Pyrolysis temperature-regulated gas transport and aging properties in 6FDA-DAM polyimide-derived carbon molecular sieve membranes

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ABSTRACT

Carbon molecular sieve (CMS) membranes with exceptional separation performance and scalable processing are promising for precise gas separation. However, their broad applicability is hampered owing to stability issues, mainly resulting from physical aging. Herein, we manipulate the pyrolysis temperature (550 °C, 650 °C and 750 °C) to regulate the gas transport properties and control the physical aging of CMS membranes derived from 6FDA-DAM polyimide. The morphology, chemical composition and pore size of the membranes were characterized using SEM, IR, XPS and XRD. Results demonstrated that the pore structure of CMS membranes shows densification with increasing the pyrolysis temperature, affording enhanced separation efficiency for gas pairs: H₂/N₂, H₂/CH₄ and CO₂/CH₄ pairs based on the size-sieving effect. Moreover, the effect of aging is more considerable for membranes pyrolyzed at a higher temperature. In addition, the membrane subjected to pre-aging treatment via vacuum storage exhibit better, stable gas separation performance beyond the upper-bond for polymeric membranes. The separation mechanism of the CMS membranes reveals that gas permeation behavior is dominated by diffusion. Tailoring gas permeation and physical aging can provide an alternative approach to tune the gas transport properties of CMS membranes.

1. Introduction

Membrane based gas separation with low energy consumption and high efficiency has been demonstrated as an alternative to traditional separation processes (e.g., cryogenic distillation and adsorptive separation) [1–3]. Conventional membrane materials are dominated by polymers, but they generally suffer from a trade-off relationship between permeability and selectivity [4]. As next-generation molecular selective membranes, carbon molecular sieve (CMS) membranes with a simple preparation process and high separation performance have triggered a great deal of attention [5–12]. CMS membranes are formed via the pyrolysis of polymers with suitable microstructures at temperature exceeding their glass transition temperature (Tg), which comprise disordered sp²-hybridized carbon sheets, exhibiting an idealized bimodal pore distribution with ultramicropores (~3–7 Å) and micropores (~7–20 Å). The micropores could accelerate gas diffusion and the ultramicropores confer strong size-sieving ability, which may discriminate between gases with a small size difference, overcoming the trade-off limitations of polymeric membranes [13–18].

However, the development of CMS membranes is hampered by aging, which causes permeance loss and selectivity gain over time [16,19–21]. Various strategies have been proposed to suppress the aging effect. Tseng et al. demonstrate a polymer coating strategy to enhance the anti-aging ability of CMS membrane [22]. By using a hydrophobic polymer layer coated on the surface, the water and oxygen adsorption capacity effectively decreased, significantly improving the CMS membrane stability. However, extra transport resistance is inevitable to sacrifice gas permeability. Qiu et al. reported an engineered post-pyrolysis hyperaging treatment of CMS membrane at moderate elevated temperatures [14]. Results show that hyperaging also stabilizes CMS materials against physical aging and the performance of H₂ separation during long-term operation. Nanoparticles introduction is also an effective approach to inhibit structural change to enhance anti-aging ability of CMS membrane. Musselman et al. introduced metal – organic polyhedra-18 (MOP-18) into PIM-1 to prepare a hybrid membrane [20]. During the pyrolysis of resulted membrane, copper metal nanoparticles in situ generated, which acted as pillars for the graphene sheets within the CMS membrane, preventing the collapse of the micropores, thus minimizing the aging of the CMS membrane. In addition, it has been also found that the pyrolysis temperature considerably

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CMS membranes were fabricated by a broader array of pyrolysis temperature leading to highly permeable CMS membranes (Fig. 1). Meanwhile, it can be converted into a carbon material by a simple pyrolysis process. The bulky 6FDA moiety could provide a high fractional free volume, pore structures by regulating the pyrolysis temperature for gas separation. The effects of pyrolysis temperature on the aging and molecular transport performance [16,23]. However, there is lack of a systematic study about the effects of pyrolysis temperature on the aging and molecular transport properties of CMS membranes.

