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High-performance carbon molecular sieve membranes for ethylene/ethane separation derived from an intrinsically microporous polyimide

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Abstract

An intrinsically microporous polymer with hydroxyl functionalities, PIM-6FDA-OH, was used as a precursor for various types of carbon molecular sieve (CMS) membranes for ethylene/ethane separation. The pristine polyimide films were heated under controlled N₂ atmosphere at different stages from 500 to 800 °C. All CMS samples carbonized above 600 °C surpassed the polymeric ethylene/ethane upper bound. Pure-gas selectivity reached 17.5 for the CMS carbonized at 800 °C with an ethylene permeability of about 10 Barrer at 2 bar and 35 °C, becoming the most selective CMS for ethylene/ethane separation reported to date. As expected, gravimetric sorption experiments showed that all CMS membranes had ethylene/ethane solubility selectivities close to

one. The permselectivity increased with increasing pyrolysis temperature due to densification of the micropores in the CMS membranes, leading to enhanced diffusivity selectivity. Mixed-gas tests with a binary 50:50 v/v ethylene/ethane feed showed a decrease in selectivity from 14 to 8.3 as the total feed pressure was increased from 4 to 20 bar. The selectivity drop under mixed-gas conditions was attributed to non-ideal effects: (i) Competitive sorption that reduced the permeability of ethylene and (ii) dilation of the CMS that resulted in an increase in the ethane permeability.

Keywords:

ethylene/ethane separation, carbon molecular sieve, polyimide of intrinsic microporosity, mixed-gas permeation

1. Introduction

The worldwide ethylene production by steam cracking was 141 million tons in 2011 which is higher than that of any other organic compound [1]. The ethylene-rich stream exiting the cracker must be separated from other organic compounds such as ethane. The ethylene/ethane separation step is extremely challenging due to the similarities in size of the molecules (Lennard-Jones diameter: 4.23 Å for ethylene and 4.42 Å for ethane [2] and condensability (critical temperature: 9.2 °C for ethylene and 32.3 °C for ethane). In current practice this separation is accomplished by highly energy-intensive cryogenic distillation. Membranes separate mixtures without requiring a phase change [3], so incorporating a membrane into the cryogenic process can potentially reduce its energy consumption, provided that a suitable membrane material can be developed. Recent process modeling indicated that coupling the ethylene/ethane distillation column with a membrane process to debottleneck the operation could potentially save energy [4-6]. However, the advantages of using a hybrid system will only outweigh the cost of implementation if a membrane material exhibits high ethylene/ethane selectivity (15-20) and withstands realistic process conditions [7].

Currently available commercial membrane materials used for gas separation mainly comprise low-free-volume, solution-processable, glassy polymers, which exhibit an inverse relationship between permeability and selectivity [8, 9]. In 2013, Rungta and Koros reported the polymer upper bound for the ethylene/ethane system [10] based on pure-gas permeation properties, with 6FDA-NDA copolymers providing the highest combination of permeability and selectivity [11, 12]. To date, the best performing polymers offer pure-gas ethylene/ethane selectivities of < 7 , even at low pressures. Under high feed pressure mixed-gas conditions (i.e. high hydrocarbon activities) penetrant-induced plasticization typically causes even lower selectivity [13].

Recent research efforts have been devoted to the study of polymers of intrinsic microporosity (PIMs) for various gas separation applications [14-20]. PIMs possess high BET surface area (up to $1000 \text{ m}^2/\text{g}$) with pores of less than 2 nm. Remarkably, PIM polymers have a large free volume fraction of finer pores $< 7 \text{ \AA}$ (i.e. ultra-micropores), which may discriminate between gases with small differences in molecular dimensions and some types have significantly surpassed previously reported 2008 polymeric upper bound performance for air and hydrogen separation [21]. So far, pure-gas ethylene/ethane separation performance of PIM-materials has only been reported for PIM-1 [22], which offered poor separation due to its very broad pore size distribution (PSD). Tailoring microporosity is essential to developing advanced materials for ethylene/ethane separation.

In general, polymers can gain microporosity if they are heated beyond their degradation temperature. Reactions that occur when the polymer is heated depend on reaction conditions (temperature [23], thermal-soak [24], and atmosphere composition [25, 26]), and the nature of the precursor itself [27-29]. Pyrolysis of the polymer chains leads to the formation of carbon molecular sieves (CMS) [30-32]. CMS membranes have narrower PSDs than polymers and, therefore, better molecular sieving capabilities [33]. Furthermore, carbon membranes have

shown chemical stability after long-term exposure to hydrocarbons at low pressures [34, 35], which makes them promising candidates for olefin/paraffin separation. Thermal treatment may lead to materials with the PSD and stability needed to meet the benchmarks for improving ethylene/ethane separation. In fact, the ethylene/ethane transport properties of CMS materials usually surpass the polymeric upper bound due to their high permselectivities ($\alpha_{C_2H_4/C_2H_6} \sim 7-12$) [35-41].

