Ethylene/ethane permeation, diffusion and gas sorption properties of carbon molecular sieve membranes derived from the prototype ladder polymer of intrinsic microporosity (PIM-1)

Octavio Salinas, Xiaohua Ma, Eric Litwiller, Ingo Pinnau

PII: S0376-7388(15)30400-2
DOI: <http://dx.doi.org/10.1016/j.memsci.2015.12.052>
Reference: MEMSCI14192

To appear in: *Journal of Membrane Science*

Received date: 29 October 2015
Revised date: 12 December 2015
Accepted date: 24 December 2015

Cite this article as: Octavio Salinas, Xiaohua Ma, Eric Litwiller and Ingo Pinnau Ethylene/ethane permeation, diffusion and gas sorption properties of carbon molecular sieve membranes derived from the prototype ladder polymer of intrinsic microporosity (PIM-1), *Journal of Membrane Science* <http://dx.doi.org/10.1016/j.memsci.2015.12.052>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ethylene/ethane permeation, diffusion and gas sorption properties of carbon molecular sieve membranes derived from the prototype ladder polymer of intrinsic microporosity (PIM-1)

Octavio Salinas, Xiaohua Ma, Eric Litwiller, Ingo Pinnau*

Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, Chemical and Biological Engineering Program, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

*Corresponding author: King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering Al-Jazri Bldg. 4, Thuwal 23955-6900, Saudi Arabia, Tel: +966-12-808-2406

E-mail address: ingo.pinnau@kaust.edu.sa (I. Pinnau)

Abstract

Fine-tuning the microporosity of PIM-1 by heat treatment was applied to develop a suitable carbon molecular sieve membrane for ethylene/ethane separation. Pristine PIM-1 films were heated from 400 to 800 °C under inert N₂ atmosphere (< 2 ppm O₂). At 400 °C, PIM-1 self-cross-linked and developed polar carbonyl and hydroxyl groups due to partial dioxane splitting in the polymer backbone. Significant degradation occurred at 600 °C due to carbonization of PIM-1 and resulted in 30% increase in cumulative surface area compared to its cross-linked predecessor. In addition, PIM-1-based CMS developed smaller ultramicropores with increasing pyrolysis temperature, which enhanced their molecular sieving capability by restricted diffusion of ethylene and ethane through the matrix due to microstructural carbon densification. Consequently, the pure-gas ethylene permeability (measured at 35 °C and 2 bar) decreased from 1600 Barrer for the pristine PIM-1 to 1.3 Barrer for the amorphous carbon generated at 800 °C, whereas the ethylene/ethane pure-gas selectivity increased significantly from 1.8 to 13.

Keywords: ethylene/ethane separation, intrinsically microporous polymer, PIM-1, carbon molecular sieve

1. Introduction

Ethylene/ethane separation is accomplished through equilibrium-based energy-intensive distillation processes [1]. Alternatively, membrane technology could offer substantial savings to this application because membranes do not require a phase change for the separation of the feed components [2]. In recent years, gas separation with membranes has successfully found large-scale commercial use for natural gas upgrading and nitrogen production from air [3, 4]. To date, however, polymer membranes have not reached the minimum requirements for viable ethylene/ethane separation due to: i) Insufficient selectivity (e.g. ~ 3 -6 under ideal pure-gas permeation conditions) and low permeability [5-10] and ii) potential penetrant-induced plasticization leading to reduced mixed-gas selectivity [9]. The former issue can be addressed by rational design of the pore size and pore distribution (PSD) of the membrane material, while the latter demands materials that can withstand the high activities of the ethylene/ethane feed under realistic industrial conditions.

Intrinsically microporous polymers (PIMs) represent the state-of-the-art among known solution-processable organic membrane materials for gas separation [11-16]. PIMs often define the permeability/selectivity performance upper bounds of gas transport through polymers [17] as defined by Robeson [18, 19] by virtue of their contorted and rigid polymer backbones that allow them to capitalize on interconnected pore sizes of less than 2 nm [20, 21]. The prototype of the ladder-type PIM-family, PIM-1, was synthesized by polycondensation reaction of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane and tetrafluoroterephthalonitrile. The polymer structure is shown in **Fig. 1**. The tetrahedral-spirobisindane moiety in its backbone promotes inefficient packing of its chains in the solid state [12, 20, 22]. Although the gas separation performance of PIM-1 has been placed on the upper bounds for several gas pairs, such as O_2/N_2 and H_2/CH_4 , it is an inadequate material for ethylene/ethane separation with a high ethylene permeability of 573 Barrer but very low ethylene/ethane selectivity of 1.4 (measured at 25 °C and 1 atm) [23].