Herein, we report the fabrication of CMS membranes with tunable pore structures by regulating the pyrolysis temperature for gas separation. The 6FDA-DAM polyimide was chosen as the precursor given that the bulky 6FDA moiety could provide a high fractional free volume, leading to highly permeable CMS membranes (Fig. 1). Meanwhile, it can be converted into a carbon material by a simple pyrolysis process. The CMS membranes were fabricated by a broader array of pyrolysis temperature (550 °C, 650 °C and 750 °C), which differs from what was done in the literature reported by Arab et al. [24]. Moreover, the relationship between gas permeation and physical aging property of the membranes and the pyrolysis temperature was investigated in detail. Further, the gas transport mechanism of the membranes was revealed. The resulting separation performance of the optimal CMS membranes is beyond the performance upper-bond limits for polymeric membranes.

2. Experimental

2.1. Materials

4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, >99%) and 2,4-diaminomesitylene (DAM, ≥98%) were used as the reactive monomers for synthesis of 6FDA-DAM polymers and were obtained from Aladdin Bio-CheM Technology Co., Ltd. 1-Methyl-2-pyrroldione (NMP, ≥99%) was used as the solvent for polymer synthesis. Tetrahydrofuran (THF, ≥99%) was the solvent for membrane fabrication and methanol (>99.7%) was used to wash the obtained polymers to remove excess NMP in the polymers. NMP, THF and methanol were provided by Shanghai Aladdin Co., Ltd. All chemicals were used without further purification.

2.2. Synthesis of polymers

The 6FDA-DAM polymers were synthesized via condensation of dianhydride monomers with diamine according to the previously reported method [25,26]. Typically, stoichiometric amounts of monomers were agitated and reacted in a NMP solution under N2 atmosphere at low temperature (~5 °C) for one day to produce a polyamide-acid solution. Then imidization was achieved with the presence of beta picoline and acetic anhydride at ambient temperature for another one day under N2 purge. The resulted polymers were precipitated and washed with methanol and dried at 200 °C under vacuum for 24 h to remove residual solvent.

2.3. Preparation of pristine polyimide dense films

6FDA-DAM powder was dried at 120 °C under vacuum overnight before being dissolved in THF to form a 20 wt% casting solution. The solution was stirred on a rolling mixer for 24 h at room temperature. Then the resulting solution was poured onto a smooth glass plate, which was stored in a glove bag with saturated THF vapor. After casting the solution using a draw knife, pure 6FDA-DAM dense films with desired thickness (typically 50–70 μm) could be formed on the glass plate, following by being left in the glove bag to endow THF solvents to evaporate slowly. Finally, the resulted film was further dried at 120 °C under vacuum for 24 h to remove residual solvent.

2.4. Preparation of CMS films

To prepare CMS films, the obtained 6FDA-DAM films were cut into circular pieces with diameter of 25 mm, which were sandwiched between two clean quartz plates and left into the center of a tube furnace. As shown in Fig. 2, the pyrolysis program was set as follows: the temperature was ramped up from ~ 50 °C to 250 °C at ~ 7 °C/min, then to (Tc–15) °C (Pyrolysis temperature, 550 °C, 650 °C and 750 °C) at ~ 4 °C/min, finally to Tc at 0.25 °C/min and then the films were soaked for 120 min. At last, the tube furnace was allowed to cool naturally to room temperature. During the pyrolysis process, the whole system was under ultra-low vacuum of < 0.0075 Torr, and the corresponding concentration of O2 was < 2 ppm, the influence of these factors on membrane performance can be negligible. The membranes generated from pyrolysis temperature of 550 °C, 650 °C and 750 °C were denoted as CMS-550 °C, CMS-650 °C and CMS-750 °C, respectively. The thickness of resulted CMS film was measured by a high-precision micrometer.

