A review of polymer-derived carbon molecular sieve membranes for gas separation

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Abstract: Membrane technology for gas separation and purification has unique economic and environmental advantages over conventional purification processes. Carbon molecular sieve membranes (CMSMs) have a higher gas permeability, selectivity, chemical resistance, and better thermal stability than polymer membranes, and have therefore received more attention. CMSMs are commonly fabricated by the pyrolysis of polymer precursors such as polyimides, resins, cellulose and polyetherimide. The reported fabrication process and gas separation performance of CMSMs made from various precursors are summarized and discussed. Both the chemical and physical structures of the precursor membranes affect the carbon structures and gas separation performances of the resulting CMSMs. Overall, the gas separation performance of CMSMs has been significantly improved in the last 20 years, and their possible commercial use is not far away. An in-depth understanding of this progress on CMSMs should provide researchers from different fields an understanding of how to promote their fabrication and applications.

Key words: Precursor; Carbon molecular sieve membranes; Gas separation performance; Permeability; Selectivity

1 Introduction

The purification and separation of gas are essential for most gas applications. So far, the demand of highly purified industrial gases has been increasing at a rate of ~10% per year, and the annual growth rate of global gas industry output value is ~12%. Separation technology plays a major role in gas industry. Up to the date, various traditional gas separation technologies, such as cryogenic distillation and pressure swing adsorption, have been widely employed. In order to lower the gas price, researchers and manufacturers are continuously making efforts to develop novel separation technologies with higher efficiency, lower energy conservation, and better environmental protection. Compared with traditional separation technologies, the membrane separation technology exhibits its unique advantages on low cost, easy scale up, and little footprint, and has been widely used in a variety of industrial applications since 1960s[1].

Polymer membranes with low cost and easy processability have become prominent in gas separation. However, there are also many disadvantages for polymer membranes, such as poor thermal stability, poor chemical resistance, and possible plasticization by surrounding gas. Additionally, the gas permeability and selectivity are normally a pair of balancing factors. It is extremely difficult to achieve both high permeability and high selectivity. A critical limitation, permeability selectivity trade-off, is defined to evaluate the membrane separation performance, and the permeability selectivity trade-off boundary is continuously improved. Inspired by other types of carbon materials, a serial of carbon molecular sieving membranes (CMSMs) has been prepared through the pyrolysis and carbonization of polymer precursors, and the resulting CMSM exhibits good thermal stability, excellent chemical resistance, as well as both high permeability and high selectivity compared with polymer membranes. The CMSM was firstly prepared as early as in 1970s from thermosetting organic materials[2–4]. The high carbon content and strong C—C bonding lead to excellent structural integrity and stability. Most CMSMs exhibit superior gas permeability and selectivity that could easily exceed the trade-

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off boundary of polymer membrane. Also, the CMSMs could be operated in a broad temperature range, especially at high temperature. Due to the advantages of CMSMs in gas separation, such as, the purification of H_2, the recovery of CO_2, the separation of O_2/N_2, and the separation of olefins/alkanes, more and more attentions have been attracted to the development of novel CMSMs.

CMSMs are commonly fabricated from polymer precursors. A typical structural evolution of CMSMs from polymer to carbon is summarized in Fig. 1. During pyrolysis, the polymer chains decompose, fragmentize, and aromatize to form carbon "strands" and "plates". Finally, turbostratic carbon structures composing of slit-liked ultra-micropores (<0.6 nm) among carbon strands and micro-cavities (0.6-2 nm) between aggregated carbon plates are formed in the resulting carbon membranes[5].

The pores of CMSM decide its gas separation performance. Pores with different sizes play different roles (Fig. 2), and the ultra-micropore is the key for gas separation efficiency of CMSMs[6]. The pore formation is complex and could be affected by many factors, including polymer precursor[7], chain aggregation, pyrolysis conditions[8–11], gas environments[12], pre- or post-treatment[13,14], and tension or stretching. Among these factors, the most prominent one is the chemical structure of the precursor, which is the dominante factor affecting chain softness temperature (glass transition temperature, T_g), rigidity, aggregation state, fractional free volume (FFV), and chain rigidity. There are extensive studies on making CMSMs from various precursors, such as polyimide (PI), phenolic resin (PR), cellulose, polymer of intrinsic microporosity (PIM), polyetherimide (PEI), polybenzimidazole (PBI), polyvinylidene chloride (PVDC), polyfurfuryl alchohol (PFA), and ether ketone. It is noted that the structural evolution from polymer to carbon is very complex, and the detailed conversion mechanisms are still not well understood. Additionally, the physical aggregation state of polymer precursor (crystalline/amorphous, orientation) and pyrolysis conditions (tension) have been proven to be important factors affecting the resulting carbon structures, but have been rarely studied in making CMSMs. In order to improve the gas separation performances and overcome the disadvantages of CMSMs, various modification methods, such as blending, doping, thinning, and surface treating, have been adopted.