Fig. 1. Chemical structure of PIM-1.

To achieve higher selectivity, the PSD in PIM-1 can be tailored by chemical and/or thermal means to potentially improve its gas separation properties. One possibility simply requires post-synthesis addition of functionalities to the polymer matrix to increase inter- and intra-chain interactions [24], which leads to enhanced densification of the polymer micropore structure. For example, the nitrile groups in PIM-1 can be substituted with polar moieties, such as carboxyl, amidoxime thioamide or tetrazole, to enhance its permselectivity [24-27]. Another relevant approach to densify the PSD of PIM-1 is via thermal annealing [28-32] or by further heat treatment so that specific chain degradation reactions are triggered. For example, PIM-1 self-cross-linked under vacuum at 300 °C showed a 400% increase in CO₂/CH₄ pure-gas selectivity, reportedly via triazine formation [33]. A different mechanism was proposed in a subsequent study [34], where it was reported that O₂ was responsible of covalently bridging the PIM-1 chains starting at heat treatment around 300 °C. Fine-tuning of the microporosity in PIM-1 was performed by varying the O₂ content in the heating atmosphere (< 200 ppm) available prior to the onset of the polymer backbone decomposition (i.e. < 450 °C).

Pyrolysis of a polymer beyond its initial decomposition temperature under essentially inert conditions produces carbon molecular sieve (CMS) membranes, which can display outstanding gas separation performance [35]. CMS have strongly size-sieving PSDs by virtue of their large array of ultramicropores (i.e. < 0.7 nm) [36], which are instrumental in distinguishing permeants based on the small differences of their molecular dimensions [37]. Furthermore, CMS membranes may be stable under harsh hydrocarbon saturated atmospheres, as demonstrated in previous studies [38, 39]. However, in spite of their

promising properties, only a few studies of CMS membranes have been reported for ethylene/ethane separation [38, 40-45].

The CMS separation performance is controlled by a wide variety of parameters involved in the pyrolysis process. For example, the heating protocol [46-48] and the atmospheric composition [43, 49-51] may lead to distinctly different microstructures in the CMS. Furthermore, the gas permeation properties of CMS membranes are also influenced by several polymer-precursor-determined properties: i) Pendant groups [52, 53], ii) glass transition temperature [54], and iii) free volume [53, 55, 56]. PIM-1 represents an extreme case in all of these categories as it possesses polar cyanide groups, undetectable glass transition temperature and, at the same time, it is one of the most permeable glassy polymers known to date due to its high free volume [57]. To the best of our knowledge, there is no rigorous assessment available for the gas transport properties of CMS membranes generated from the spirobisindane-ladder prototype PIM-1. Here, ethylene and ethane sorption, diffusion and permeation data are reported for the first time in partially and fully carbonized membranes derived via thermal treatment from pristine PIM-1 films.

2. Experimental

2.1 Materials and characterization

Pristine PIM-1 was synthesized according to a previously reported procedure by Du et al. [58]. The molecular weight of PIM-1 was determined by gel permeation chromatography (Malvern HT-350). The M_n was 6.9×10^4 g/mol with a PDI of 2.42. A thermogravimetric analyzer (TGA, TA Instruments) was used to measure sample weight loss as a function of pyrolysis temperature. Evolved gases were identified with a quadrupole mass spectrometer (Hiden Analytical) coupled to the TGA with N_2 as the carrier gas. Fourier transform infrared (FTIR) spectra were acquired using a Thermo Nicolet iS10 infrared micro-spectrometer. X-ray diffraction (XRD) scattering was conducted on a Bruker D8 Advance diffractometer. Raman spectra of the carbonized films were obtained with a Horiba LabRam HR visible microscope. The internal structure of the samples was studied by CO_2 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 PIM-1 films fabrication and thermal annealing at 250 °C

Dense PIM-1 films were made by slowly evaporating 3% w/v polymer/THF solutions from a covered glass Petri dish under ambient conditions. The resulting 100 ± 10 μm films (as measured with a digital micrometer) were then air dried for 12 h, methanol soaked for 12 h, and finally thermally annealed at 250 °C for 24 h under vacuum. The densities of the films of known thickness were determined gravimetrically by measuring the weight of the samples using a microbalance (Mettler Toledo) as well as their area with a scanner.

