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**Ultra-selective carbon molecular sieve membranes for natural gas separations
based on a carbon-rich intrinsically microporous polyimide precursor**

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ABSTRACT

A highly contorted, carbon-rich intrinsically microporous polyimide (PIM-PI) made from spirobifluorene dianhydride and 3,3-dimethylnaphthidine (SBFDA-DMN) was employed as a precursor for the formation of carbon molecular sieve (CMS) membranes at pyrolysis temperatures from 550 to 1000 °C. The high carbon content of SBFDA-DMN (~84%) resulted in only 28% total weight loss during pyrolysis under a nitrogen atmosphere at 1000 °C. The development of the various microstructural textures was characterized by gas sorption analysis, Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction, Raman spectroscopy, electrical conductivity, and gas transport properties. Heat treatment of a pristine SBFDA-DMN membrane at 550 °C resulted in reduced permeability for all gases (e.g.: P_{CO_2} dropped from 4700 to 1500 barrer) as well as lower BET surface area from 621 to 545 m² g⁻¹. At 600 °C, new pores induced by pyrolysis increased the BET surface area to nearly that of the precursor and significantly improved gas separation performance. Above 600 °C, a progressive collapse of the micropores became evident with CMS membranes showing higher gas-pair selectivity but lower permeability. At 1000 °C, ultra-micropores comparable in size with the kinetic diameter of CH₄ emerged and induced a prominent molecular sieving effect resulting in very high CH₄ rejection. This strong size exclusion effect, further supported by gravimetric gas sorption measurements, resulted in unusually high N₂/CH₄ and CO₂/CH₄ selectivities of 35 and 1475, respectively.

1. Introduction

The worldwide natural gas (NG) production has increased by ~25% from 2941 billion m³ in 2007 to 3680 billion m³ in 2017 [1]. This enormous increase in NG production due to higher energy consumption drives the worldwide market for new natural gas processing plants and advanced separation technologies [2,3]. While methane is always the major component of natural gas (75 - 90%), some undesirable contaminants, such as water vapor, carbon dioxide, nitrogen, and hydrogen sulfide may also be present, and their removal is of vital importance to meet pipeline specifications [3]. Despite the existence of well-established gas separation technologies (e.g., amine absorption, pressure swing adsorption, molecular sieves, cryogenic distillation, etc.), membrane technology offers a very attractive alternative given its potentially low energy consumption relative to existing conventional technologies [3-5]. However, two main challenges exist for membrane technology in natural gas processing – the first is the necessity to improve the membrane separation performance, that is, to develop advanced *materials* with high permeability coupled with high gas-pair selectivity. The second is the difficulty in preparing robust *thin, defect-free membranes* that can endure the harsh NG feed process conditions [5,6]. As a consequence of these challenges, membrane-based gas separations currently account only for ~5% of the NG market [3].

The available commercial polymeric membrane materials that are used for the removal of CO₂ from natural gas (e.g., cellulose triacetate, polyimide, etc.) exhibit relatively moderate properties with performance below the 2008 pure-gas [7] and 2018 mixed-gas [8] CO₂/CH₄ permeability/selectivity trade-offs. This ordinary performance is directly related to the limited size sieving properties of conventional polymeric materials. Recent work demonstrated that rigid microporous membrane materials (pore size < 20 Å), such as (i) intrinsically microporous ladder polymers (PIMs) or polyimides of intrinsic microporosity (PIM-PIs), (ii) thermally-rearranged (TR) polymers, and (iii) carbon molecular sieves (CMSs), can break conventional polymer permeability/selectivity trade-offs. Optimized PIMs and PIM-PIs have demonstrated enhanced gas permeability and improved molecular sieving capability for some gas pairs, such as O₂/N₂, H₂/N₂, and H₂/CH₄, with performance defining the 2015 permeability/selectivity polymer upper bounds [9-12]. These outstanding properties arise from their rigid and contorted molecular structures, which frustrate chain packing to create a favorable size-sieving pore size distribution

and high internal surface area. Furthermore, –OH and –COOH-functionalized PIM-PIs are among classes of advanced polymers displaying the most promising gas separation performance for CO₂/CH₄ separation [13-15]. The design of TR polymers, made by thermal conversion of polyimides containing OH groups in ortho position to the imide linkages at 400 - 450 °C, is another potential route to introduce microporosity into membrane materials to enhance their gas separation performance, especially for CO₂/CH₄ separation [16].