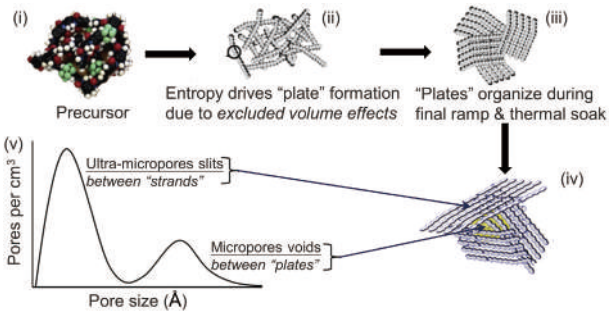

Fig. 1　Possible scheme of the structural transformation and pore formation from polymer to carbon[5]. (Reprinted with permission).

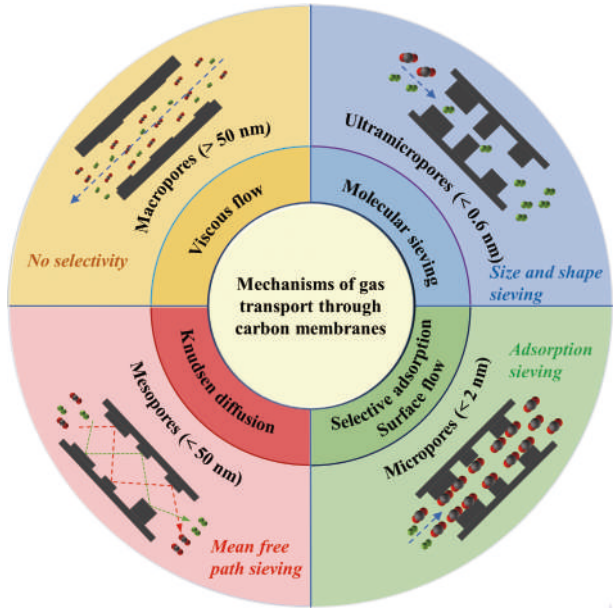

Fig. 2　Scheme of main mechanisms for gas transport through carbon membranes.

The ultimate target of investigation for CMSM is to realize its commercial applications. For the product form, like polymer membranes, hollow fiber type is highly preferred due to high packing density and high separation efficiency. The industrialization of CMSM not only depends on its gas separation performance, but also relies on economic benefits. Comprehensive programs have been developed to evaluate CMSMs' benefits, including but not limited to equipment cost, energy consumption, operation, separation efficiency,

feeding gas requirements, and product purity. Due to the complex fabrication process, the manufacturing cost of CMSMs has been estimated to be 10-50 times higher than polyimide membrane. Also, the structural fragility, adverse aging effect, and poor moisture resistance of CMSMs all challenge their applications.

Overall, as compared with polymer membrane, CMSM is considered as the next generation of membrane separation technology due to its excellent gas separation performances, and potential for organic molecule separations. In this dawn stage, we believe that the commercialization of CMSMs would happen in the next few years. This review systematically compares, analyzes, and summarizes both advantages and disadvantages of various types of CMSMs, and tends to understand the correlation between gas separation performances and precursor structures. These discussions would be beneficial to potential researchers and manufacturers to work on CMSMs.

2 CMSMs from various precursors

The chemical structures of precursor and physical structure of the membrane which depends on processing method have significant effects on the gas separation performance of the resulting CMSMs. In this section, CMSMs derived from various precursors are systematically analyzed to show their advantages and shortages.

2.1 PI-based CMSMs

PI is one of the high-performance engineering plastics with excellent physical and chemical properties, and has been widely used in the various area including aerospace, electrical electronics, precision machinery and membrane separation. Although PI-based membrane exhibits appreciable performances for gas separation, the adverse plasticization under high pressure and difficulty to breakthrough trade-off limitation are the major challenges. The highly aromatic structure of PI makes good thermal stability, leading to a high char yield after pyrolysis. Hither to now, PI is the most developed and promising precursor for making CMSMs[15,16]. PI is a serial of polymers synthesized from dianhydride and diamine monomers, and there are abundant types of PI with different chemical structures. It has been observed that the subtle structural change of the side groups in feeding dianhydride or diamine might affect the rigidity and aggregation of the resulting PI[17–19], and further significantly change the gas separation performance in the resulting CMSMs.

Literatures have proven a tentative correlation between gas permeability of CMSM and FFV of the precursor. In Fig. 3, the summarized data show that CO_2 permeability of CMSM normally increases while FFV of the precursor increases (black dotted lines). For example, introducing methyl side group into 1,3-Phenylenediamine (m-PDA) causes a higher FFV and T_g in PI, and the resulting CMSM has an enhanced gas permeability[23]. Also, the 6FDA/BPDA-DAM has a higher FFV than Matrimid, and so is the gas permeability in the resulting CMSMs[7]. Furthermore, contorted groups, such as Tröger's Base unit, have been incorporated into 6FDA-based PI to reach much higher FFV, and the resulting CMSM exhibits a high H_2 permeability (> 14 000 Barrer)[24].