2.3 Cross-linking and carbonization of PIM-1 films

Round 25 mm diameter films of thermally annealed PIM-1 films were placed inside a Carbolite three-zone tube furnace in a quartz tube supplied with $1000 \text{ cm}^3(\text{STP})/\text{min}$ of N_2 from a mass flow controller. 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 confirmed to be less than 2 ppm at all times. The furnace temperature was ramped at 3 °C/min and then held isothermally for 30 minutes for each thermal stage, leading to: (i) cross-linking at 400 °C and (ii) CMS formation at 600 and 800 °C, respectively. After the isothermal soak, the furnace was allowed to cool down to room temperature. The gas permeation properties of the films were immediately tested after removal from the furnace. These measures were used to ensure data reproducibility.

2.4 Gravimetric sorption

Ethylene and ethane 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 [59]:

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

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 [60]:

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

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

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

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

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

2.5 Pure-gas permeation experiments

Gas permeation experiments were performed at 35 °C in a constant-volume/variable-pressure apparatus as described in detail elsewhere [61]. The films were masked with special care to prevent damage under vacuum as previously described [62]. Samples were degassed for at least 24 h to remove adsorbed molecules. 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. The pure-gas selectivity was calculated as the ratio of the pure-gas permeabilities:

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

3. Results and discussion

3.1 Thermal annealing and CMS formation of pristine PIM-1 films

The pure-gas H₂, N₂, O₂, CH₄ and CO₂ permeation properties of methanol-exchanged PIM-1 films, followed by thermal annealing at 250 °C for 24 h under vacuum, and previously reported data for PIM-1 films made under a variety of conditions are shown in **Table 1**. The significant variance in the permeation properties of PIM-1 found in the literature can mainly be attributed to the casting solvent type, solvent exchange procedure as well as annealing temperature selected for removal of solvent traces from the film [21, 23, 63]. In all cases PIM-1 exhibited very high gas permeability with low- to moderate gas selectivity.

Table 1 Permeation data of PIM-1 films prepared under different protocols.

Drying temperature (°C)	Permeability (Barrer) ^d			$\alpha_{x/y}$ (-)	
	N ₂	O ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂
80 ^a	252	969	5303	3.8	21.0
100 ^b	687	1521	8460	2.2	12.3
250 ^c	434	1220	6400	2.8	14.7

^a Previous work; film was cast from CHCl₃, dried and then tested at 25 °C [23].

^b Previous work; film was cast from CHCl₃, methanol soaked, dried for 24 h and then tested at 25 °C [27].

^c This work; films were cast from THF, methanol soaked, dried for 24 h and then tested at 35 °C.

^d 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

The thermal decomposition mechanisms of PIM-1 under inert nitrogen atmosphere (i.e. O_2 concentration < 2 ppm) were characterized by the evolution of specific gaseous products (**Fig. 2**). Heat treatment of PIM-1 at 400 °C for 30 min caused only 1% weight loss which was related to CO_2 evolution from the partial thermolysis of its dioxane rings as previously proposed by Song et al. [34]. Evidence of the splitting of the dioxane-ether linkage is shown in the FTIR spectra of the samples (**Fig. 3a**). The ether linkage (1110 cm^{-1}) decreased in intensity, whereas the -OH stretch (3400 cm^{-1}) and C=O (1700 cm^{-1}) increased significantly. In addition, the pristine fluorescent yellow PIM-1 films became brown after heat treatment at 400 °C and became partially insoluble in THF. Thermal treatment of PIM-1 at 400 °C for 30 min under < 2 ppm O_2 atmosphere effectively created an insoluble, cross-linked intermediate system with enhanced intra-chain interactions by virtue of the hydrogen bonding between the created polar hydroxyl groups and the other polar segments of the chain; in a similar fashion to other hydrogen-bonded-PIM-1 examples [24-27].