Recently, a polyimide with intrinsic microporosity (PIM-PI), PIM-6FDA-OH, containing hydroxyl functionalities in ortho position relative to the imide linkage showed enhanced inter- and intra-chain interactions [42]. As a result, the polymer matrix was more diffusion-selective compared to the prototypes from the PIM-polyimide family [43]. Previous studies indicated that CMS derived from PIM-6FDA-OH showed attractive pure-gas selectivity for CO_2/CH_4 and O_2/N_2 separations [44]. In addition, the mixed-gas CO_2/CH_4 permeation properties of carbonized samples derived from PIM-6FDA-OH were assessed while increasing the feed pressure to realistic industrial values [45]. It was shown that the mixed-gas carbon dioxide permeability decreased, most likely due to competitive sorption, whereas the methane permeability increased as a result of a small CMS matrix dilation at higher feed pressures.

In this work, carbonized PIM-6FDA-OH samples were evaluated for ethylene/ethane separation. Pure-gas ethylene and ethane permeation properties of isotropic films prepared under a range of treatment conditions are reported. The effect of pressure on membrane performance was evaluated for a 50:50 mixed-gas feed. These results are complemented with sorption isotherms at 35 °C where the appropriate sorption models were fitted to the data.

2. Experimental

2.1 *Materials and characterization methods*

Pristine PIM-6FDA-OH was synthesized according to our previously reported method [42]. A thermogravimetric analyzer (TGA, Q5000 TA Instruments) was used to measure sample weight loss as a function of pyrolysis temperature. Evolved gases were studied with a quadrupole mass spectrometer (Hiden Analytical) coupled to the TGA with N₂ as the carrier gas. Raman spectra of the carbonized films were obtained with a Horiba LabRam HR visible microscope. The internal structure of the samples was studied by CO₂ sorption at 0 °C using a Micromeritics 2020. The pore size distribution was calculated using the nonlocal density functional theory (NLDFT) model assuming a carbon-slit pore geometry using the software version 4.02 provided by Micromeritics.

2.2 *Dense pristine polyimide film*

Dense polyimide films were made by slowly evaporating 3% w/v polymer/THF solutions cast on a leveled glass plate. The resulting 90 µm films (± 1 µm as measured with a digital micrometer) were then air dried for 12 h, and conditioned at 250 °C for 24 h under vacuum to remove traces of solvent without the need of a solvent-exchange step. TGA confirmed that the precursor polyimide film did not contain any solvent. After heat treatment at 500 °C, the film thickness increased by 10 $\pm$ 1% compared to that of pristine PIM-6FDA-OH. Further carbonization at higher temperature did not cause significant additional variation in the thickness of the membranes. The densities were calculated gravimetrically by measuring the weight of the samples using a microbalance (Mettler Toledo) as well as their area with a scanner. Like all thick, isotropic carbon membranes, the dense CMS derived from PIM-6FDA-OH were brittle; however, the films were mechanically strong enough to withstand up to 20 bar pressure difference during the gas permeation tests.

2.3 Carbonization in three-zone tube furnace

Round 25 mm diameter films were placed inside a Carbolite three zone tube furnace in a quartz tube supplied with 1000 cm³(STP)/min of N₂ from a mass flow controller. The temperature was measured with a thermocouple adjacent to the sample. The concentration of oxygen exiting the furnace was continuously measured at all times with a Cambridge Sensotec Rapidox 3100 and confirmed to be less than 2 ppm. The furnace temperature was ramped at 3 °C/min and then held isothermally for 30 minutes (**Fig. 1**). After this isothermal stage, the furnace was allowed to cool down to room temperature. The films were immediately tested after removal from the furnace to prevent any significant oxygen chemisorption. These measures were used to ensure data reproducibility.

Fig. 1. Heat-treatment procedure of PIM-6FDA-OH films in a three-zone Carbolite tube furnace. The thermal soak time was 30 minutes for each degradation stage.

2.4 Gas permeation measurements

Gas permeation experiments were performed at 35 °C in a constant-volume/variable-pressure apparatus as described in detail elsewhere [46]. The films were masked with special care to prevent damage under vacuum as previously described [47]. Samples were degassed under high vacuum for at least 24 h to remove adsorbed gases. Pure-gas permeability was calculated according to the following equation:

$$P_i = \frac{V_d l}{P_U T R A} \frac{dp_i}{dt}$$

where P_i is the pure-gas permeability, V_d is the downstream volume, l is the membrane thickness, P_U is the upstream pressure, T is the temperature in absolute units, R is the gas constant, A is the active permeation area and dp_i/dt is the steady-state rise in pressure with respect to time. Pure-gas selectivity was calculated as the ratio of the pure-gas permeabilities:

$$\alpha_{i/j} = \frac{P_i}{P_j}$$

The mixed-gas permeability was measured with a 50:50 v/v ethylene/ethane mixture by the general technique described by O'Brien et al. [48]. The experiments were performed at 35 °C and the total feed pressure was set at 4, 8, 12 and 20 bar, respectively; the permeate pressure was essentially 0 bara. The stage-cut, that is, the permeate to feed flow rate, was less than 1%. Under this condition, the feed and residue concentrations were essentially equivalent. The feed and permeate compositions were determined with an Agilent 3000A Micro GC. Mixed-gas permeabilities were calculated as follows:

$$P_i = \frac{y_i V_d l}{x_i P_U T R A} \frac{dp}{dt}$$

where P_i is the permeability of the component i , y_i and x_i are the molar fractions of i in the permeate and feed, respectively. Finally, the mixed-gas selectivity was calculated by:

$$\alpha_{i/j} = \frac{y_i/x_i}{y_j/x_j}$$

2.5 Gravimetric sorption

Sorption isotherms in the pressure range from 1 to 15 bar were determined at 35 °C with a Hiden IGA apparatus. Gas sorption in organic glassy polymers can be described by the dual-mode sorption model [49]:

$$C = K_D p + \frac{C_H b p}{1 + b p}$$

where C is the total gas concentration in the glassy polymer, K_d is the Henry's law coefficient, C_H is the Langmuir hole capacity, b is the interaction parameter, and p is the gas pressure. Gas isotherms of carbon materials are typically expressed by the Langmuir model [50]:

$$C = \frac{C_H b p}{1 + b p}$$

The gas solubility can be calculated for a fixed thermodynamic state as:

$$S = \frac{C}{p}$$

Then, the diffusion coefficient, D , can be estimated from the basic permeability definition as:

$$D = \frac{P}{S}$$

3. Results and discussion

3.1 Thermal-treatment of dense-PIM-6FDA-OH

3.1.1 Thermal annealing of PIM-6FDA-OH

Freshly-cast films showed an increase in bulk density from 1.22 g/cm³ for the 120 °C-dried film reported in [42] to 1.28 g/cm³ for a 250 °C-annealed film reported in this study. This densification due to thermal annealing decreased the permeability of H₂, N₂, O₂, CH₄ and CO₂ in PIM-6FDA-OH by about 50%, as shown in the **Table 1**. Annealing microporous functionalized polyimides is known to be beneficial for their selectivity due to the formation of charge transfer complexes (CTCs) [51, 52].

Table 1. Gas permeation properties of thermally annealed PIM-6FDA-OH measured at 2 bar and 35 °C.

Drying protocol (°C)	Permeability (Barrer) ^c							$\alpha_{x/y}$ (-)		
	H ₂	N ₂	O ₂	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	O ₂ /N ₂	CO ₂ /CH ₄	C ₂ H ₄ / C ₂ H ₆
120 ^a	259	11	45	9	251	16.6	6	4.2	28	2.8
250 ^b	181	5.5	23.8	3.4	119	5.5	1.4	4.4	35	4

^a Previous communication; the film was conditioned for 24 h at 120 °C [55]

^b This work

^c 1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ or 7.5×10^{-18} m³ (STP) m m⁻² s⁻¹ Pa⁻¹

3.1.2 Carbonization of PIM-6FDA-OH

As reported previously, the onset of the decomposition temperature of PIM-6FDA-OH is ~380 °C [44]. CO₂ evolution occurred mainly from 400 to 450 °C, while H₂O peaked at 550 °C confirming backbone scission reactions (**Fig. S1**). The carbonization of PIM-6FDA-OH was related to the decrease in infrared-sensitivity (i.e. loss of functionalities) of the PIM-PI for pyrolysis above 500 °C (**Fig. S2**). The weight loss of PIM-6FDA-OH for each heat-treatment temperature is shown in **Fig. 2(a)**. After 30 min thermal soak at 500 °C, PIM-6FDA OH lost ~30% of its initial (pristine) weight and the films became pitch-black. In addition, the samples gained Raman sensitivity (**Fig. S3**), which proved the existence of graphene in its damaged form [53].

The thermal degradation of the samples can be divided into two prominent regimes: i) Pore opening and ii) pore sintering. The former is associated with nearly 30% of the weight loss, (i.e. for a pyrolysis temperature of 500 °C) whereas the latter showed only 15% mass loss above 600 °C. These pore formation mechanisms can be elucidated from the XRD spectra shown in **Fig. 2(b)**. Degradation of the pristine PI at 500 °C increased the d-spacing from 5.53 to 6.22 Å by virtue of the formation of damaged graphene. Carbonization above 600 °C was related to internal reconfigurations towards a more ordered molecular sieve, as demonstrated in the bimodal XRD spectra. An increase in the intensity of the 2.05 Å (1 0 0) graphene plane peak [54] indicated an enhancement of the ultramicroporosity in the samples. The larger d-spacing reached a minimum of 3.75 Å for samples made at 800 °C. However, even the most carbonized samples had wide halos in the XRD spectra, indicating a high percentage of amorphous material was still imbedded in the final structure. The carbonization process is depicted in **Fig. 3**.

Fig. 2. (a) Weight loss of PIM-6FDA-OH for each isothermal stage of degradation. Shaded areas show the dominating porosity evolution mechanisms during heat treatment while the dashed line was the actual soak time used in the pyrolysis protocol; (b) XRD spectra of all samples.

Fig. 3. Carbonization of PIM-6FDA-OH. At 500 °C the polymer structure degrades into turbostratic graphene layers that sinter as the pyrolysis temperature increases. Non-carbon impurities (as significant as 10% molar [44]) are contained within the honeycomb array of the turbostratic graphene sheets (generated in Material Studio, version 8.0).