2.5. Characterizations

Thermal properties of 6FDA-DAM membrane were investigated by thermal gravimetry analysis (TGA, NETZSCH STA 449F3) at a heating rate of 10 °C/min under a nitrogen atmosphere. The film morphologies were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscope (TEM, JEM2100F, Japan Electron Optics Laboratory Co., Ltd., Japan). Attenuated total reflectance-Fourier transform infrared spectra (ATR-FTIR, Thermo, Nicolet Nexus 470 spectrometer, USA) was used to analyze the chemical properties of films in the range of 750–4000 cm⁻¹. X-ray diffraction (XRD, Rigaku, Smartlab 3 KW, Japan) was measured on a Rigaku diffractometer operating with Cu Kα radiation at a wavelength of 1.54 Å, in the 2θ range of 5–40°. Gas (H2, CO2, N2 and CH4) adsorption capacity of films was investigated by BELSORP-HP (MicrotracBEL Corp., Japan).
2.6. Gas permeation measurement

2.6.1. Pure-gas permeation

The constant-volume permeation system was used to measure the pure gas permeability and ideal selectivity [27]. In detail, the membranes were sealed in the middle of the test cell and the whole system was degassed using a vacuum pump. Then the pure gas was flowed into the upstream slowly. After the system reached stability, all the gas permeation measurements were performed at least three times. The gas permeability can be calculated according to the following equation:

$$P = \frac{V_m \times I}{R \times T \times A \times \Delta p} \times \frac{dp}{dt}$$

(1)

where \( P \) represents the pure gas permeability (Barrer, 1 Barrer = \( \times 10^{-10} \) cm\(^2\) cm\(^-1\) s\(^-1\) cmHg\(^-1\)), \( R \) is the operating temperature (K), \( V_m \) stands for the downstream volume (cm\(^3\)), \( I \) is the membrane area (cm\(^2\)), \( \Delta p \) represents the transmembrane pressure (cmHg\(^-1\)) and \( t \) refers to the permeation time (s).

The ideal gas selectivity is calculated based on the ratio of pure gas permeabilities according to the following equation:

$$\alpha_{ij} = \frac{P_i}{P_j}$$

(2)

2.6.2. Mixed-gas permeation

The mixed-gas permeation was measured with a 50/50 v/v gas mixture (H\(_2\)/CH\(_4\) or CO\(_2\)/CH\(_4\)) by the constant-pressure permeation system [28,29]. The experiments were performed at 35 °C and the total pressure of 3 atm. In order to avoid the concentration polarization, the stage-cut (also known as the permeate to feed flow rate) was maintained <1%. The composition in permeation side was determined by gas chromatography (Agilent 8860, USA).

The mixed-gas selectivity was calculated by Eq. (2) in which the gas permeability can be obtained as follows:

$$P_i = \frac{V \times I \times x_i \times \frac{\partial p}{\partial t}}{A \times R \times T \times \Delta p}$$

(3)

where \( P_i \) is the permeability of component \( i \), \( x_i \) stands for the molar fraction in the permeation side.

2.7. Gas adsorption measurement

Besides, the permeability can also be expressed as the product of the sorption coefficient (\( S \)) and the diffusion coefficient (\( D \)):

$$P = S \times D$$

(4)

The sorption coefficient (\( S \)) can be obtained from the gas sorption measurement, which was carried out by a high-pressure physical adsorption apparatus (BELSORP-HP, MicrotracBEL Corp., Japan). The sorption coefficient can be calculated by the following equation:

$$S_i = \frac{c_i}{f_i}$$

(5)

where \( c_i \) is the total gas concentration in the membrane sample, \( f_i \) stands for the corresponding upstream fugacity driving force of component \( i \). Here, the gas adsorption concentration of CMS was described using the dual-mode sorption model, which is expressed as follows [10]:

$$c_i = k_{i,0} \rho + \frac{c_{i,H_2} \cdot \rho}{1 + \beta}$$

(6)

where \( k_{i,0} \) refers to the Henry’s solubility coefficient of component \( i \), \( c_{i,H_2} \) is the Langmuir saturation constant and \( \beta \) stands for the Langmuir affinity constant.

3. Results and discussion

3.1. Characterizations of CMS membranes

Owing to the CMS membranes are typically derived from the pyrolysis of the polymers in the range between 500 and 1000 °C, it is very crucial to examine thermal decomposition and stability of the polymers. Thus, TGA analysis was employed to observe the thermal property of the 6FDA-DAM membrane. As shown in Fig. 3, a small weight loss of ~1.13% was observed in the temperature range from room temperature to 100 °C, which corresponded to the removal of a trace amount of a residual solvent in the membrane. Besides, the 6FDA-DAM membrane maintained stability until ~480 °C, at which decarboxylation occurred. Generally, carbonization starts from the rapid degradation of the polymer above its \( T_g \). For the 6FDA-DAM polymer membrane, fast weight loss started at ~500 °C, and beyond 750 °C, the degradation rate became quite low. At this stage, the disappearance of functional groups and the release of small gas molecules occurred, gradually generating the CMS membrane.