PIM-1 samples treated above 600 °C resulted in degradation of the cross-linked chains as shown by the peaks in evolution of both H_2O and CO_2 during the degradation process (**Fig. 2**). During this thermal step, the initial weight decreased by ~26%, leading to the formation of amorphous carbon as revealed by the loss of functionalities in their FTIR spectra (**Fig. 3b**). In addition, a rise in Raman activity of the D and G peaks (1300 cm^{-1} and 1600 cm^{-1} respectively) (**Fig. 4**) confirmed the content of amorphous graphene in the carbon network [60]. It can be hypothesized that the ratio of intensities between the D and G peaks tend to reflect a maximum value as the matrix reconfigured at higher degradation temperatures into more ordered carbon molecular sieves [64]. Furthermore, complimentary XRD analysis supported the strong collapse in porosity towards CMS (**Fig. 5**). The broad trimodal XRD spectra of pristine and partially degraded PIM-1 (~ $3.74 - 7\text{ Å}$) sintered into amorphous carbon configurations with average d-spacing < 3.8 Å . The characteristic (1 0 0) graphene plane was associated with the 2.05 Å peak displayed in the spectrum of the carbon pyrolyzed at 800 °C [65]. Increased ultramicroporosity occurred simultaneously due to dehydrogenation of the carbon matrix which was related to <1% weight loss from 700 to 800 °C.

Fig. 2. Thermal gravimetric analysis of PIM-1 under an inert N₂ atmosphere at a ramping rate of 3 °C/min. Mass spectroscopy qualitatively shows H₂, H₂O and CO₂ evolution. Shaded areas represent the dominating degradation mechanisms: i) Partial dioxane splitting, ii) complete dioxane and methyl group degradation, iii) matrix dehydrogenation.

Fig. 3. FTIR spectra of (a) polymeric heat-annealed PIM-1 and (b) its CMS derivatives.

Fig. 4. Raman spectra of CMS generated from PIM-1 at 600 and 800 °C.

Fig. 5. XRD spectra of pristine (250 °C) and cross-linked (400 °C) PIM-1 and its heat-derived CMS analogs (600 and 800 °C).

3.2 Surface area and PSD estimation of PIM-1 and its heat-derived CMS

NLDFT applied to CO₂ sorption data obtained at 0 °C can be used to *qualitatively* assess the PSD of a microporous membrane material [66]. CO₂ sorption in PIM-1 and its CMS counterparts (**Fig. 6a**) showed a very steep linear increase in concentration at very small relative pressures (i.e. $p/p_0 < 10^{-3}$), a common characteristic found in other microporous materials [67]. Interestingly, the CO₂-NLDFT method confirmed that the pores of < 0.7 nm found in pristine PIM-1 contribute to a large fraction of its total surface area, if compared to the BET surface area for the whole pore range determined with N₂ sorption

at -196 °C [25, 68]. Furthermore, carbonization of the cross-linked PIM-1 yielded a significant rise of a bimodal ultramicroporous distribution (**Fig. 6b**). In addition, the surface area of PIM-1 carbonized at 800 °C increased by 30% compared to the cross-linked precursor produced at 400 °C (**Table 2**), from 530 m²/g to 700 m²/g. Likewise to other CMS reported in the literature [53], PIM-1-derived carbons had higher densities than their precursor polymers (**Table 2**).

Fig. 6. (a) CO₂ sorption isotherms at 0 °C in heat-annealed PIM-1 (250 and 400 °C) and its CMS derivatives (600 and 800 °C). The lower right corner depicts low-pressure sorption. (b) Pore size distribution computed from this sorption data by NLDFT using Micromeritics software version 2.0.

Table 2 Bulk density and internal surface area of PIM-1 and its CMS derivatives.

Treatment Temperature (°C)	Bulk density ^a (g/cm ³)	Cumulative ^b NLDFT CO ₂ surface area (m ² /g)
250	1.04±0.01	513
400	1.04±0.01	530
600	1.39±0.01	690
800	1.43±0.01	700

^a Measured gravimetrically, $\rho = (\text{weight of sample}) / (\text{volume})$

^b Total surface area of pores smaller than 7.2 Å according to the NLDFT method.

3.3. Pure-gas sorption isotherms of ethylene and ethane in PIM-1 and its heat-derived CMS analogs

Sorption of ethylene and ethane at 35 °C was determined gravimetrically (**Fig. 7a**). As expected from the qualitative PSD description based on the XRD and NLDFT studies discussed above, cross-linked PIM-1 at 400 °C did not change its ethylene uptake due to the very slight variations in its PSD distribution before and after the partial dioxane degradations at 400 °C. Sorption in the carbonized samples derived from PIM-1 showed Langmuir-like behavior, with ~100% increase in the sorption capacity of ethylene at 1 bar, from 32 cm³(STP)/cm³ in PIM-1 to 64 cm³(STP)/cm³ in the 800 °C-derived CMS. Remarkably, the total ethylene uptake at 15 bar in the polymeric PIM-1 samples surpassed the uptake of the CMS generated at 600 °C due to sintering of the CMS-micropores >0.7 nm during the pyrolysis procedure. Furthermore, solubility selectivity increased by ~30%, from its value of 0.95 in pristine PIM-1 to 1.25 for CMS carbonized at 800 °C (**Fig. 7b**). Possible π - π interactions between ethylene and the walls of the amorphous carbon sheets could have caused this small preferential sorption effect, as proposed elsewhere [45].