3.2 CO_2 sorption for PSD estimation

CO_2 sorption can be used to probe CMS ultramicropores [55], which could potentially discriminate ethylene from ethane. PIM-6FDA-OH derived CMS samples exhibited a larger CO_2 uptake in the low-pressure range (i.e. $p/p_0 < 10^{-3}$) as the carbonization temperature increased, as shown in **Fig. 4**. The carbonization of PIM-6FDA-OH at 500 °C amplified the ultramicroporous gates that connect the initially generated microporous cavities. In addition, CO_2 uptake nearly doubled after PIM-6FDA-OH was carbonized at 500 °C, from 35 $\text{cm}^3(\text{STP})/\text{g}$ to 60 $\text{cm}^3(\text{STP})/\text{g}$ at p/p_0 of 0.028. Uptake then further increased to 80 $\text{cm}^3(\text{STP})/\text{g}$ at 600 °C and 90 $\text{cm}^3(\text{STP})/\text{g}$ at 800 °C, respectively.

Fig. 4. Physisorption of CO₂ at 0 °C in PIM-6FDA-OH and its heat-derived CMS membranes. Low-pressure sorption is shown in the upper left corner of the graph.

In order to obtain the pore size distribution of the CMS membranes, the incremental surface area was calculated using the NLDFT model assuming carbon-slit pore geometry using the software version 4.02 provided by Micromeritics. The PSD obtained from CO₂ sorption at 0 °C is shown in **Fig. 5**. A bimodal ultramicropore distribution was detected in all samples. It can be seen that there was a strong growth of the 3.6 Å pores with an increase in pyrolysis temperature. Similarly, the fraction of larger pores from 4.5 - 6 Å increased after heat treatment of 500 °C or higher.

Fig. 5. PSD from the NLDT method derived from CO₂ sorption data at 0 °C for the pristine PIM-6FDA-OH conditioned at 250 °C and its heat-derived CMS samples.

Steel and Koros proposed an idealized pore structure model that can be used to qualitatively describe the molecular sieving mechanism in a CMS membrane [56]. PIM-6FDA-OH is a rigid polymer with entrapped free volume (intrinsic microporosity) that remains “static” compared to the time scale of molecular diffusion. Therefore, the Steel and Koros model may be applied to elucidate changes on the critical dimension, d_c , of the ultramicropores responsible for the separation. The overall effect of heat-treating PIM-6FDA-OH is shown schematically in **Fig. 6**. At 250 °C, PIM-6FDA-OH was thermally annealed where small micropores (indicated by a red arrow) were frozen in the intrinsically microporous polymer structure. After heating to 500 °C, the polymer started to form a partially carbonized structure, which resulted in pore enlargement, and, consequently, a significant increase in ethylene permeability and loss in ethylene/ethane selectivity (**Fig. 7**) was observed. Heating to 600 and 800 °C, respectively, further completed the formation of the amorphous CMS structure, and importantly, pore densification in the carbon matrix. Accordingly, the ethylene permeability dropped continuously due to pore sintering from

600 to 800 °C. During this process, a finely ultramicroporous CMS structure developed, which led to a significant increase in ethylene/ethane selectivity, as discussed below (section 3.3).

Fig. 6. Schematic pore evolution of PIM-6FDA-OH and its heat-derived CMS samples. The red arrow represents the critical dimension d_c of ultramicropores, which determines the molecular sieving behavior of the membranes.

3.3 Ethylene/ethane pure-gas permeation properties

Ethylene/ethane pure-gas permeabilities and ideal selectivities are shown in **Fig. 7**. The 250 °C-annealed PIM-6FDA-OH showed modest performance with a selectivity of 4 and an ethylene permeability of 5.5 Barrer. Heat treatment at 500 °C increased the ethylene permeability of the CMS by a factor of 50 but selectivity decreased from 4 to 2.9. The 500 °C-treated sample was the most ethylene permeable film tested in this work, with a value of 276 Barrer. This is most likely due to the formation of some larger pores around 4.5 to 6 Å, as shown in **Fig. 5**. Heat treatment at higher temperatures reduced permeability, as a result of the pore contraction

confirmed by XRD and CO₂ sorption tests. From 600 to 800 °C, ethylene permeability decreased from 66.1 to 10.4 Barrer. All samples treated at temperatures above 600 °C surpassed the polymeric ethylene/ethane upper bound. At 800 °C a pure-gas selectivity of 17.5 was reached, which is the highest reported value to date for CMS membranes.

Fig. 7. Pure-gas ethylene/ethane permeation properties of CMS membranes derived from PIM-6FDA-OH. The polymer upper bound is represented with the bold black line [10].

3.4 Gravimetric sorption isotherms at 35 °C for ethylene and ethane

Sorption isotherms of ethylene and ethane, shown in **Fig. 8**, were determined by gravimetric sorption. Gas uptake for the 250 °C annealed PIM-6FDA-OH displayed the expected dual-mode sorption behavior for both gases. The CMS derivatives presented much larger sorption capacity than their polyimide precursor. The shapes of the CMS isotherms resembled Langmuir sorption behavior due to the significant growth of their ultramicroporous domains (i.e. the smaller pores are filled at low pressures). Fitted dashed curves followed the dual-mode sorption model for

the polymeric PIM-PI sample heated at 250 °C, whereas the Langmuir model was used to describe sorption in the CMS.