In some cases, the changes of CO_2 permeability in CMSM don't always follow the changes of FFV of the precursor, which indicates that the FFV of precursor is an important factor for the gas permeability of CMSMs, but not the only factor. Hu et al. observed that CMSMs made from ODPA-FDA have higher O_2 permeability and higher selectivity of O_2/N_2 than that made from Matrimide[25]. The improvement is

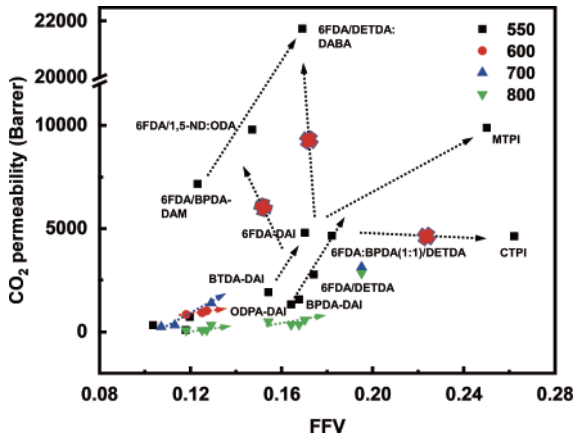

Fig. 3 Relationship of CO_2 permeability and precursor FFV for PI-based CMSMs, the final thermal treatment temperatures are noted by different colored symbols.

ascribed to the enhanced chain rigidity which leads to a narrower FFV distribution, like Matrimid after bromination modification[26]. Besides FFV, other structures of precursors, including chain rigidity, flatness, linearity, functional group type, and so on, also play roles on the pore structure and performances of the resulting CMSM.

The chemical structure of PI is the most important factor for the gas separation performances of the resulting CMSMs. The polymer chain configuration is directly related to chain packing density or FFV. The PPD, ODA, BAPP/BDAF types of diamines represent rod-like, curved, and helical chain configurations, respectively (Fig. 4a)[20]. The CMSM prepared from PPD-PMDA with linear chains has the lowest CO_2 permeability, the CMSM made from BAPP-PMDA with a helical configuration and larger dihedral angle exhibits a much higher gas permeability, and the CMSM made from BDAF-PMDA with extra steric hindrance of -CF_3 groups has the highest permeability. Jin et al. prepared CMSMs from PABZ-6FDA with both flat and contorted structures, and the CMSM has both high H_2 permeability (9 500 Barrer) and high selectivity of H_2/CH_4 (96, Fig. 4b)[21]. Similarly, the gas separation performance of CMSM could be tailored by polymerizing isomers (asymmetric BPDA monomer, aBPDA, and symmetrical BPDA, sBPDA) into PI, the aBPDA has a more winding structure which leads to more packing-inhibitable carbon structures, and the resulting CMSM has a CO_2 permeability 80% higher than pure sBPDA-based CMSM (Fig. 4c)[22].

The functional groups also affect the structural evolutions during pyrolysis, and could improve the gas performance of CMSMs. Koros et al. prepared the CMSMs from PI containing carboxyl functionalized DABA. Randomly cross-linking occurs after decarboxylation during heating treatments, and the formation of network disrupts the orderly packing of graphitic sheets, causes the formation of micro-voids, and finally improves the gas permeance of the resulting CMSM[27–30]. The works also show that the formation of a thermally cross-linked network before carbonization could slow down the adverse aging effect of the resulting CMSMs[31]. Furthermore, if there are sufficient amount of side groups in precursor chains, micro-pores or micro-channels could possibly form during their decomposition. For example, the binaphthol-6FDA type PIs with naphthol groups or acetyl groups were synthesized by an azeotropic imidization and acetic anhydride method, respectively. The CMSMs from PI with the esterification of naphthol exhibit the highest gas permeability, which is ascribed to the pore generation during the destruction of hydrogen between PI chains[32]. Also, the work shows that the incorporation of large amount of —CF_3 groups in Matrimid would create much more ultra-micropores in the resulting CMSMs which leads to a higher permeability[7].