Fig. 7. (a) Pure-gas sorption isotherms of ethylene at 35 °C in pristine PIM-1-250 °C (■), its cross-linked PIM-1-400 °C derivative (◆), CMS-600 °C (▼) and CMS-800 °C (●) derivatives. Fitted dashed curves follow the dual-mode sorption model for the polymeric PIM-1 and its analog cross-linked samples, whereas the Langmuir model was used to

describe sorption in the CMS. (b) Ethylene/ethane solubility selectivity as a function of pressure for all samples.

The parameters of the fitted sorption models are summarized in **Table 3**. The overall trend indicated an increase of C_H and b with increasing treatment temperature. For example, ethylene C_H of the 800 °C-treated PIM-1 sample had a value of 98 cm³(STP)/cm³, around 70% higher than that of the original PIM-1 precursor thermally annealed at 250 °C for 24 h. This result was consistent with the CO₂-based NLDFT surface area data of heat-treated PIM-1 derivatives reported in the previous section of this work.

Table 3 Parameters obtained from fitting experimental ethylene and ethane sorption data to the dual-mode (polymers) and the Langmuir isotherms (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	3.1	58.1	1.4
	Ethane	3.9	56.0	1.4
400	Ethylene	3.6	56.8	1.4
	Ethane	3.4	55.2	1.4
600	Ethylene	-	78.2	2.0
	Ethane	-	67.8	2.5
800	Ethylene	-	98.1	2.4
	Ethane	-	79.7	2.4

3.4. *Pure- gas ethylene/ethane permeation properties*

The ethylene/ethane permeation properties of heat-treated PIM-1 and its CMS samples are presented in **Table 4**. Additional gas permeation data of heat-treated PIM-1 and its CMS derivatives for H₂, N₂, O₂, CH₄, and CO₂ are listed in **Table S2**. The permeability and diffusivity coefficients of ethylene and ethane decreased with increasing treatment temperature of the membrane. The pristine PIM-1 showed poor performance for ethylene/ethane separation with an ethylene permeability of 1640 Barrer and a selectivity of only 1.8. Nevertheless, in the beginning of the thermal treatment, formation of crosslinks at 400 °C increased selectivity to 2.4 with a concurrent reduction in the

permeability of ethylene by 60% and of ethane by 200%. At 2 bar, there was no significant difference between the solubility coefficients of the pristine PIM-1 and its cross-linked analog (400 °C). Therefore, the drop in permeability can be attributed primarily to a decrease in diffusion coefficients. Degradation of the cross-linked PIM-1 into the CMS membrane at 600 °C, caused a ~60% increase in solubility of both hydrocarbons in the membranes at 2 bar due to the creation of ultramicroporous voids. A significant drop occurred for the CMS membranes generated at 600 and 800 °C in the ethylene permeability from 44 and 1.3 Barrer, respectively. In a similar fashion, the diffusion coefficient of ethylene decreased 2000-fold from its original value of 5.6×10^{-7} cm²/s in pristine PIM-1 to its minimum value of 2.6×10^{-10} cm²/s in the CMS produced at 800 °C. The decrease in diffusion coefficients coupled with enhanced diffusion selectivities was a clear effect of the sintering of the dimensions of the ultramicropores in the CMS as suggested by the XRD and NLDFT results.

Table 4 Pure-gas permeability, diffusivity and solubility coefficients of ethylene and ethane at 35 °C and 2 bar for heat-treated PIM-1 and its CMS derivative samples.

Treatment temperature (°C)	Permeability (Barrer)		Solubility ^a (cm ³ /cm ³ cmHg)		Diffusivity ^b (10 ⁻¹⁰ cm ² /s)	
	Ethylene	Ethane	Ethylene	Ethane	Ethylene	Ethane
250	1640	906	0.29	0.31	5600	2900
400	1082	439	0.28	0.30	3900	1500
600	44	7	0.38	0.35	116	20
800	1.3	0.1	0.51	0.42	2.6	0.24

^a Solubility calculated from the gravimetric sorption uptake at 2 bar.