Fig. 8. Pure-gas sorption isotherms of C_2H_4 and C_2H_6 at 35 °C in PIM-6FDA-OH and its CMS derivatives. Fitted dashed curves follow the dual-mode sorption model for the polymeric PIM-PI annealed at 250 °C, whereas the Langmuir model was used to describe sorption in the CMS samples.

The parameters of the fitted sorption models are summarized in **Table 2**. The overall trend indicates an increase of C_H and b with increasing treatment temperature. For example, ethylene C_H of the 800 °C-treated film has a value of 125 cm³(STP)/cm³, three times higher than the C_H of the original polymeric precursor annealed at 250 °C. This result is consistent with the enhanced CO₂ sorption uptake for carbonized PIM-6FDA-OH shown previously.

Table 2. Parameters obtained from fitting experimental data to the dual-mode model (pristine PIM-6FDA-OH) and the Langmuir model (carbons).

Treatment Temperature (°C)	Gas	K_D (10 ⁻² cm ³ cm ⁻³ cmHg ⁻¹)	C_H (cm ³ cm ⁻³)	b (10 ⁻² cmHg ⁻¹)
250	Ethylene	1.53	42.0	0.62
	Ethane	1.65	34.1	1.25
500	Ethylene	-	91.4	1.29
	Ethane	-	83.5	3.07
600	Ethylene	-	114.3	1.91
	Ethane	-	103.3	2.48
800	Ethylene	-	125.0	2.83
	Ethane	-	110.6	3.91

3.5 Pure-gas solubility and diffusivity of ethylene and ethane

The solubility coefficients of PIM-6FDA-OH and its heat-treated samples are shown in **Fig. 9**. Carbon formation in samples treated above 500 °C led to considerable enhancement in solubility of both gases. Ethylene solubility increased from 0.17 at 250 °C to 0.39 at 500 °C, and then to

0.66 cm³(STP)/(cm³ cmHg) in the most graphitic 800 °C sample. However, solubility selectivity in all samples remained very close to 1 due to the very similar condensabilities of both hydrocarbons.

Ethylene and ethane diffusion coefficients of all membranes are shown in **Fig. 10**. The evolution of the pore structure is the most important factor influencing diffusivity. Intermediate carbonization at 500 °C resulted in a 20-fold increase in ethylene diffusivity and a 30-fold increase in ethane diffusivity compared to the pristine PI. At 800 °C, pore collapse and the rise of the ultramicroporosity in the CMS decreased diffusion coefficients 44-fold from 7.1x10⁻⁸ to 1.6x10⁻⁹ cm²/s for ethylene and 255-fold from 2.5x10⁻⁸ to 9.8x10⁻¹¹ cm²/s for ethane. The diffusivity ratio essentially matched the actual pure-gas permselectivity for the whole temperature range, verifying the dominance of the molecular sieving mechanism (**Fig. 11**).

Fig. 9. Solubility of C₂H₄ and C₂H₆ in PIM-6FDA-OH (●) and its CMS (▲) derivatives at 35 °C and 2 bar.

Fig. 10. Diffusivity of C₂H₄ and C₂H₆ in PIM-6FDA-OH (●) and its CMS (▲) derivatives at 35 °C and 2 bar.

Fig. 11. C₂H₄/C₂H₆ diffusivity and solubility selectivities in PIM-6FDA-OH (●) and its CMS derivatives (▲). The fitted lines are drawn to guide the eye.

3.6 *Mixed-gas permeability and selectivity of the 800 °C CMS membrane*

The PIM-6FDA-OH sample carbonized at 800 °C was tested with a 50:50 v/v ethylene/ethane mixture and the results are shown in **Fig. 12(a)**. Ethylene permeability decreased from 10.6 Barrer at 4 bar total pressure to 9.6 Barrer at 20 bar, possibly due to competitive sorption of ethylene and ethane in the CMS. On the other hand, ethane permeability increased from 0.75 to 1.16 Barrer over the same pressure range, which could be the result of a subtle dilation of the critical ultramicropores in the presence of ethylene. The strongly time-dependent effect of the pressure on the mixed-gas selectivity is illustrated in **Fig. 12(b)**. At a feed pressure of 4 bar it took about 300 hours to reach pseudo-equilibrium state. At intermediate pressures of 8 to 12 bar the equilibration time was reduced to about 120 hours. A similar carbon matrix dilation was observed previously for the CO₂/CH₄ gas pair for PIM-6FDA-OH-derived CMS membranes [45]. Despite the losses in selectivity, the performance remains above the pure-gas polymer upper bound, as seen in **Fig. 13**.

Fig. 12. (a) Pressure dependence of the mixed-gas permeation properties of a 1:1 ethylene/ethane binary mixture and (b) time required to reach pseudo-equilibrium at each pressure for the CMS membrane heat-treated at 800 °C derived from PIM-6FDA-OH.