Besides adjusting the chemical structures of pre-

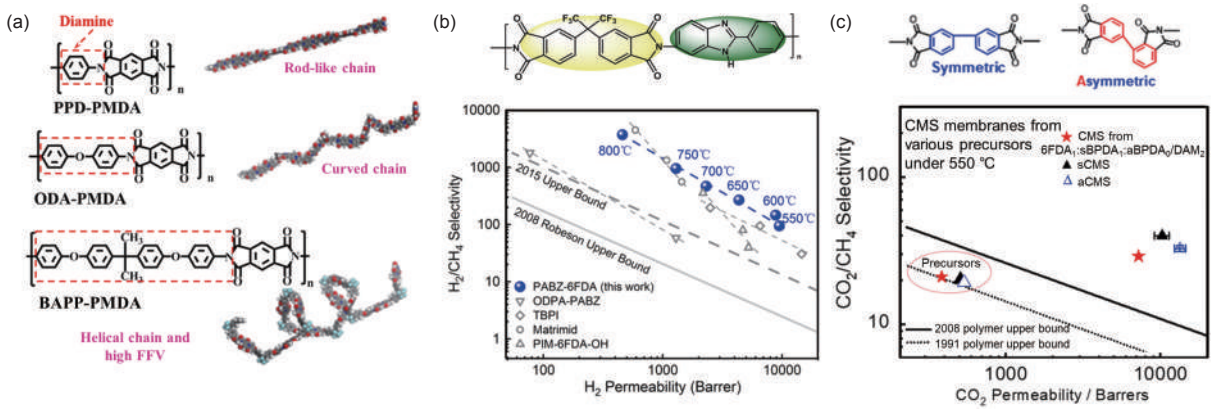

Fig. 4　(a) Chemical structures and optimized local conformations of single PI chain with different configurations[20]; (b) Chemical structure of PABZ-6FDA-PI and gas permeability and selectivity of H_2/CH_4 of the resulting CMSMs[21]; (c) Gas separation properties of aBPDA and sBPDA containing PI-based CMSMs for CO_2/CH_4[22]. (Reprinted with permission).

cursor, compounding PI with other fillers could also improve the gas performances of the resulting CMSMs[11,35,36]. The thermally unstable polymers added into PI membrane, such as polyethylene glycol, cellulose, polyvinylpyrrolidone (PVP) and cellulose acetate, would decompose and create extra pores to improve the gas permeability of resulting CMSMs[39,40]. Whereas, if the polymer additive has a high char yield, the resulting CMSM would have a heterogeneous structure at microlevel. Both PI and additive phases play roles on gas separation. During the preparation of composite membranes, the decomposition of PI and additives might have different pyrolysis behaviors. And our previous study suggests that the gas separation performances of the composite membranes depend on the evolved structures after thermal treatments, and could either improve or decrease the gas separation performances[37,41–43]. Additionally, if solid fillers, such as particles or rods, are mixed into PI matrix, the inherent properties of the fillers are important to the composites. For example, zeolites and MOFs could diffuse small size gas molecules (H_2 and CO_2) and block large size molecules by themselves. The incorporation of zeolites and MOFs could possibly simultaneously increase both gas permeability and selectivity in the composite membranes (Fig. 5)[33,38,44,45]. Also, the gas separation process involves both molecule diffusion and sorption. The incorporation of metal ions, which interact with gas molecules by adsorption, could potentially increase the gas sorption selectivity[30,46,47].

During the conversion from precursor to carbon structures, the temperature, especially the final carbonization temperature, is vital for the resulting carbon structure. Normally, a higher carbonization temperature improves carbon structural integrity and reduces porosity, which commonly leads to a higher gas selectivity but a lower permeability. For example, the CMSM derived from $6FDA_2$:$sBPDA_1$:$aBPDA_0$/DAM_3 exhibited a CO_2 permeability of 10 195 Barrer, and a CO_2/CH_4 selectivity of 40 after pyrolysis at 550 °C. When the carbonization temperature increased to 800 °C, the CO_2/CH_4 selectivity increased to 83, but the CO_2 permeability decreased to 2 649 Barrer[22].

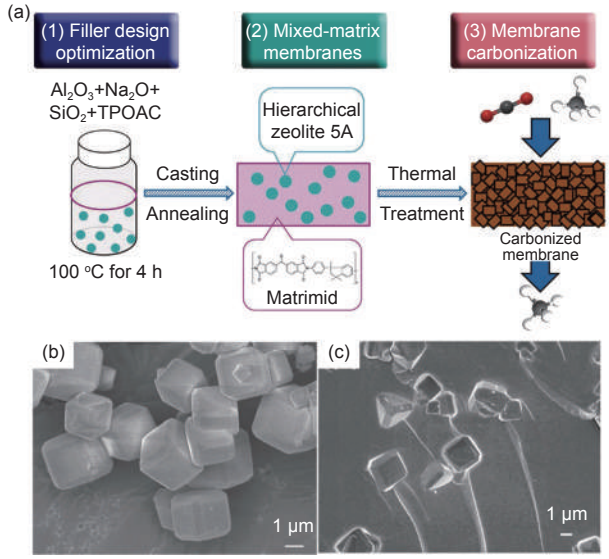

Fig. 5 (a) Synthesis procedure of mixed CMSM; (b) SEM images of zeolite 5A; (c) cross-sectional SEM morphologies of the mixed CMSMs[33]. (Reprinted with permission).