^b Average diffusion coefficient calculated from $D = P/S$.

The ethylene/ethane separation performance of heat-treated PIM-1 and its CMS derivatives is compared against existing polymer and other CMS membranes in **Fig. 8**. The polymeric PIM-1 and its cross-linked analog did not present high enough selectivity to transcend the upper bound of the polymeric performance, whereas the carbonized

PIM-1 samples exhibited selectivities very close to the previously reported values of carbons generated from Matrimid®, a low-free-volume polyimide. Interestingly, PIM-1 treated at 600 °C produced carbon membranes with moderate ethylene/ethane selectivities (i.e. 6 - 8) that match those generated from other polymeric precursors with clear structural differences (e.g. lower free volume and measureable Tg). It is interesting to note, however, that high-temperature pyrolysis (800 °C) of the intrinsically microporous PIM-1 showed about 10-fold higher ethylene permeability compared to low-free-volume Matrimid® polyimide. This result indicates that intrinsically microporous polymers, such as PIM-1, may provide a new platform as precursors for the generation of more permeable and highly selective CMS membranes. However, to further support this preliminary conclusion drawn from this work, additional studies with structurally different PIMS are required. In addition, to assess the full potential of PIM-derived CMS membranes, future studies require high-pressure mixed ethylene/ethane permeation experiments, as previously demonstrated for a hydroxyl-functionalized PIM-PI precursor CMS membrane [69].

Fig. 8. Pure-gas ethylene/ethane permeation properties of heat-derived PIM-1 membranes (stars) from right to left: Pristine thermally annealed at 250 °C, cross-linked at 400 °C followed by CMS produced at 600 °C and 800 °C, respectively. For comparison, previously reported Matrimid® polyimide derived CMS heated to 550 and 800 °C [45]. Shaded areas represent the two main mechanisms of carbon tailoring. The polymer upper bound is represented with the bold black line [5].

4. Conclusions

PIM-1 was heat-treated under inert N₂ atmosphere to provide materials with enhanced performance for ethylene/ethane separation and to provide insight about the pore evolution mechanism during carbon formation derived from intrinsically microporous polymer precursors. The pristine dense films of PIM-1 were thermally treated at 400 °C to form a cross-linked structure which exhibited 36% increase in pure-gas ethylene/ethane selectivity from 1.8 to 2.4 with respect to its pristine precursor. Carbonization of the films at 600 °C enhanced the sorption capacity of both ethylene and ethane at lower pressures, as observed from the Langmuir behavior in their sorption isotherms measured at 35 °C. Sintering in the microporous region >0.7 of the amorphous carbon membranes derived from PIM-1 prevented additional sorption of hydrocarbons at high pressures compared to their polymeric precursors. XRD and NLDFT were used to qualitatively confirm the growth in the ultramicroporous distribution found in the isotropic carbon films. The diffusion coefficients of ethylene decreased by 2000-fold as the pristine PIM-1 samples sintered into their final 800 °C-carbonaceous form, from 5.6×10^{-7} cm²/s to 2.6×10^{-10} cm²/s, while ethane decreased even 12000-fold, from 2.9×10^{-7} cm²/s to 2.4×10^{-11} cm²/s; therefore, confirming the strong molecular sieving improvement after shrinkage of the PSD closer to the molecular dimensions of ethylene and ethane.

Acknowledgments

This work was supported by KAUST funding for Prof. Ingo Pinnau (BAS/1/1323-01-01).

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.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.
- [3] R.W. Baker, *Membrane technology and applications*, Wiley, 2004.

- [4] R.W. Baker, B.T. Low, Gas separation membrane materials: A perspective, *Macromolecules*, 47 (2014) 6999-7013.
- [5] 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.
- [6] K. Tanaka, A. Taguchi, J. Hao, H. Kita, K. Okamoto, Permeation and separation properties of polyimide membranes to olefins and paraffins, *J. Membr. Sci.*, 121 (1996) 197-207.
- [7] O.M. Ilinitich, G.L. Semin, M.V. Chertova, K.I. Zamaraev, Novel polymeric membranes for separation of hydrocarbons, *J. Membr. Sci.*, 66 (1992) 1-8.
- [8] 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.
- [9] C. Staudt-Bickel, W.J. Koros, Olefin/paraffin gas separations with 6FDA-based polyimide membranes, *J. Membr. Sci.*, 170 (2000) 205-214.
- [10] R. Faiz, K. Li, Polymeric membranes for light olefin/paraffin separation, *Desalination*, 287 (2012) 82-97.
- [11] 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.
- [12] N.B. McKeown, P.M. Budd, K.J. Msayib, B.S. Ghanem, H.J. Kingston, C.E. Tattershall, S. Makhseed, K.J. Reynolds, D. Fritsch, Polymers of intrinsic microporosity (PIMs): Bridging the void between microporous and polymeric materials, *Chem. Eur. J.*, 11 (2005) 2610-2620.