Fig. 13. Single ethylene permeability and ethylene/ethane selectivity of CMS derived from PIM-6FDA-OH (red closed squares). Mixed-gas selectivity dropped from 14 to 8.3 as the feed pressure was increased from 4 to 20 bar (open squares). Matrimid® polyimide-based CMS (blue) pure-gas permeation properties at 35 °C and 3.4 bar [40].

4. Conclusions

Carbon membranes derived from an intrinsically microporous PIM-6FDA-OH precursor via thermal treatment were evaluated for ethylene/ethane separation. Separation performance increased dramatically with temperature for the carbonized samples. In contrast to CMS membranes derived from lower-free-volume polyimides (e.g. Matrimid®), the CMS derived from PIM-6FDA-OH underwent degradations that prevented the full collapse (shift to smaller pore size) of its PSD even for the most carbonized sample, retaining a pure-gas ethylene permeability of about 10 Barrer. With an ethylene/ethane pure-gas selectivity of 17.5, the carbon generated at 800 °C represents the highest performing CMS membrane for this application to date. It is suggested that the spiro-containing PIM-6FDA-OH possesses properties (high free

volume, chain rigidity and thermal stability) responsible for hindering sintering of the graphene sheets during the pyrolysis process.

Mixed-gas permeation experiments for the CMS membrane pyrolyzed at 800 °C performed at a feed pressure of 20 bar showed that the ethylene permeability dropped by ~10%, most likely due to competitive sorption effects. On the other hand, slight dilation of the CMS ultramicropore structure resulted in an increase in the ethane permeability by 54%. Consequently, the mixed-gas ethylene/ethane selectivity dropped from a pure-gas value of 17.5 at 2 bar to 8.3 at a feed pressure of 20 bar. Our study provides further evidence that the choice of the polymer precursor strongly determines the final structure and gas transport properties of CMS membranes.

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Appendix A. Supplementary materials

TGA-MS of the pristine polymer, FTIR and the Raman spectra of its heat-derived CMS samples are reported in the supplementary information, along with the tabular form of the permeation properties.

References

- [1] T. Ren, M. Patel, K. Blok, Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes, *Energy*, 31 (2006) 425-451.
- [2] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, M.G. Mayer, *Molecular theory of gases and liquids*, Wiley New York, 1954.

- [3] R.W. Baker, J.G. Wijmans, J.H. Kaschemekat, The design of membrane vapor–gas separation systems, *J. Membr. Sci.*, 151 (1998) 55-62.
- [4] J.A. Caballero, I.E. Grossmann, M. Keyvani, E.S. Lenz, Design of hybrid distillation-vapor membrane separation systems, *Ind. Eng. Chem. Res.*, 48 (2009) 9151-9162.
- [5] A. Motelica, O.S.L. Bruinsma, R. Kreiter, M. den Exter, J.F. Vente, Membrane retrofit option for paraffin/olefin separation—a technoeconomic evaluation, *Ind. Eng. Chem. Res.*, 51 (2012) 6977-6986.
- [6] J. Ploegmakers, A.R.T. Jelsma, A.G.J. van der Ham, K. Nijmeijer, Economic evaluation of membrane potential for ethylene/ethane separation in a retrofitted hybrid membrane-distillation plant using unisim design, *Ind. Eng. Chem. Res.*, 52 (2013) 6524-6539.
- [7] R.W. Baker, B.T. Low, Gas separation membrane materials: A perspective, *Macromolecules*, 47 (2014) 6999-7013.
- [8] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165-185.
- [9] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, 320 (2008) 390-400.
- [10] M. Rungta, C. Zhang, W.J. Koros, L. Xu, Membrane-based ethylene/ethane separation: The upper bound and beyond, *AIChE Journal*, 59 (2013) 3475-3489.
- [11] S.S. Chan, R. Wang, T.-S. Chung, Y. Liu, C2 and C3 hydrocarbon separations in poly(1,5-naphthalene-2,2'-bis(3,4-phthalic) hexafluoropropane) diimide (6FDA-1,5-NDA) dense membranes, *J. Membr. Sci.*, 210 (2002) 55-64.