Compared to polymeric membrane materials, carbon molecular sieve (CMS) membranes exhibit superior thermal and chemical stability as well as extraordinary gas separation performance for a variety of highly energy demanding gas separation applications, such as CO₂/CH₄, N₂/CH₄, C₂H₄/C₂H₆, C₃H₆/C₃H₈ etc. [17-20]. Their exceptional performance originates from the strong size exclusion capability caused by their highly rigid, slit-like pore structure and narrow pore size distribution. In 1983, Koresh and Soffer prepared the first carbon molecular sieve membranes by thermal decomposition of different polymeric precursors [21]. Since then, extensive research has been devoted to the effect of the polymeric precursor on the resultant CMS membranes, including polyacrylonitrile [22], polyimides [23,24], phenolic resin [25,26], polyfurfuryl alcohol [27], and others [28,29]. Among these polymers, polyimides are the most widely studied precursors for the preparation of CMS membranes due to their versatile chemistry and excellent mechanical and thermal properties [30, 31].

Many earlier studies investigated the effects of various preparation parameters (e.g., polymer precursor, pyrolysis temperature, heating rate, holding time, and pyrolysis atmosphere) on the performance of the resultant CMS membranes [18,28-31]. Increasing the pyrolysis temperature typically produces CMS membranes with higher selectivity and lower permeability, but enhanced brittleness [29-32]. The average interplanar spacing reveals the microstructural changes caused by pyrolysis, which is ultimately linked to the CMS gas separation performance. Pyrolysis is most commonly carried out at temperatures ranging from 500 to 800 °C [6,33,34]. CMS membranes made at temperatures >800 °C are rarely reported in the literature with the exception of some works on Kapton and Matrimid polyimides (**Fig. 1**) [35-38]. Suda and Haraya observed continuous reductions in gas permeability coupled with steeply increasing gas-pair selectivity for CMS membranes based on Kapton polyimide by raising the pyrolysis temperature

from 600 to 1000 °C [36]. Recently, Zhang and Koros studied the molecular sieving effect of CMS hollow fiber membranes made from Matrimid polyimide precursor at elevated pyrolysis temperatures from 750 to 900 °C. X-ray diffraction showed broad peaks with average d-spacings in the range of 3.70-3.86 Å. Such CMS membranes present the best performing molecular sieves reported to date. Matrimid-derived CMS pyrolyzed at 900 °C showed ultra-high selectivity for all gas pairs (e.g. $\text{CO}_2/\text{CH}_4 = 3650$, $\text{N}_2/\text{CH}_4 = 63$, etc.) [35].

Fig. 1. Chemical structures of Kapton, Matrimid, and SBFDA-DMN (this study) with simulated three-dimensional conformations obtained by Materials Studio 6.0 (Biovia). The light blue shadow is used to highlight the molecular orientations of the precursors.

Our group investigated the gas separation performance of CMS membranes derived from ladder PIMs, such as PIM-1, and polyimides of intrinsic microporosity (PIM-PIs) [39-44]. We demonstrated that the intrinsic microporosity of the polymeric precursor can have significant effects on the formation of the ultimate microporous structure of the CMS membranes. Ma et al. reported CMS membranes based on a PIM-PI precursor using PIM-6FDA-OH [39]. The CMS membrane obtained by pyrolyzing the PIM-PI precursor at 800 °C exhibited excellent gas separation properties, well above the permeability-selectivity trade-off curves of polymeric membranes with a CO_2 permeability of 556 Barrer and CO_2/CH_4 selectivity of 93. Salinas et al. employed a hydroxyl-free spirobisindane-based PIM-PI precursor (PIM-6FDA), to prepare CMS membranes for ethane/ethylene separation [43]. Carbon membranes derived from PIM-6FDA pyrolyzed at 800 °C showed an exceptional separation performance for ethylene/ethane with a mixed-gas selectivity of 16 obtained for a 1:1 $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ feed at 20 atm and 35 °C – the best

performance of any materials class for ethylene/ethane separation reported to date. Recently, Jin's group applied a Tröger's base derived PIM-PI, named TB-PI, as precursor material for formation of CMS membranes pyrolyzed at 550, 650 and 800 °C, respectively [34]. The TB-PI-based CMS membrane pyrolyzed at 800 °C showed excellent performance for natural gas applications, far above the 2008 Robeson upper bound, with a CO₂ permeability of 1406 barrer and CO₂/CH₄ selectivity of 112.