The cross-sectional SEM images of the pristine 6FDA-DAM membrane and the resulting CMS membranes are shown in Fig. 4. The 6FDA-DAM membrane is highly smooth without any bulges (Fig. 4a), whereas at high magnifications, it shows a coarse nodular structure (Fig. 4b and c). However, after the carbonization of the polymer to form the CMS membrane, the intrinsic nodular-like morphology of the 6FDA-DAM membrane disappeared and the cross-sectional and surface SEM images of the CMS membrane exhibited a smooth morphology (Fig. 4d-f). Furthermore, the microstructure of the CMS membrane was characterized using TEM. As shown in Fig. 4f, the pore structure constructed by disorder turbostratic carbon sheets revealed the distribution of micropore size in carbon.

ATR-FTIR analysis was used to investigate the chemical properties of the 6FDA-DAM and CMS membranes. As shown in Fig. 5a, the 6FDA-DAM membrane showed three characteristic peaks at approximately 1100, 1370, and 1720 cm\(^-1\), which corresponded to the stretching of C-N-C, C-N and C = O, respectively [30,31]. In addition, compared with the 6FDA-DAM membrane, with the increase in the pyrolysis temperature, the intensity of the vibration peaks gradually weakened and almost disappeared when the carbonization temperature was 750 °C. To better analyze the chemical properties changes in the 6FDA-DAM and CMS membranes, X-ray photoelectron spectroscopy (XPS) was performed. Fig. 5b and Table 1 show that no F element was found in CMS membrane, indicating that the -CF\(_3\) group has been completely removed after the carbonization of polymer. Meanwhile, the concentrations of O and N elements decreased (from 9.28% to 3.23% for O and from 6.39% to 3.36% for N) with the pyrolysis temperature, indicating that the
polymer continued to be carbonized. It is worth noting that the concentration of N is slightly higher than that of neat polymeric membrane, probably due to the adsorbed impurity on the membrane surface and test error. At 750 °C, the degree of carbonization was considerable, evidenced by the high carbon concentration (93.41%, Table 1). In addition, the ratio of sp³ to sp² hybridized carbon decreases from 0.60 to 0.41 with increasing pyrolysis temperature, indicating that more graphitic sp²-hybridized carbon forms under higher pyrolysis temperatures (Fig. 5c). Meanwhile, decreased BET surface areas as increasing pyrolysis temperature was also observed (Fig. S1). These results further revealed that the chemical groups gradually decreased during the carbonization process with increasing temperature.

We further employed XRD to observe the lattice spacing (d spacing) of CMS membranes generated using different pyrolysis temperatures.
The pure-gas permeation results measured at 35 °C for the 6FDA-DAM and CMS membranes are shown in Fig. 7. It was found that the permeability of H₂, CO₂, N₂, and CH₄ for all CMS membranes pyrolyzed at different temperatures showed the following order: P(H₂) > P(CO₂) > P(N₂) > P(CH₄). This is a reverse order of their kinetic diameters: H₂ (2.89 Å) < CO₂ (3.3 Å) < N₂ (3.64 Å) < CH₄ (3.8 Å), indicating that size plays an important role in the gas permeation behavior of CMS membranes. Meanwhile, gas permeability decreased with increasing pyrolysis temperature (Fig. 7a). This is due to that increasing pyrolysis temperature could further facilitate the pore densification in the carbon matrix, as confirmed by the variation of d-spacing in Fig. 6. It was reported that increasing content of heteroatoms (e.g., F and N element) could facilitate the transport of CO₂ molecule owing to enhanced sorption ability. However, we found the CO₂ permeability of the neat 6FDA-DAM membrane with higher heteroatoms content is lower than that of CMS-550 °C or CMS-650 °C membrane with lower heteroatoms content (Fig. 7a and Table 1). This probably is due to that different structures in polymeric and CMS membranes. The 6FDA-DAM membrane with polymeric segment interactive network possesses fewer adsorption sites. The CMS-550 membrane showed the highest H₂ permeability of 8461.1 Barrer with a modest H₂/CH₄ selectivity of 92.8. Pyrolysis at a higher temperature reduced H₂ permeability due to pore contraction, considerably improving gas selectivity. At 750 °C, H₂ permeability decreased to 2321.5 Barrer and a H₂/CH₄ selectivity of 246.9 was achieved (Fig. 7b). A similar trend was also observed for H₂/N₂ and CO₂/CH₄. Nevertheless, it was also noticed that the H₂ permeability CMS membranes with a smaller pore dimension outperformed that of polymeric membranes with a bigger pore dimension. Probably due to that different from CMS membranes with unique bimodal distribution of pores structure, polymer membrane is generated by interleaving polymer chain segments, leading to a long transport path. The H₂ molecule will encounter higher resistance to pass through the precursor polymeric membrane. These results further demonstrated that tailoring the pyrolysis temperature can be used to regulate gas separation performance.