- [12] S.S. Chan, T.-S. Chung, Y. Liu, R. Wang, Gas and hydrocarbon (C₂ and C₃) transport properties of co-polyimides synthesized from 6FDA and 1,5-NDA (naphthalene)/Durene diamines, *J. Membr. Sci.*, 218 (2003) 235-245.
- [13] C. Staudt-Bickel, W.J. Koros, Olefin/paraffin gas separations with 6FDA-based polyimide membranes, *J. Membr. Sci.*, 170 (2000) 205-214.
- [14] P.M. Budd, K.J. Msayib, C.E. Tattershall, B.S. Ghanem, K.J. Reynolds, N.B. McKeown, D. Fritsch, Gas separation membranes from polymers of intrinsic microporosity, *J. Membr. Sci.*, 251 (2005) 263-269.
- [15] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials, *Chem. Commun.*, (2004) 230-231.
- [16] P.M. Budd, N.B. McKeown, D. Fritsch, Polymers of intrinsic microporosity (PIMs): High free volume polymers for membrane applications, *Macromol. Symp.*, 245-246 (2006) 403-405.
- [17] Y. Zhuang, J.G. Seong, Y.S. Do, H.J. Jo, Z. Cui, J. Lee, Y.M. Lee, M.D. Guiver, Intrinsically microporous soluble polyimides incorporating Tröger's base for membrane gas separation, *Macromolecules*, 47 (2014) 3254-3262.
- [18] B.S. Ghanem, R. Swaidan, E. Litwiller, I. Pinnau, Ultra-microporous triptycene-based polyimide membranes for high-performance gas separation, *Adv. Mater.*, 26 (2014) 3688-3692.
- [19] M. Carta, M. Croad, R. Malpass-Evans, J.C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanč, N.B. McKeown, Triptycene induced enhancement of membrane gas selectivity for microporous Tröger's base polymers, *Adv. Mater.*, 26 (2014) 3526-3531.
- [20] N. Du, H.B. Park, G.P. Robertson, M.M. Dal-Cin, T. Visser, L. Scoles, M.D. Guiver, Polymer nanosieve membranes for CO₂-capture applications, *Nat. Mater.*, 10 (2011) 372-375.

- [21] R. Swaidan, B. Ghanem, I. Pinnau, Fine-tuned intrinsically ultramicroporous polymers redefine the permeability/selectivity upper bounds of membrane-based air and hydrogen separations, *ACS Macro Lett.*, (2015) 947-951.
- [22] P. Li, T.S. Chung, D.R. Paul, Gas sorption and permeation in PIM-1, *J. Membr. Sci.*, 432 (2013) 50-57.
- [23] L. Shao, T.-S. Chung, G. Wensley, S.H. Goh, K.P. Pramoda, Casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA-TMMDA copolyimide membrane and its derived carbon membranes, *J. Membr. Sci.*, 244 (2004) 77-87.
- [24] K.M. Steel, W.J. Koros, An investigation of the effects of pyrolysis parameters on gas separation properties of carbon materials, *Carbon*, 43 (2005) 1843-1856.
- [25] M. Kiyono, P.J. Williams, W.J. Koros, Effect of pyrolysis atmosphere on separation performance of carbon molecular sieve membranes, *J. Membr. Sci.*, 359 (2010) 2-10.
- [26] Q. Song, S. Cao, R.H. Pritchard, B. Ghalei, S.A. Al-Muhtaseb, E.M. Terentjev, A.K. Cheetham, E. Sivaniah, Controlled thermal oxidative crosslinking of polymers of intrinsic microporosity towards tunable molecular sieve membranes, *Nat. Commun.*, 5 (2014).
- [27] M. Kiyono, P.J. Williams, W.J. Koros, Effect of polymer precursors on carbon molecular sieve structure and separation performance properties, *Carbon*, 48 (2010) 4432-4441.
- [28] P.S. Tin, Y. Xiao, T.S. Chung, Polyimide - carbonized membranes for gas separation: Structural, composition, and morphological control of precursors, *Sep. Purif. Rev.*, 35 (2006) 285-318.
- [29] Y. Xiao, T.-S. Chung, M.L. Chng, S. Tamai, A. Yamaguchi, Structure and properties relationships for aromatic polyimides and their derived carbon membranes: Experimental and simulation approaches, *J. Phys. Chem. B*, 109 (2005) 18741-18748.

- [30] S.M. Saufi, A.F. Ismail, Fabrication of carbon membranes for gas separation—a review, *Carbon*, 42 (2004) 241-259.
- [31] M. Inagaki, N. Ohta, Y. Hishiyama, Aromatic polyimides as carbon precursors, *Carbon*, 61 (2013) 1-21.
- [32] M. Yoshimune, K. Mizoguchi, K. Haraya, Alcohol dehydration by pervaporation using a carbon hollow fiber membrane derived from sulfonated poly(phenylene oxide), *J. Membr. Sci.*, 425–426 (2013) 149-155.
- [33] M. Mulder, *Basic Principles of Membrane Technology*. Kluwer, Dordrecht, 1991.
- [34] I. Menendez, A.B. Fuertes, Aging of carbon membranes under different environments, *Carbon*, 39 (2001) 733-740.
- [35] A.B. Fuertes, I. Menendez, Separation of hydrocarbon gas mixtures using phenolic resin-based carbon membranes, *Sep. Purif. Technol.*, 28 (2002) 29-41.
- [36] J.-i. Hayashi, H. Mizuta, M. Yamamoto, K. Kusakabe, S. Morooka, S.-H. Suh, Separation of ethane/ethylene and propane/propylene systems with a carbonized BPDA–pp'ODA polyimide membrane, *Ind. Eng. Chem. Res.*, 35 (1996) 4176-4181.
- [37] K.-i. Okamoto, S. Kawamura, M. Yoshino, H. Kita, Y. Hirayama, N. Tanihara, Y. Kusuki, Olefin/paraffin separation through carbonized membranes derived from an asymmetric polyimide hollow fiber membrane, *Ind. Eng. Chem. Res.*, 38 (1999) 4424-4432.
- [38] H. Suda, K. Haraya, Alkene/alkane permselectivities of a carbon molecular sieve membrane, *Chem. Commun.*, (1997) 93-94.