Thus far, no data have been reported for CMS membranes made at higher pyrolysis temperature than 800 °C based on ladder PIM or PIM-PI precursors. Here, we report the properties of a heat-treated carbon-rich intrinsically microporous polyimide (SBFDA-DMN) to produce: (i) an amorphous carbon intermediate at 550 - 600 °C and (ii) amorphous turbostratic carbon molecular sieve membranes from 600 to 1000 °C. The rigid and contorted structure of the highly aromatic PIM-PI precursor (**Fig. 1**) was designed to control the collapse of micropores during carbonization at high pyrolysis temperatures. In this work, we report how the gradual changes in the membrane microstructure affected the resulting gas transport properties of the pyrolyzed SBFDA-DMN polyimide precursor material.

2. Experimental

2.1 Materials and characterization methods

The pristine polymer used as the CMS precursor was a PIM-PI made by polycondensation reaction of a spirobifluorene-based dianhydride with 3,3'-dimethylnaphthidine (SBFDA-DMN) according to a previously reported method [45]. A thermogravimetric analyzer (TGA, TA Instruments) was used to measure the weight loss as a function of the pyrolysis temperature. X-ray diffraction (XRD) experiments were conducted on a Bruker D8 Advance diffractometer at a scanning rate of 0.5° min⁻¹ from 6 to 70°; the d-spacings were calculated with Bragg's law. The surface area and pore size distribution (PSD) at each pyrolysis temperature were obtained by N₂ adsorption at 77 K and CO₂ adsorption at 273 K using a Micromeritics ASAP 2020 adsorption apparatus with micropore option. Before measurement, the samples were degassed at 120 °C for 24 h. The Brunauer-Emmett-Teller (BET) surface area was determined over a relative pressure range of 1×10⁻⁸ to 0.99. The pore size distribution was obtained by the Nonlinear Density

Functional Theory (NLDFT) model assuming carbon-slit pore geometry. Raman spectra were acquired with a Horiba LabRam HR800 Raman spectrometer at 473 nm wavelength and electrical conductivity of the CMS samples were measured with a DM-200 digital multimeter. The x-ray photoelectron spectroscopy (XPS) experiments were performed on a Kratos Axis Supra instrument equipped with a monochromatic Al K α x-ray source ($h\nu = 1486.6$ eV). The geometric density of the CMS membranes was determined by accurately measuring the thickness, area and weight of each pyrolyzed sample *immediately* after removing the membranes from the furnace.

2.2 Membrane precursor fabrication

The polymer precursor (SBFDA-DMN) was dissolved in chloroform (~3 weight %) and the solution was then filtered using a 0.45- μm PTFE cartridge into a glass petri dish with a syringe. The solvent was slowly evaporated from the polymer solution that was covered by a larger glass petri dish under ambient conditions. After two days, the dry membranes (~ 60 to 70 μm thick) were soaked in methanol for 24 h to remove any solvent trapped in the micropores and then heated at 120 $^{\circ}\text{C}$ for 24 h under high vacuum.

2.3 Polymer to carbon molecular sieve transformation

Round polymeric membrane samples (**Fig. S1**) were placed inside a Carbolite three-zone tube furnace supplied with 1000 cm^3 (STP) min^{-1} of N_2 . The temperature was measured with a thermocouple adjacent to the sample. The concentration of oxygen exiting the furnace was measured with a Cambridge Sensotec Rapidox 3100 and did not exceed 2 ppm. The precursor was heated at a ramp rate of 3 $^{\circ}\text{C min}^{-1}$ to set point temperatures from 550 to 1000 $^{\circ}\text{C}$ and then held isothermally for 60 minutes. After the isothermal soak, the furnace was allowed to passively cool to room temperature, which took around 9 h (**Fig. S2**). The gas permeation properties of the membranes were tested immediately after removal from the furnace. A description of the heating protocol used in this study is illustrated in **Fig. 2**.

Fig. 2. The heating protocol of the SBFDA-DMN polyimide precursor to produce carbon molecular sieve membranes.

2.4 Gas permeation measurements

Gas permeation experiments were performed at 35 °C and 2 atm in a constant volume/variable-pressure apparatus [46] using ultrahigh purity gases in increasing order of condensability (He, N₂, O₂, CH₄, and CO₂). The membranes were degassed for about 24 h to remove adsorbed molecules.

2.5 Gravimetric sorption

Gravimetric sorption isotherms for pure nitrogen, methane and carbon dioxide at 35 °C up to 15 atm were determined with a Hiden Isochema IGA apparatus (Warrington, UK).

3. Results and discussion

3.1 Carbon molecular sieve structural evolution during pyrolysis

Carbonization is a process of continuous thermal decomposition of polymer chains and partial elimination of elements other than carbon to yield an amorphous turbostratic structure (**Fig. 3**).