Similar to glass polymers, CMS membranes generally suffer from physical aging over time, along with enhanced selectivity between penetrants [16,34]. Because the sub-Å pore structure...
of CMS membranes changes during the aging process, it is hard to detect subtle changes using conventional characterization method. Therefore, we used gas molecules, H₂, CO₂, N₂, and CH₄, as probes to systematically study the relation between CMS membranes pyrolyzed at different temperature and physical aging. Vacuum storage has been demonstrated as an effective strategy to prevent the blocking of pores owing to the chemisorption of oxygen and water in air during the aging process [16,35,36]. It has also been used as an optimization strategy for 6 h and 24 h vacuum equilibration of asymmetric CMS fibers prepared from 6FDA:BPDA-DAM at 550 °C, 600 °C and 650 °C [24]. The separation performances of fresh and 7 d-aged CMS membranes for H₂/N₂, H₂/CH₄ and CO₂/CH₄ pairs were tested by exposing upstream and downstream surfaces to < 0.5 torr at 35 °C. As shown in Fig. 8, compared with the fresh CMS membranes, the permeabilities of all gases decrease in case of the 7 d-aged CMS membranes obtained using different pyrolysis temperatures. Moreover, the ideal gas selectivities obtained for H₂/N₂ and H₂/CH₄ pairs considerably increased. This can be ascribed to the aging process, enabling the densification and contraction of the pore structure of CMS membranes [37]. Notably, regarding the selectivity of the CO₂/CH₄ pair, the aging effect is less considerable, which is partially...
attributed to the smaller size difference of CO$_2$/CH$_4$ pair (0.50 Å) compared with those of H$_2$/N$_2$ pair (0.75 Å) and H$_2$/CH$_4$ pairs (0.91 Å).

To better understand the effect of pyrolysis temperature on the aging rate of CMS membranes, we investigated the rate of change in gas permeability and selectivity in detail. It can be seen from Fig. 5a that the percentage of permeability reduction for CMS membranes after 7 d of vacuum aging increased as the pyrolysis temperature increased. This is the typical phenomenon of physical aging. Particularly, CMS membranes pyrolyzed at 550 °C exhibit a 17% permeability reduction for H$_2$, while the membranes pyrolyzed at 750 °C showed a 60% loss in permeability. A similar tendency was also observed for other gas molecules (e.g., CO$_2$, N$_2$, and CH$_4$). The effects of physical aging in permeability reduction are considerable for gas molecules with larger kinetic diameters (e.g., CO$_2$, N$_2$, and CH$_4$), affording selectivity gain for their gas pairs (Fig. 9b). Similarly, the rate of increase in gas pair selectivity shows a positive relation with pyrolysis temperature. These trends can be explained as follows. At a lower pyrolysis temperature, despite the pores of CMS membranes would tighten during the aging process, they are still large enough for the permeation of small-sized gas molecules. In addition, a higher pyrolysis temperature is able to facilitate rapid physical aging process, which can be ascribed to the following aspect. During the pyrolysis process, the polymer precursor starts a decomposition process, wherein gaseous species (e.g., CF$_3$H, HF, CO$_2$, CO and H$_2$) are evaluated. This process could cause aromatization and associated linearization of polymer segments, following by a fragmentation process to form shorter strands. Ultramicropores can form by arrangement of carbon strands into plates, while large micropores form between neighboring plates. Notably, higher final pyrolysis temperatures can lead to more tightly packed carbon strands in the walls of micropores, thus, partial densification of the stacked plates occur, leading to the average distance between the plates reduction [24,38]. Upon slight pore tightening, a lower permeability of small and large-sized molecules tends to exist, while large-sized molecules could bear a larger steric hindrance through CMS membranes pyrolysis at higher temperature, causing higher selectivity gain. Thus, the aging behavior of CMS membranes can be manipulated by controlling the pyrolysis temperature.