- [13] R. Swaidan, M. Al-Saeedi, B. Ghanem, E. Litwiller, I. Pinnau, Rational design of intrinsically ultramicroporous polyimides containing bridgehead-substituted triptycene for highly selective and permeable gas separation membranes, *Macromolecules*, 47 (2014) 5104-5114.
- [14] 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.
- [15] 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.
- [16] 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.
- [17] 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.
- [18] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165-185.
- [19] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, 320 (2008) 390-400.
- [20] 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.

- [21] 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.
- [22] 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.
- [23] P. Li, T.S. Chung, D.R. Paul, Gas sorption and permeation in PIM-1, *J. Membr. Sci.*, 432 (2013) 50-57.
- [24] N. Du, G.P. Robertson, J. Song, I. Pinnau, M.D. Guiver, High-performance carboxylated polymers of intrinsic microporosity (PIMs) with tunable gas transport properties, *Macromolecules*, 42 (2009) 6038-6043.
- [25] R. Swaidan, B.S. Ghanem, E. Litwiller, I. Pinnau, Pure- and mixed-gas CO₂/CH₄ separation properties of PIM-1 and an amidoxime-functionalized PIM-1, *J. Membr. Sci.*, 457 (2014) 95-102.
- [26] C.R. Mason, L. Maynard-Atem, N.M. Al-Harbi, P.M. Budd, P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen, Polymer of intrinsic microporosity incorporating thioamide functionality: Preparation and gas transport properties, *Macromolecules*, 44 (2011) 6471-6479.
- [27] N. Du, G.P. Robertson, M.M. Dal-Cin, L. Scoles, M.D. Guiver, Polymers of intrinsic microporosity (PIMs) substituted with methyl tetrazole, *Polymer*, 53 (2012) 4367-4372.
- [28] 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.

- [29] 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.*, 495 (2015) 235-241.
- [30] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, Plasticization-resistant glassy polyimide membranes for CO₂/CO₄ separations, *Sep. Purif. Technol.*, 14 (1998) 27-39.
- [31] F. Zhou, W.J. Koros, Study of thermal annealing on Matrimid® fiber performance in pervaporation of acetic acid and water mixtures, *Polymer*, 47 (2006) 280-288.
- [32] E.D. Wachsman, C.W. Frank, Effect of cure history on the morphology of polyimide: Fluorescence spectroscopy as a method for determining the degree of cure, *Polymer*, 29 (1988) 1191-1197.
- [33] F.Y. Li, Y. Xiao, T.-S. Chung, S. Kawi, High-performance thermally self-cross-linked polymer of intrinsic microporosity (PIM-1) membranes for energy development, *Macromolecules*, 45 (2012) 1427-1437.
- [34] 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).
- [35] S.M. Saufi, A.F. Ismail, Fabrication of carbon membranes for gas separation—a review, *Carbon*, 42 (2004) 241-259.
- [36] 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.
- [37] K.M. Steel, W.J. Koros, Investigation of porosity of carbon materials and related effects on gas separation properties, *Carbon*, 41 (2003) 253-266.

- [38] A.B. Fuertes, I. Menendez, Separation of hydrocarbon gas mixtures using phenolic resin-based carbon membranes, *Sep. Purif. Technol.*, 28 (2002) 29-41.
- [39] I. Menendez, A.B. Fuertes, Aging of carbon membranes under different environments, *Carbon*, 39 (2001) 733-740.
- [40] 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.
- [41] 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.
- [42] H. Suda, K. Haraya, Alkene/alkane permselectivities of a carbon molecular sieve membrane, *Chem. Commun.*, (1997) 93-94.
- [43] 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.
- [44] 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.
- [45] 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.
- [46] 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.