Fig. 3. Schematic of chemical transformation occurring during pyrolysis; the structure on the right is a possible CMS morphology; structures generated by Materials Studio 6.0 (Biovia).

The weight loss of the SBFDA-DMN polyimide during the heating process up to 1000 °C is depicted in **Fig. 4**. The TGA thermogram can be divided into three regions: (i) degradation of the precursor started to occur at ~ 550 °C demonstrating the high thermal stability of the SBFDA-DMN precursor. At 550 °C, the BET surface area dropped from 621 to 545 m²/g (**Fig. 5**); (ii) the maximum weight loss rate was observed around 600 - 650 °C; in this region, the weight decreased by 10 - 15% forming an intermediate amorphous carbon structure [47,48] with evolved pores increasing the BET surface area to 615 m²/g; (iii) from 650 to 1000 °C, the degradation rate started to decline, and the CMS membranes bulk density began to increase indicating formation of a tighter and more ordered structure (**Fig. 5**). Densification of the CMS structure resulted in a tightly sintered carbon matrix which hindered the diffusion of the probing N₂ molecules into pores by gas sorption and, as a result, very limited contribution of ultra-micropores to the BET surface area could be detected for the 700 to 1000 °C-heat-treated membranes, as shown in **Fig. 5**. From 900 to 1000 °C, the degradation rate reached a very low value as seen by the small decrease in the weight loss. The relatively small overall weight loss at 1000 °C (~28%) is consistent with the high carbon content (~ 84%) of the SBFDA-DMN precursor. As expected, XPS analysis of various CMS samples (**Table S1** and **Fig. S3**) showed a continuous increase in carbon content concurrent with decrease in oxygen and nitrogen contents as pyrolysis temperature increased.

Fig. 4. Weight loss of SBFDA-DMN polyimide for each isothermal stage of degradation. The dashed curve represents the total degradation rate of the precursor upon pyrolysis.

Fig. 5. BET surface areas and bulk densities of heat-treated SBFDA-DMN polyimide and CMS membranes.

3.2 CO_2 and N_2 sorption isotherms and pore size distributions

N_2 and CO_2 are often used as probe molecules in gas sorption experiments to provide assessments of the surface area and pore size distribution of CMS membranes [49]. N_2 adsorption with a relative pressure (p/p_o) ranging from 1×10^{-8} to 0.99 at 77 K was used in this

study to investigate the microporosity (< 2 nm) of the CMS membranes. The main disadvantage of this method is the hindered diffusion of N_2 into the narrow pores (< 0.5 nm) in the low relative pressure range (10^{-3} - 10^{-8}), which results in less reliable pore size distribution data in the ultra-microporous region [49]. N_2 isotherms for the SBFDA-DMN and its derived CMS membranes exhibited a steep uptake in the low pressure range (i.e., $p/p_o < 10^{-3}$), as shown in **Fig. 6a**. The tuning of porosity by carbonizing the polymer structure is typically expected to increase the sorption capacity of the membrane [50]. Nevertheless, the magnitude of this change is less noticeable if the precursor is a high-free-volume material as in the case of the SBFDA-DMN polyimide (**Fig. 6a**). Heating the pristine PIM-PI sample isothermally at 550 °C for 1 h shifted the intrinsic micropores slightly towards smaller micropores (**Fig. 6b**) which resulted in reduced sorption uptake (**Fig. 6a**). SBFDA-DMN thermally treated at 600 °C displayed a maximum sorption uptake and an apparent shift in the pore size distribution towards the ultra-microporous region (< 7 Å). However, for the 700 to 1000 °C-heat-treated membranes N_2 molecule diffusion into the ultra-micropores was hindered by the tightly sintered carbon matrix; consequently, the contribution of the ultra-micropores deduced from the N_2 sorption uptake could not be detected as shown in **Fig. 6a**.

To overcome this problem, low-pressure CO_2 adsorption at 273 K was employed [49]. Using the smaller CO_2 as a molecular probe allows for better access into the smaller ultra-micropores and, therefore, results in a better structure/porosity assessment. Progressive increase in the sorption uptake as a consequence of the evolution of pores was observed for the pristine precursor up to the 800 °C-heat-treated CMS membranes (**Fig. 6c**). The SBFDA-DMN treated at 800 °C exhibited maximum sorption uptake (**Fig. 6c**) with an apparent increase in the ultra-micropores volume fraction, as shown in **Fig. 6d**. Treating the SBFDA-DMN above 800 °C resulted in a tighter carbon matrix, which limited CO_2 diffusion into the pores, therefore probably affecting the accurate estimation of pores in the ultra-microporous region. Another approach to assessing the shift in the pore size distribution at the critical region of high pyrolysis temperature is x-ray diffraction, which is discussed in Section 3.3.