Accordingly, CMS-550 °C membrane with high gas permeability and desired gas pair selectivity is a better candidate for long-term applications. Therefore, we further investigated the separation performance for equimolar CO$_2$/CH$_4$ and H$_2$/CH$_4$ gas mixtures. It can be seen from Fig. 10 that the mixed gas permeability and actual selectivity were lower than the pure gas permeability and ideal selectivity (Fig. 8), which can be attributed to the competitive sorption of gases. Meanwhile, during 14 d of continuous operation, the CMS-550 °C membrane showed a 17.4% loss of H$_2$ permeability with decreasing from 8074 Barrer to 6667 Barrer. Meanwhile, a 26.7% gain of H$_2$/CH$_4$ selectivity with increasing from 85.7 to 108.6 was achieved (Fig. 8a). The separation performance of CO$_2$/CH$_4$ gas mixture exhibited similar variation trends with that of H$_2$/CH$_4$ gas mixture. These results indicate the typical physical aging phenomenon of CMS membrane. In addition, owing to H$_2$/CH$_4$ gas pair possesses a larger size difference (0.91 Å) than the CO$_2$/CH$_4$ pair (0.50 Å). The effect of physical aging is more considerable for H$_2$/CH$_4$ mixed gas separation. The CO$_2$/CH$_4$ selectivity maintained stable at ~ 44 during the first week and then slowly increased to ~ 46, while the H$_2$/CH$_4$ selectivity steadily increased over time (Fig. 8b). Besides, it should be noted that the separation performance of our developed CMS-550 °C membranes differed from the same 6FDA-DAM precursor but pyrolyzed...
under an inert argon atmosphere [35], which may be ascribed to the
different pyrolysis atmosphere [39].

Pre-vacuum aging has been demonstrated as an attractive strategy to
improve the stability of CMS membranes. The CMS membrane, CMS-
550 °C membrane exemplified here, was stored in the oven with a
vacuum of ~ 0.75 Torr for 30 days. Before the membrane stability
evaluation, we first observe whether it was physical or chemical aging in
CMS membrane treated by vacuum storage. No external species (e.g.,
water, oxygen) adsorption was observed (Fig. S2), indicating vacuum
aging belongs to physical aging. We observed the long-term gas sep-
ration performance of the CMS membrane. As shown in Fig. 11, the
CMS-550 °C membrane with 30 d of vacuum storage exhibited stable
CO₂ permeability of ~ 1100 Barrer with a CO₂/CH₄ selectivity of > 50
and H₂ permeability of ~ 4850 Barrer with a H₂/CH₄ selectivity of > 320,
respectively, during long-term testing for over 120 h, indicating
that pre-vacuum aging endows the CMS membranes with excellent anti-
aging properties. This could be attributed to that pre-vacuum storage
accelerate aging to some extent that could enable surface energy

![Figure 12](image12.png)

**Fig. 12.** Comparison of CO₂/CH₄ and H₂/CH₄ separation performance of CMS membranes.

![Figure 13](image13.png)

**Fig. 13.** (a) H₂, (b) CO₂, (c) N₂ and (d) CH₄ adsorption isotherms of CMS membranes aged for 7 d at 35 °C.
reduction and approach to a thermodynamically stable state in the absence of penetrant self-diffusion throughout the micropores [24]. In addition, pre-aging tightens the pore structure, which is further confirmed by XRD analysis (Fig. S3). It has a more significant impact on the gas permeation behavior of large gas molecules. Thus, owing to the absence of penetrant self-diffusion throughout the micropores [24]. In ambient condition, water and oxygen molecules could be strongly adsorbed on CMS membranes. It will reduce the pore volume and pore size, thereby decreasing the gases permeability and enhancing selectivity [48].