- [39] M. Yamamoto, K. Kusakabe, J.-i. Hayashi, S. Morooka, Carbon molecular sieve membrane formed by oxidative carbonization of a copolyimide film coated on a porous support tube, *J. Membr. Sci.*, 133 (1997) 195-205.
- [40] M. Rungta, L. Xu, W.J. Koros, Carbon molecular sieve dense film membranes derived from Matrimid® for ethylene/ethane separation, *Carbon*, 50 (2012) 1488-1502.
- [41] L. Xu, M. Rungta, W.J. Koros, Matrimid® derived carbon molecular sieve hollow fiber membranes for ethylene/ethane separation, *J. Membr. Sci.*, 380 (2011) 138-147.
- [42] X. Ma, R. Swaidan, Y. Belmabkhout, Y. Zhu, E. Litwiller, M. Jouiad, I. Pinnau, Y. Han, Synthesis and gas transport properties of hydroxyl-functionalized polyimides with intrinsic microporosity, *Macromolecules*, 45 (2012) 3841-3849.
- [43] B.S. Ghanem, N.B. McKeown, P.M. Budd, N.M. Al-Harbi, D. Fritsch, K. Heinrich, L. Starannikova, A. Tokarev, Y. Yampolskii, Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic microporosity: PIM-polyimides, *Macromolecules*, 42 (2009) 7881-7888.
- [44] X. Ma, R. Swaidan, B. Teng, H. Tan, O. Salinas, E. Litwiller, Y. Han, I. Pinnau, Carbon molecular sieve gas separation membranes based on an intrinsically microporous polyimide precursor, *Carbon*, 62 (2013) 88-96.
- [45] R. Swaidan, X. Ma, E. Litwiller, I. Pinnau, High pressure pure- and mixed-gas separation of CO₂/CH₄ by thermally-rearranged and carbon molecular sieve membranes derived from a polyimide of intrinsic microporosity, *J. Membr. Sci.*, 447 (2013) 387-394.
- [46] D.G. Pye, H.H. Hoehn, M. Panar, Measurement of gas permeability of polymers. I. Permeabilities in constant volume/variable pressure apparatus, *J. Appl. Polym. Sci.*, 20 (1976) 1921-1931.

- [47] T.T. Moore, S. Damle, P.J. Williams, W.J. Koros, Characterization of low permeability gas separation membranes and barrier materials; design and operation considerations, *J. Membr. Sci.*, 245 (2004) 227-231.
- [48] K.C. O'Brien, W.J. Koros, T.A. Barbari, E.S. Sanders, A new technique for the measurement of multicomponent gas transport through polymeric films, *J. Membr. Sci.*, 29 (1986) 229-238.
- [49] W.R. Vieth, P.M. Tam, A.S. Michaels, Dual sorption mechanisms in glassy polystyrene, *J. Colloid Interf. Sci.*, 22 (1966) 360-370.
- [50] L. Xu, M. Rungta, J. Hessler, W. Qiu, M. Brayden, M. Martinez, G. Barbay, W.J. Koros, Physical aging in carbon molecular sieve membranes, *Carbon*, 80 (2014) 155-166.
- [51] R. Swaidan, B. Ghanem, E. Litwiller, I. Pinnau, Effects of hydroxyl-functionalization and sub-T_g thermal annealing on high pressure pure- and mixed-gas CO₂/CH₄ separation by polyimide membranes based on 6FDA and triptycene-containing dianhydrides, *J. Membr. Sci.*, 475 (2015) 571-581.
- [52] R.J. Swaidan, X. Ma, E. Litwiller, I. Pinnau, Enhanced propylene/propane separation by thermal annealing of an intrinsically microporous hydroxyl-functionalized polyimide membrane, *J. Membr. Sci.*, doi:10.1016/j.memsci.2015.08.015.
- [53] A.C. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, *Phys. Rev. B*, 64 (2001) 075414.
- [54] L. Shao, T.-S. Chung, K.P. Pramoda, The evolution of physicochemical and transport properties of 6FDA-durene toward carbon membranes; from polymer, intermediate to carbon, *Microporous Mesoporous Mater.*, 84 (2005) 59-68.

[55] M.C. Campo, F.D. Magalhães, A. Mendes, Comparative study between a CMS membrane and a CMS adsorbent: Part I—Morphology, adsorption equilibrium and kinetics, *J. Membr. Sci.*, 346 (2010) 15-25.

[56] K.M. Steel, W.J. Koros, Investigation of porosity of carbon materials and related effects on gas separation properties, *Carbon*, 41 (2003) 253-266.

HIGHLIGHTS

- First report of ethylene/ethane separation of a PIM-polyimide.
- PIM-6FDA-OH-derived CMS (pyrolyzed at 800 °C) exhibits the highest pure-gas selectivity reported to date ($\alpha_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6} \sim 18$).
- Permselectivity of the CMS membranes is completely dominated by diffusivity selectivity.
- Mixed-gas ethylene/ethane permselectivity decreased from 14 at 4 bar to 8.3 at 20 bar feed pressure (1:1 $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ feed).

Graphical Abstract