Fig. 6. (a) Physisorption of N₂ at -196 °C; (b) N₂ sorption isotherm-derived pore size distribution for SBFDA-DMN and its CMS derivatives; (c) physisorption of CO₂ at 0 °C and (d) CO₂ sorption isotherm-derived pore size distribution for SBFDA-DMN and its CMS derivatives.

3.3 XRD and Raman analysis

XRD patterns of the SBFDA-DMN polyimide and the derived CMS membranes are shown in **Fig. 7**. All spectra exhibit broad peaks, which are indicative of the amorphous nature of the precursor and the heat-treated CMS samples. The PIM-PI precursor showed a bimodal distribution indicated by two broad peaks with corresponding d-spacings of 7.4 Å and 4.4 Å. SBFDA-DMN thermally treated at 600 °C appeared to have one broad amorphous peak with a much higher average d-spacing of ~8.7 Å compared to the pristine polyimide. However, significant changes in the diffraction patterns were observed for samples carbonized at higher pyrolysis temperatures, as evidenced by the continuous shift and narrowing of the peaks. The 2θ

peak around 44° with an average d-spacing of 2.0-2.1 Å corresponds to the (100) plane in the graphite lattice and indicates the average space between the neighboring carbon atoms within graphene planes [23]. By raising the pyrolysis temperature from 600 to 1000 °C, the intensity of this peak became more pronounced suggesting the formation of more ordered graphitic-like carbonaceous structures. The main amorphous peak shifted significantly to the higher 2θ values for 800 and 1000 °C CMS samples compared to the pristine and 600 °C CMS sample. The average inter-plane distances (d_{002}), which are calculated from the diffraction peaks at the disordered graphitic (002) planes, slightly decreased from 4.0 to 3.8 Å between 800 and 1000 °C. Although the diffraction peaks of these CMS samples exhibited amorphous and disordered nature with the d_{002} values higher than the d_{002} of graphite (~ 3.4 Å), the evolution of XRD patterns clearly shows the development towards a more ordered graphitic structure and smaller pores for CMS samples prepared at higher pyrolysis temperature (**Table S2**). X-ray diffraction of CMS membranes derived from Matrimid showed a d-spacing of 3.80 Å at 800 °C [23], whereas increasing the pyrolysis temperature up to 900 °C resulted in a reduced d-spacing of 3.70 Å [35]. The larger d-spacing of SBFDA-DMN-derived CMS membranes, relative to Matrimid and Kapton, indicates a higher resilience of SBFDA-DMN to maintain its amorphous structure and collapse of its micropores which is consistent with the gas separation performance discussed in the next section.

Besides the average inter-plane distances of disordered graphitic plane (002), other structural parameters of SBFDA-DMN-based CMS membranes, including the apparent crystallite thickness (L_c) and the apparent layer-plane length (L_a) can also be used as measure to evaluate the development of a graphitic-like structure in carbon materials [51]. These parameters were calculated based on the Scherrer formula from XRD spectra (see **Fig. S4**). The average apparent layer-plane length (L_a) increased from 13 to 23 Å as the pyrolysis temperature increased from 700 to 1000 °C, as shown in **Table S2**. Moreover, the average apparent crystallite thickness (L_c) also increased from 7.2 to 8.2 Å from 700 to 1000 °C. Both increase in the crystallite thickness L_c and the layer-plane length L_a indicated that more ordered graphitic structures were developed as the pyrolysis temperature increased.

The Raman spectra of the SBFDA-DMN-derived carbons from 700 to 1000 °C are shown in **Figs. S5-S6**. All samples exhibited two prominent broad peaks: the D peak (~ 1360 cm⁻¹,

indicative of the defective structure of graphite) and the G peak ($\sim 1590\text{ cm}^{-1}$, indicative of the regular graphite structure). All peak-fitting results of the peak position, peak width, peak intensity based on peak area, and peak area ratio of D and G bands are summarized in **Table S3**. As the pyrolysis temperature increased, the D peak was narrower with an accompanying decrease in its intensity $I(D)$, whereas the G peak experienced an increase in its intensity $I(G)$. A lower $I(D)/I(G)$ ratio is likely to be associated with smaller defects density, higher order in graphitic materials [52]. The interpretation of lower $I(D)/I(G)$ ratio referring to a higher graphitization level is only valid when the crystal size is larger than 20 Å [53]. Based on XRD analysis, the crystallite size, which was calculated at different pyrolysis temperatures, increased from 20.2 to 22.8 Å in the temperature range of 800 to 1000 °C . Therefore, Raman analysis indicated that a higher graphitization level occurred for CMS membranes at higher pyrolysis temperature consistent with the XRD results.