Furthermore, the strong size-sieving effect endowed the CMS membranes with excellent gas separation performance, which exceeds the 2008 upper bound and are competitive compared with microporous membranes such as zeolite and silica membranes for CO₂/CH₄ and H₂/CH₄ separation [28,40–47] (Fig. 12), showing considerable potential for gas separation applications. It is worth noting that the gas permeabilities of aged-550 °C-30 d CMS membranes are lower than that of fresh CMS-550 °C membranes (Fig. 10), further indicating pre-vacuum treatment of aged-550 °C membranes are lower than that of fresh CMS-550 °C membranes (Fig. 10), pre-vacuum aging can afford a ~ 242% selectivity increase for H₂/CH₄, whereas the same membrane shows a ~ 25% selectivity increase for CO₂/CH₄.

3.3. Gas separation mechanism of CMS membranes

To understand the transport mechanism in CMS membranes, the permeability (P) was deconvoluted into the product of sorption coefficient (solubility, S) and diffusion coefficient (diffusivity, D) according to the solution-diffusion model [49]. Gas solubility is generally calculated from the gas adsorption capacity. We first employed high-pressure physical adsorption measurement to investigate the gas adsorption capacity (H₂, CO₂, N₂ and CH₄) of fresh and 7 d vacuum aged CMS membranes. As shown in Fig. 13, it can be seen that the gases adsorption capacity of the CMS membranes decreased as the final pyrolysis temperature increased. This could be because the physical aging effect is significant at a higher pyrolysis temperature, increasing the densification of the pore structure. Besides, the H₂ and N₂ uptake for CMS-750 °C membrane dropped considerably after 7 d of aging compared with the uptake of CO₂ and CH₄ because CMS membranes possess high vol% Langmuir pores with molecular sieving slit pore walls, thus, the physical aging process can enable pore densification, decreasing the gas adsorption capacity. The effect is much more significant for noncondensable gas molecules (e.g., H₂ and N₂) compared with relatively condensable molecules (e.g., CO₂ and CH₄).

Accordingly, the solubility (S, 10⁻² cm³ (STP) cm⁻³ cmHg⁻¹) and diffusivity (D, 10⁻⁸ cm² s⁻¹) coefficients of four gases (H₂, CO₂, N₂ and CH₄) and the corresponding selectivities were calculated, as shown in Fig. 14 and Table 2. It was found that the solubility and diffusivity coefficients of all the gases show a decreased tendency with increasing pyrolysis temperature for various CMS membranes, owing to the shrinkage of transport channels (Fig. 6) caused by pore structure densification. Meanwhile, the CMS membranes exhibited ultralow

Fig. 14. Solubility and diffusivity of fresh and aged CMS membranes pyrolyzed at different temperatures. (a) H₂, (b) CO₂, (c) N₂ and (d) CH₄ of the solubility (S) and the diffusivity (D), S: 10⁻² cm³ (STP) cm⁻³ cmHg⁻¹, D: 10⁻⁸ cm² s⁻¹.

Table 2

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<th>Membrane sample</th>
<th>CO₂/CH₄</th>
<th>H₂/N₂</th>
<th>H₂/CH₄</th>
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<tr>
<td></td>
<td>α₀</td>
<td>α₀</td>
<td>α₀</td>
</tr>
<tr>
<td>CMS-550 °C</td>
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<td>0.37</td>
<td>0.16</td>
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<tr>
<td>Aged-550 °C</td>
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<td>Aged-750 °C</td>
<td>2.53</td>
<td>0.12</td>
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To understand the transport mechanism in CMS membranes, the permeability (P) was deconvoluted into the product of sorption coefficient (solubility, S) and diffusion coefficient (diffusivity, D) according to the solution-diffusion model [49]. Gas solubility is generally calculated from the gas adsorption capacity. We first employed high-pressure physical adsorption measurement to investigate the gas adsorption capacity (H₂, CO₂, N₂ and CH₄) of fresh and 7 d vacuum aged CMS membranes. As shown in Fig. 13, it can be seen that the gases adsorption capacity of the CMS membranes decreased as the final pyrolysis temperature increased. This could be because the physical aging effect is significant at a higher pyrolysis temperature, increasing the densification of the pore structure. Besides, the H₂ and N₂ uptake for CMS-750 °C membrane dropped considerably after 7 d of aging compared with the uptake of CO₂ and CH₄ because CMS membranes possess high vol% Langmuir pores with molecular sieving slit pore walls, thus, the physical aging process can enable pore densification, decreasing the gas adsorption capacity. The effect is much more significant for noncondensable gas molecules (e.g., H₂ and N₂) compared with relatively condensable molecules (e.g., CO₂ and CH₄).

