membranes derived from a novel method, which was first proposed for another DABA containing precursor and referred to as precrosslinking, was shown in this study to be attractive with significantly improved gas permeability and slightly drop in selectivity.

The results reported in this study serve as a guide for future optimization study on CMS membranes. The optimized pyrolysis conditions will be highly dependent on the type of the CMS membrane used and the targeted gas pairs. For example, an optimized pyrolysis condition effective for CO₂/CH₄ separation is not necessarily ideal for O₂/N₂ separation. Different final pyrolysis temperatures or different amount of O₂ doping might be favored for different gas pair separations. Moreover, the combination of different tuning methods might also be attractive for some specific applications.

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