Fig. 7. X-ray diffraction of the SBFDA-DMN polyimide precursor and its heat-derived CMS membranes. Vertical lines are used to highlight the shift in the peak.

3.4 Gas transport properties

The pure gas (He , N_2 , O_2 , CH_4 , and CO_2) permeabilities of the SBFDA-DMN precursor and the derived carbon membranes were determined at 2 atm and 35 °C (**Table 1**). The pristine PIM-PI precursor exhibited the highest gas permeabilities relative to all carbonized membranes – this is unusual compared to all previously reported CMS precursors including PIM materials

[34,39,40]. After heating the precursor isothermally at 550 °C, the permeability dropped significantly and resulted in a small increase in selectivity. After partial degradation of the polymer backbone at 600 °C, permeability of the CMS increased significantly relative to the 550 °C sample, likely as a result of the generation of new pores and pore opening. This is indicated by widening of the average d-spacing as shown in XRD spectra (**Fig. 7**) and the increase in BET surface area (**Fig. 5**). Previous studies showed that such an intermediate state CMS usually exhibits the highest gas permeability compared to the polymeric precursors [34,39,40,47,48].

In the case of SBFDA-DMN, the intrinsic polymer permeability was very high due to its high BET surface area resulting from its contorted rigid structure - this signifies one of the important differences between the high BET surface area PIM-PIs and conventional low-free-volume polyimide (Matrimid, P84, and others) carbon precursors. Consequently, while the intermediate state 600 °C CMS exhibited a loss in permeability relative to the SBFDA-DMN precursor, it showed a significant increase in selectivity. For example, the CO₂ permeability dropped from 4700 barrer for the pristine polymer to 2853 barrer for the 600 °C heat-treated membrane with a concurrent ~ 3-fold increase in the CO₂/CH₄ selectivity from 14 to 37. The decrease in gas permeability for the 700 to 1000 °C heat-treated CMS membranes resulted from gradual pore shrinkage. The increase in He/CO₂ selectivity observed at 700 °C is evidence for the formation of a tighter ultra-microporous molecular sieve structure. The magnitude of the permeability decrease scaled with the gas size in the order: He < CO₂ < O₂ < N₂ < CH₄. Owing to the development of tighter ultra-micropores the membranes pyrolyzed at higher temperatures exhibited extremely high gas-pair selectivity. For example, the 1000 °C heat-treated CMS membrane displayed extremely high CO₂/CH₄ and N₂/CH₄ selectivity of 1475 and 35, respectively, combined with CO₂ and N₂ permeabilities of 30 and 0.7 barrer. The extraordinarily high rejection of CH₄ of the CMS membrane made at this pyrolysis temperature can be related to the comparable d-spacing of the turbostratic carbon structure with the kinetic diameter of CH₄ (3.80 Å), as evidenced by the WAXD analysis discussed above. This ultra-high selectivity has been unachievable so far by polymeric membranes, specifically for penetrants with similar molecular size such as N₂/CH₄ [7]. Unlike the progressive increase in selectivity for CO₂/CH₄ and N₂/CH₄ from the pristine polyimide to the 1000 °C heat-treated CMS membrane, O₂/N₂ selectivity already reached a plateau at 800 °C and did not change significantly at higher

pyrolysis temperatures. This interesting effect may be related to the similar effect of pore collapse encompassing both O₂ and N₂ molecule dimensions of 3.46 and 3.64 Å, respectively, which resulted only in a drop in permeability for both gases.

Table 1. Gas permeability and selectivity of pristine and heat-treated SBFDA-DMN membranes.

Temperature (°C)	Permeability (barrer) ^a					Ideal Selectivity $\alpha_{x/y}$			
	He	N ₂	O ₂	CH ₄	CO ₂	He/CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	N ₂ /CH ₄
Pristine ^b	1340	226	850	326	4700	0.29	3.8	14	0.70
550	442	66	266	72	1500	0.30	4.0	21	0.92
600	1073	110	663	77.5	2853	0.38	6.0	37	1.42
700	903	8.75	85	5.7	236	3.83	9.8	41	1.54
800	418	3.23	35	0.93	105	3.98	11	113	3.5
900	250	1.6	20	0.27	60	4.17	13	222	5.9
950	132	1.06	12	0.104	39	3.38	11	375	10
1000	96	0.7	7.52	0.02	30	3.25	11	1475	35
1000 ^c	78	0.48	5.62	0.013	22	3.55	11.7	1732	38

^a 1 barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹ or 7.6×10^{-18} m³ (STP) m m⁻² s⁻¹ Pa⁻¹. The measurements were carried out at 35 °C; upstream pressure was 2 atm.