- [47] A.C. Lua, J. Su, Effects of carbonisation on pore evolution and gas permeation properties of carbon membranes from Kapton® polyimide, *Carbon*, 44 (2006) 2964-2972.
- [48] V.C. Geiszler, W.J. Koros, Effects of polyimide pyrolysis conditions on carbon molecular sieve membrane properties, *Ind. Eng. Chem. Res.*, 35 (1996) 2999-3003.
- [49] 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.
- [50] J.-i. Hayashi, M. Yamamoto, K. Kusakabe, S. Morooka, Effect of oxidation on gas permeation of carbon molecular sieving membranes based on BPDA-pp'ODA polyimide, *Ind. Eng. Chem. Res.*, 36 (1997) 2134-2140.
- [51] 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.
- [52] Y. Xiao, Y. Dai, T.-S. Chung, M.D. Guiver, Effects of brominating matrimid polyimide on the physical and gas transport properties of derived carbon membranes, *Macromolecules*, 38 (2005) 10042-10049.
- [53] Y.K. Kim, J.M. Lee, H.B. Park, Y.M. Lee, The gas separation properties of carbon molecular sieve membranes derived from polyimides having carboxylic acid groups, *J. Membr. Sci.*, 235 (2004) 139-146.
- [54] S. Fu, E.S. Sanders, S.S. Kulkarni, W.J. Koros, Carbon molecular sieve membrane structure–property relationships for four novel 6FDA based polyimide precursors, *J. Membr. Sci.*, 487 (2015) 60-73.

- [55] H.B. Park, Y.K. Kim, J.M. Lee, S.Y. Lee, Y.M. Lee, Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes, *J. Membr. Sci.*, 229 (2004) 117-127.
- [56] 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.
- [57] S. Thomas, I. Pinnau, N. Du, M.D. Guiver, Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1), *J. Membr. Sci.*, 333 (2009) 125-131.
- [58] N. Du, J. Song, G.P. Robertson, I. Pinnau, M.D. Guiver, Linear high molecular weight ladder polymer via fast polycondensation of 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethylspirobisindane with 1,4-dicyanotetrafluorobenzene, *Macromol. Rapid Commun.*, 29 (2008) 783-788.
- [59] R.M. Barrer, J.A. Barrie, J. Slater, Sorption and diffusion in ethyl cellulose. Part III. Comparison between ethyl cellulose and rubber, *J. Polym. Sci.*, 27 (1958) 177-197.
- [60] 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.
- [61] 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.
- [62] 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.

- [63] C.L. Staiger, S.J. Pas, A.J. Hill, C.J. Cornelius, Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer, *Chem. Mater.*, 20 (2008) 2606-2608.
- [64] L.G. Cançado, A. Jorio, E.H.M. Ferreira, F. Stavale, C.A. Achete, R.B. Capaz, M.V.O. Moutinho, A. Lombardo, T.S. Kulmala, A.C. Ferrari, Quantifying defects in graphene via raman spectroscopy at different excitation energies, *Nano Lett.*, 11 (2011) 3190-3196.
- [65] 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.
- [66] J. Landers, G.Y. Gor, A.V. Neimark, Density functional theory methods for characterization of porous materials, *Colloids Surf., A*, 437 (2013) 3-32.
- [67] A. Wahby, J. Silvestre-Albero, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, CO₂ adsorption on carbon molecular sieves, *Microporous Mesoporous Mater.*, 164 (2012) 280-287.
- [68] B.S. Ghanem, N.B. McKeown, P.M. Budd, J.D. Selbie, D. Fritsch, High-Performance Membranes from Polyimides with Intrinsic Microporosity, *Adv. Mater.*, 20 (2008) 2766-2771.
- [69] O. Salinas, X. Ma, E. Litwiller, I. Pinnau, High-performance carbon molecular sieve membranes for ethylene/ethane separation derived from an intrinsically microporous polyimide, *J. Membr. Sci.*, 500 (2016) 115-123.

Ethylene/ethane permeation, diffusion and gas sorption properties of carbon molecular sieve membranes derived from the prototype ladder polymer of intrinsic microporosity (PIM-1)

Octavio Salinas, Xiaohua Ma, Eric Litwiller, Ingo Pinnau*

- First report of ladder PIM-1-derived CMS membranes for ethylene/ethane separation.
- PIM-1-derived CMS (pyrolyzed at 800 °C) shows high pure-gas selectivity ($\alpha_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6} \sim 13$).
- Ethylene/ethane permselectivity of the CMS membrane is dominated by diffusivity selectivity.
- Intrinsic polymer precursor microporosity appears to have influence on CMS gas permeability.