Accordingly, the solubility (S, 10⁻² cm³ (STP) cm⁻³ cmHg⁻¹) and diffusivity (D, 10⁻⁸ cm² s⁻¹) coefficients of four gases (H₂, CO₂, N₂ and CH₄) and the corresponding selectivities were calculated, as shown in Fig. 14 and Table 2. It was found that the solubility and diffusivity coefficients of all the gases show a decreased tendency with increasing pyrolysis temperature for various CMS membranes, owing to the shrinkage of transport channels (Fig. 6) caused by pore structure densification. Meanwhile, the CMS membranes exhibited ultralow
sorption selectivity of 0.05 ~ 2.53, indicating that the gas separation in CMS membranes is dominated by the diffusion process. In addition, in the fresh CMS-550 °C membrane, non-condensable H₂ displays much higher diffusivity of 1618.8 × 10⁻⁶ cm² s⁻¹ than that of CH₄ (2.7 × 10⁻⁸ cm² s⁻¹), due to the smaller size (H₂: 2.89 Å; CH₄: 3.8 Å), thereby indicating ultrahigh H₂/CH₄ diffusion selectivity of 599.6 and high H₂/CH₄ permeation selectivity of 92.9. This implies the molecular sieving effect. With increasing the pyrolysis temperature to 750 °C, the diffusivity of H₂ decreased to 814.3 × 10⁻⁶ cm² s⁻¹, two times lower than that of CMS-550 °C membrane, owing to the decreased pore size. While the effect of pore size shrinkage is more obvious for large-sized molecules, the diffusivity of CH₄ sharply reduced to 0.38 × 10⁻⁶ cm² s⁻¹, leading to remarkable enhanced H₂/CH₄ diffusion selectivity and permeation selectivity to 2142.9 and 246.9, respectively. Besides, owing to pore structure densification, the diffusivity coefficient of all the gases decreased for the CMS membrane after the preaging treatment. Meanwhile, the percentage increase in the H₂/CH₄ diffusion selectivity of aged CMS membrane spiked to 410% at pyrolysis temperature of 750 °C, nearly 100 times higher than that at 550 °C (4.2%). A similar phenomenon was also found in the H₂/N₂ pair, whereas it was absent for CO₂/CH₄ owing to the smaller size difference (CO₂/CH₄: 0.50 Å; H₂/ N₂: 0.75 Å; H₂/CH₄: 0.91 Å). Therefore, the manipulation of the gas transport and physical aging behavior of CMS membranes was achieved by tuning the pyrolysis temperature.

4. Conclusions

In this work, the effects of pyrolysis temperature on the gas transport properties and aging of CMS membranes prepared from high free volume 6FDA-DAM membranes were investigated. The manipulation of pyrolysis temperature rationally tuned the pore size to achieve controllable gas transport and aging properties of CMS membranes. The gas permeability decreased, while the selectivity increased with increasing the pyrolysis temperature. The effect of aging is more significant for membranes prepared at higher temperatures. In addition, compared with fresh CMS membranes, after preaging treatment, the CMS membrane showed more stable separation performance during 120 h permeation tests for CO₂/CH₄ and H₂/CH₄. This work provides additional insight into the formation and aging of CMS membranes. Notably, the implementation of vacuum pyrolysis is not easily scalable and the study of inert gas pyrolysis is underway. Moreover, this fundamental study was focused on CMS symmetric dense film, in which the transport behavior and aging property are distinct from CMS asymmetric hollow fiber. More systematic study on CMS hollow fiber is needed as applying the finding in this work.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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