^b Permeation data were obtained from reference [45].

^c Sample tested after 250 days.

Physical aging is a process of gradual structural materials relaxation towards an equilibrium state over time, which can lead to significant changes in gas transport properties. This phenomenon has been extensively studied for glassy polymeric materials [45,54-56] but has rarely been investigated for CMS materials [57]. In this study, the physical aging effect on CMS-1000 °C derived from SBFDA-DMN polyimide was studied over 250 days of storage under ambient conditions (**Table 1**). Permeability decreased for all gases but to a relatively moderate extent with a small commensurate increase in gas-pair selectivity, demonstrating good stability of the CMS membrane toward physical aging. For example, the CO₂ permeability decreased from 30 barrer for a fresh CMS sample to 22 barrer upon aging with a concurrent increase in CO₂/CH₄ selectivity from 1465 to 1732.

The performance of the SBFDA-DMN polyimide and its derived CMS membranes for CO₂/CH₄ and N₂/CH₄ separation is plotted on the 2008 upper bound of polymeric materials in **Fig. 8**. In

both plots, unlike CMS membranes derived from conventional low-free-volume polymers such as Matrimid [58], the high-free-volume SBFDA-DMN precursor exhibited the highest permeability among the studied samples. Increasing the pyrolysis temperature from 600 to 700 °C reduced the permeability significantly but showed surprisingly little effect on the selectivity of CO₂/CH₄ and N₂/CH₄ (**Fig. 8**). It is worth noting that the progressive increase in the selectivity above 700 °C correlates well with the sharp increase in the electrical conductivity of the CMS materials (**Fig. 9**). This indicates that the materials developed a more conjugated electronic structure leading to increased conductivity concurrently with an onset of tightening of the slit-like micropores.

Fig. 8. Separation performance of the SBFDA-DMN polyimide and its heat-treated CMS samples from 550 to 1000 °C. a) CO₂/CH₄, b) N₂/CH₄; blue square mark represents the 8 months aged 1000 °C sample.

Fig. 9. Relationship between the electrical conductivity of the CMS samples with increasing pyrolysis temperature.

Gravimetric N₂, CH₄, and CO₂ direct sorption measurements were carried out at 35 °C and 2 atm to further investigate the contributions of gas solubility and diffusivity on the permeability and permselectivity of SBFDA-DMN-based CMS membranes. The diffusion coefficients at 2 atm were calculated from the relationship: $D = P/S$. As anticipated, the diffusion coefficients of all gases dropped gradually for CMS membranes made at 600 to 1000 °C and scaled with the gas size, i.e. CO₂ < N₂ < CH₄ (**Fig. 10a**). The solubility coefficient of all gases increased when the heat treatment was raised from 600 to 800 °C due to the generation of the new pores (**Fig. 10b**). Increasing the pyrolysis temperature further to 900 °C showed relatively little effect on the sorption coefficients for N₂ and CO₂. The 1000 °C-heat-treated membrane showed a slight decrease in the N₂ and CO₂ sorption coefficient (6% for both); however, the sorption coefficient of CH₄ was the most affected with a drop of 35%. Consequently, the CO₂/CH₄ (**Fig. 11a**) and N₂/CH₄ (**Fig. 11b**) solubility selectivity increased. The drop in the CH₄ sorption coefficient was probably caused by the very tightly packed CMS structure, which restricted the diffusion of CH₄ into the pores. This effect was first observed and discussed by Zhang and Koros for CMS membranes derived from Matrimid [35], in which the diffusion of CH₄ was *severely* restricted to the extent where a reverse solubility selectivity favoring N₂ over CH₄ was obtained at pyrolysis of 900 °C. **Fig. 11b** depicts such progressive increase in the N₂/CH₄ solubility selectivity for the CMS derived from SBFDA-DMN heated at 1000 °C, however no reverse solubility selectivity

was observed. It is important to note that the sorption data qualitatively agree with the trend observed in the XRD results, which showed that the average d-spacing of the CMS pyrolyzed at 1000 °C approached the kinetic diameter of the CH₄ thereby limiting the accessibility of CH₄ diffusion into the pore structure of the CMS.