Table 1 summarizes the carbonization temperature, gas permeability and selectivity of PI-based CMSMs. The chemical structure of PI is definitely the most important factor for making high performance CMSMs. Lots of works are still going on to understand PI types and its CMSM performances. The major challenge is that the conversion from polymer to carbon involves complex physical and chemical changes, as well as numerous processing parameters. The extreme complexity for preparing CMSMs make it impossible to attribute the separation performances of CMSMs to single parameter. To better understand the preparation of CMSMs, the structural evolutions during pyrolysis and carbonization need to be clarified in details, even though it is extremely hard. It is highly desired to understand the structural correlation between precursor and the resulting CMSMs.

2.2 Resin-based CMSMs

Although the gas separation performance of carbon membrane is excellent, the estimated cost of carbon membrane was 10-50 times higher than that of the polyimide polymeric membrane. The cost of CMSMs includes the cost of precursor, membrane processing, and heat treatments. The cost of precursor contributes to 5%-10% of the total cost of CMSMs. Compared to the high cost of polyimide, resins are a large family of

Table 1　Gas separation performances of PI-based CMSMs.

Polymer		*T* (°C)	Permeability (Barrer)		Selectivity				Ref.
			H_2	CO_2	H_2/N_2	H_2/CH_4	CO_2/N_2	CO_2/CH_4	
BTDA–m-PDA		600		840			70		[23]
BTDA–2,4-DAT		600		925			54		
BTDA–m-TMPD		600		1017			48		
BTDA-DAI		550		1923			15	21	[34]
ODPA-DAI		550		1321			15	18	
BPDA-DAI		550		1564			14	19	
6FDA-DAI		550		4800			25	28	
Matrimid		550		1049			17	62	[7]
6FDA/BPDA-DAM		550		7170			35	29	
TB-PI		550	14600	16050	19	31	21	34	[24]
ODPA-FDA		650		5379			27.7		[25]
MAT-FDA		650		1592			28.0		
PPD-PMDA		700	366	241	73		45		[20]
ODA-PMDA		700	466	331	67	155	47	110	
BAPP-PMDA		700	1182	1392	21	41	25	48	
BDAF-PMDA		700	1673	3135	12	12	22	23	
PABZ-6FDA		550	9495	5915	56	96	35	60	[21]
		600	8845	3706	89	148	37	62	
		700	2312	525	199	475	45	108	
$6FDA_2$: $sBPDA_1$: $aBPDA_0/DAM_3$		550		10195				40	[22]
$6FDA_2$: $sBPDA_{0.5}$: $aBPDA_{0.5}/DAM_3$		550		13284				33	
6FDA/DETDA		550		2779			31	46	[27]
6FDA : BPDA(1 : 1)/DETDA		550		4663			20	24	
6FDA/DETDA : DABA (3 : 2)		550		21740			25	30	
6FDA/1,5-ND : ODA (1 : 1)		550		9791			29	45	
6FDA-6F : DABA (1 : 1)	-	576	7175	2609		125		46	[30]
	Zn	576	7078	2284		170		55	
Binaphthol-6FDA-naphthol		550		2674			37		[32]
Binaphthol-6FDA- acetyl		550		3332			32		
P84	-	800	1227 (GPU)		396				[35]
	7% NCC	800	1406 (GPU)		430				
	7% MCC	800	1341 (GPU)		418				
	9% PVP	800	1274 (GPU)		402				
6FDA-DAM : DABA (3 : 2)	-	600	3420	1659	53	54	25.5	26.3	[36]
	10% CA	600	5310	2388	42	42	25.3	25.7	
6FDA-DAM : DABA (3 : 2)	20% LPSQ	550		3789				50	[37]
	-	550		2465				56	
P84	10 % ZIF-108	600	125	25		219		130	[38]
	-	600	26	5		125		79	

low-cost polymers with a wide variety of structures, for example, PR and polyfurfuryl alchohol (PFA). These thermosetting resins have a relatively high carbon yield and could be used for fabricating CMSMs.

PR has been used for making many types of carbon materials, such as activated carbon, nano carbon fiber, and thermal resistance carbon. For PR carbonized at a temperature higher than 450 °C (normally 600-800 °C), micropores with relatively high sorption capacity and good molecular sieving ability could be formed. Due to the brittleness of PR-based carbon, PR-based CMSMs are commonly supported by commercial porous ceramic matrix through spin coating, dip coating or slip coating[48,49]. Studies have proven that 700 °C is the critical carbonization temperature for PR-based CMSMs. For the CMSMs prepared at a temperature lower or higher than 700 °C, the corresponding gas transport mechanism is either adsorption

selective or molecular sieving, respectively. The different mechanisms depend on the size of micropores. When diffusive pore size (ϕ_D) is in the range of 0.6 to 2 nm, gas molecules prefer to adsorb in the pores and create a surface flow. In this case, the adsorbed gas molecules exhibit high permeability. On the other hand, when micropore diameter is less than 0.6 nm, gas molecules would be sieved according on their dynamic diameters, and the CMSMs act as gas barriers. The pore size of PR-based CMSMs would decrease at a higher carbonization temperature. Centeno et al. prepared CMSM from Novolak-PR at temperatures from 700 to 1 000 °C, and the selectivity of hydrocarbon (such as C_2H_4, C_3H_6, and n-C_4H_{10})/N_2 increased from single digits to 90.0[50]. Additionally, the pore size and fraction could be increased by increasing oxidation degree of PR. At same carbonization temperature of 700 °C, the gas separation mechanism of the CMSMs could change from molecular sieving to adsorption-selective when oxidation is prolonged and carried out at a higher temperature[51,52].