Fig. 10. a) Diffusivity and b) solubility coefficients of CO₂, N₂ and CH₄ in CMS membranes derived from SBFDA-DMN precursor at 35 °C and 2 atm. The light blue square marks the area where the diffusivity and solubility coefficients of CH₄ dropped together, indicating limited pore access.

Fig. 11. a) CO₂/CH₄ and b) N₂/CH₄ diffusivity and solubility selectivities of CMS membranes derived from SBFDA-DMN. The dashed-lines are drawn to guide the eye.

The sorption isotherms for N₂, CH₄ and CO₂ at 35 °C in the CMS-1000 °C up to 15 atm at 35 °C are depicted in **Fig. 12a**. All isotherms were fitted with the Langmuir sorption model and the

gases did not reach their saturated adsorption capacity throughout the pressure range studied up to 15 atm. **Fig. 12b** depicts that the solubility selectivity of CO_2/CH_4 and CH_4/N_2 decreased sharply with increasing pressure.

Fig. 12. a) Sorption isotherms of N_2 , CH_4 , and CO_2 at 35 °C in CMS-1000 °C membranes derived from SBFDA-DMN; the dashed-lines are based on Langmuir-mode fitting; b) solubility selectivity of CO_2/CH_4 and CH_4/N_2 as a function of pressure; the solid lines are drawn to guide the eye.

Fig. 13 compares the progressive improvement of the gas separation performance of CMS membranes that is derived from two different precursor types – one is the carbon-rich SBFDA-DMN, the high BET surface area PIM-PI used in this study, and the second is the conventional low-free-volume Matrimid polyimide recently reported by Zhang and Koros [35]. While SBFDA-DMN with its ultrahigh permeability is located at the far right, Matrimid with its low permeability is placed at the far left in **Fig. 13**. Although, the two pristine polyimide precursors have two orders of magnitude different gas permeabilities, **Fig. 13a** indicates that pyrolyzing them at 800 °C, resulted in CMS membranes with very similar gas separation performance for He/CH_4 . However, the effect of the precursor type was more pronounced after increasing the pyrolysis temperature to 900 °C. Matrimid suffered from a 77% reduction in He permeability whereas SBFDA-DMN showed only a 40 % drop in He permeability. This observation reflects the higher thermal resistance and possibly also the higher rigidity of SBFDA-DMN, which results in less pores collapse as compared to Matrimid when they are exposed to higher pyrolysis temperatures. A similar conclusion can be drawn from **Fig. 13b**, where increasing the pyrolysis

temperature from 800 to 900 °C reduced the CO₂ permeability about 60% and 42% in CMS membranes derived from Matrimid and SBFDA-DMN, respectively.

Fig. 13. 2008 performance upper bound for a) He/CH₄ and b) CO₂/CH₄ separation performance of the SBFDA-DMN and Matrimid with their heat-treated CMS samples. The light blue rectangular marks an area where the CMS performance for both precursors is very similar.

4. Conclusions

In this study, a highly carbon-rich intrinsically microporous polyimide (SBFDA-DMN) precursor was employed to generate a systematic series of CMS membranes made at different pyrolysis temperatures. The gradual changes in the membrane microstructure affected the resulting gas transport properties of the pyrolyzed SBFDA-DMN polyimide. The rigid and contorted structure of the highly aromatic SBFDA-DMN precursor resulted in reduced collapse of micropores during pyrolysis at high temperatures. When pyrolyzed at 900 °C, SBFDA-DMN-generated CMS membranes which exhibited higher permeability but lower gas-pair selectivity than CMS membranes derived from the low-free-volume Matrimid precursor. The ultrahigh selectivity of CO₂ and N₂ over CH₄ observed for the SBFDA-DMN-derived CMS-1000 °C membrane resulted from a very tightly packed structure which severely restricted the diffusion of the CH₄ into the pores leading to reduced sorption and diffusion coefficients. This ultrahigh CH₄ rejection agreed with the XRD results which showed that the average d-spacing at 1000 °C approached the kinetic diameter of CH₄.

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Highlights

- ❖ Carbon molecular sieve membranes made from microporous SBFDA-DMN polyimide
- ❖ High temperature pyrolysis at 1000 °C leads to ultrahigh gas-pair selectivity
- ❖ CO₂/CH₄ permselectivity of 1475 boosted by diffusion- and solubility selectivity
- ❖ CMS made at 1000 °C achieved extraordinary N₂/CH₄ permselectivity of 35
- ❖ Physical aging had only moderate effect on gas permeability and gas-pair selectivity