For the gas separation performances of PR-based CMSMs, literatures suggest they have relative high selectivity of CO_2/CH_4 (>80) and O_2/N_2 (>10), and could possibly be used for purification of H_2, CO_2 and hydrocarbon gases[53–55]. The major challenges for PR-based CMSMs are how to significantly improve the gas permeability and how to prepare CMSMs with less defects[49,56]. The chemical structures of PR are important factors for the performances of the resulting CMSMs. When PR is sulfonated, the resulting CMSM shows higher gas permeabilities for H_2, CO_2 and O_2 than pristine PR, since the sulfonic acid acts as leaving groups and creates more pores[56,57]. Also, incorporation of fillers is another way to improve the gas permeability. Alumina nanowires have been added into PR-based CMSMs through the solution mixing of PR and alumina precursor, and the resulting CMSM has a more than 40% higher H_2 permeability with a high selectivity of H_2/N_2 (>100)[58–60]. Zeolite and Ag nanoparticles have also been used to prepare the composite CMSMs with much improved gas separation performances[61–63]. For the preparation of ceramic support PR-based CMSMs, the solution rheology and solidification methods have been proven to be critical for making a defect-free membrane. Most defects are created during membrane processing, and a better uniformity could be obtained by tuning solution rheology[64], optimizing solidification conditions (such as solidification form and coating times[64]), and modifying interface or interphase (introducing intermediate layer such as α-Al_2O_3[65], chemically modifying surface[66]).

Besides PR, PFA is another type of low-cost thermosetting resin, and has been used for making CMSMs. The works show that PFA develops into amorphous carbon with slightly ordered structure at a relatively lower temperature, and then grow into aromatic microdomains with more ordered structure at a higher carbonization temperature (Fig. 6a)[67]. Similar to PR, most PFA-based CMSMs need supportive matrix, and coating methods, such as dip-coating[68], brush coating[69], spray coating[70], ultrasonic deposition[71–73],

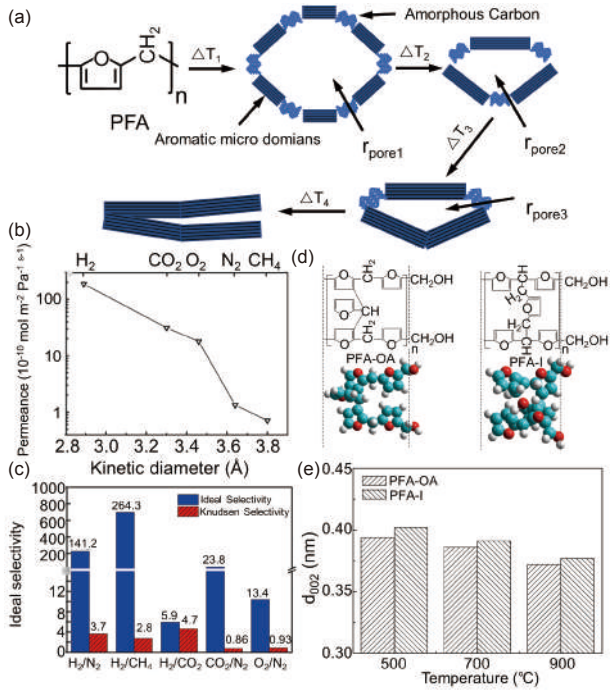

Fig. 6 (a) Conceptual model for adsorptive structure evolution in PFA-derived CMS[67]; (b) Gas permeance of the CMS/CNT membrane carbonized at 500 °C; (c) Ideal selectivities (blue bars) of the CMS/CNT membrane carbonized at 500 °C[75]; (d) Chemical structure of PFA and solidification cross-linking stage catalyzed by oxalic acid and iodine; (e) Effects of PFA chemical structure and pyrolysis temperature on their interlayer spacing d_{002}[76]. (Reprinted with permission).

ultrasonic deposition[71–73] and vapor deposition polymerization (VDP)[74], used for membrane forming. The works show that PFA-based CMSMs have very high gas selectivity that exceeds most other types of CMSMs[80,81]. Fox example, the PFA-based CMSM prepared by VDP method exhibits a H_2 permeability of 200×10^{-10} mol m^{-2} s^{-1} Pa^{-1} and a very high selectivity of H_2/CH_4 (~ 400)[74]. Interestingly, both H_2 permeability and selectivity of H_2/X (X=CO_2, CH_4 or N_2) of PFA-based CMSMs was found to increase at a higher pyrolysis temperature[83]. Furthermore, the synthesis of PFA could be catalyzed by oxalic acid or iodine, and the resulting CMSMs have different microstructure, the CMSMs from oxalic acid-PFA exhibited the lower gas permeability and higher selectivity due to the smaller d_{002} value (Fig. 6d, e)[76].

The low gas permeability of PFA-based CMSM is the major issue for its commercial applications, and a practical solution is to reduce membrane thickness. PFA-based thin CMSMs are normally supported by ceramic matrix, and the thinning of the membrane would easily introduce defects. In order to achieve thinner and defect-free PFA-based carbon layer, Wang et al. added an intermediate layer between PFA and support to improve their adhesion, and the thickness of the resulting carbon layer could be decreased to less than 4 μm. However, the enhanced H_2 permeability always accompanied with substantially declined selectivity, which indicated the presence of large defects[77,84]. Hou et al. prepared the ultrathin PFA-based CMSMs by introducing CNT nano-scaffolds to facilitate the spreading of PFA solution on support, and a uniform and continuous carbon layer with a thickness as low as 100 nm could be obtained[75]. The resulting ultrathin CMSM exhibited a reasonable H_2 permeability (455×10^{-10} mol m^{-2} s^{-1} Pa^{-1}) and a high selectivity (H_2/N_2 ~ 225, H_2/CH_4 ~ 700, Fig. 6b, c). Furthermore, lots of works improve the gas separation performances of PFA-based CMSMs by adding nano-fillers in PFA precursor[78,82,85]. For example, the addition of silica nanoparticles could reduce the solution penetration into support pores and form a uniform PFA layer. The addition of zeolite (porous, good thermal stability) could improve gas separation performance by introducing regular and orderly transport channels[78,82]. The addition of metal CMSMs could effectively change the micropore size and distribution to achieve better separation performances[85,90,91]. Palladium clusters are mixed into CMSMs by immersion with PFA precursor, and a rapid diffusive pathway of H_2 could be formed to obtain much higher permeability[82]. Table 2 summarizes the gas permeation data of PR- and PFA-based CMSMs. Although resin-based CMSMs exhibit reasonable gas separation performances, the major disadvantage is that they are normally not self-supportive. The applications of resin-based CMSMs depend on both the developments of supportive matrix and cost.

2.3 Cellulose-based CMSMs

Cellulose is a low-cost natural material that is abundant in plants and animals, and has been used for making various carbon materials, such as activated carbon and carbon fiber. Lie et al. prepared CMSMs from cellulose which showed a H_2 permeability of 940 Barrer and good selectivity of H_2/X (H_2/N_2=223.8, H_2/CH_4=204.3)[86]. The ultrahigh selectivity of cellulose based CMSMs is ascribed to their narrow size distribution of transport channel and pores. While a combination of ultra-high selectivity and good humidity stability of cellulose-based CMSMs is promising. The difficult processibility of cellulose and relatively low permeability of the resulting CMSMs are the major barriers for the applications of cellulose based CMSMs. Cellulose chains consist anhydro-glucose linked by (1,4)-*β*-*d*-glucosidic bonds. The abundant inter- and intra- hydrogen bonding of cellulose chains make them extremely difficult to be dissolved and further processed. Rogers and Zhang discovered Ionic liquids (ILs) and Urea/NaOH for the easy dissolution of cellulose[92,93]. After that, cellulose could be easily processed into membrane or fiber forms using these solvents. Hollow fiber type of cellulose-based carbon membrane (CHFMs) is promising to overcome both processibility and permeability issues. Cellulose hollow fibers have been spun from cellulose/(1-ethyl-3-methyl im-

Table 2 Gas separation performances of PR- and PFA-based CMSMs.

Polymer		Temperature (℃)	Permeability (10^{-10} mol m^{-2} s^{-1} Pa^{-1})			Selectivity					Ref.
			H_2	CO_2	O_2	O_2/N_2	H_2/N_2	H_2/CH_4	CO_2/N_2	CO_2/CH_4	
PR		700		46 (GPU)	13	10			37	85	[54]
Sulfonated PR		500	1950 (GPU)	800	240	5	42	65	17	27	[57]
45% sulfonated-PR/PR		500	1020 (GPU)	330				68		22	[56]
PR		780	270				9	10			[49]
PR		800		183					0.7		[48]
PR		500	1400	534	85	7	117		45		[58]
	11% boehmite	550	1450		30	15	725				[58]
		600	189								
	4%	550		1148 (Barrer)	153	5			35		
	6.7%	550		1499 (Barrer)	256	4			26		[59]
	9.6%	550		2017 (Barrer)	284	3			24		
PR		500	548 (Barrer)	483			222		196		[59]
		550	503 (Barrer)	223			590		261		
PR	4% boehmite	550		650 (Barrer)	90	5			35		[60]
	0.2% Ag	550		509 (Barrer)	156	7			22		[61]
PR	0% NaA-zeolite	600	58	170	48	4	5		28		[62]
	1%	600	25	39	9	6	18		28		
	2%	600	4	13	1	15	44		159		
	5%	600	9	20	4	8	18		40		
PR	0% NaA-zeolite	600		92						33	[63]
	1%	600		3390						28	
	2%	600		5680						8	
PFA	/Al_2O_3	600	1040	590	650	1	2		1		[77]
	/2H- Al_2O_3	600	490	240	140	3	10		5		
	/2B- Al_2O_3	600	350	100	75	13	58		16		
PFA	-	600	99	50			41	69	20	34	[78]
	zeolite	600	1002	572			36	63	20	36	
PFA	-	600	6		23	32					[79]
	silica	600	166		10	6	92				
PFA-OH		600	100				200				[76]
PFA-I		600	200				100				
PFA		600	68	6			272		25		[80]
		700	55	5			347		31		
		800	17	2			412		53		
		900	9	1			465		59		
PFA		600	100				125				[81]
PFA	0% zeolite-T	600	778	621			17	36	14	29	[82]
	1%	600	256	253			24	52	24	52	
	2%	600	88	83			55	103	52	97	
	3%	600	97	93			54	94	52	89	
PFA	0% Pd	700	410	100			45	100	11	24	
	0.05%	700	1440	120			225	240	19	20	
	0.1%	700	1900	130			275	317	19	22	
	0.2%	700	1800	120			286	353	19	24	
	0.4%	700	1770	110			295	377	18	23	
PFA/CNT/AAO		500	200				141	264			[75]
		600	456		21	11	225	700			

idazolium acetate/DMSO) solution[87,94,95]. The resulting CHFMs exhibit good gas separation performances (H_2 permeability 148.2 GPU, H_2/CO_2 selectivity >83.9 and H_2/CH_4 selectivity >5 700) in Fig. 7b[94]. For mixed gas test of H_2 and CO_2, the CHFMs could maintain same separation performances as pure gas

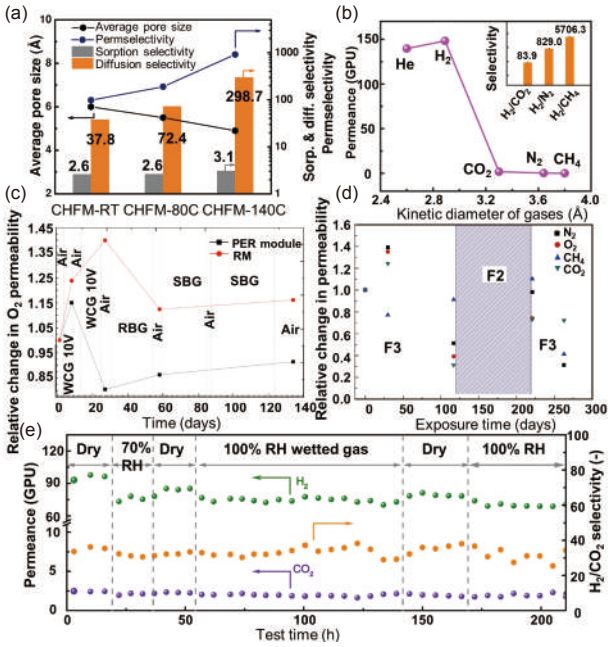

Fig. 7　(a) CO_2/CH_4 separation teasted with a 10 mol% CO_2-90 mol% CH_4 mixed gas under different feed pressures at 60 °C[88]; (b) Single-gas separation performacne of CHFM-850 as a function of gas kinetic diameter at 130 °C and 2 MPa[94]; (c) Aging of carbon membranes under different environments and effect of electrical regeneration on N_2 permeability[97]; (d) Relative change in permeability of N_2, CO_2, O_2 and CH_4 when CHFM are exposed to high H_2S concentration[95]; (e) Mixed gas dynamic durability testing (50 mol% H_2/50 mol% CO_2) of CHFM-700 under dry and humidified conditions at 1 MPa and 90 °C[94]. (Reprinted with permission).

test (Fig. 7a)[87,94,96]. The spinning conditions, modification and drying temperature would affect the micropore development in cellulose hollow fibers and cause different gas separation performances of the resulting CHFMs[88,89,95]. The low cost and good performances of CHFM make it a good candidate for commercial applications.

In order to significantly improve the gas separation performance of cellulose-based CMSMs, researchers also incorporated fillers or dopes, such as metal oxides and nitrates, into cellulose. These additives not only affect the gas performances by themselves, but also affect the structural change during the pyrolysis. The works show that the addition of Fe-nitrate in CMSMs improves O_2/N_2 and CO_2/CH_4 separation, and the addition of metal oxides leads to enhanced H_2/CO_2 separation[86].

For CMSMs, the aging phenomenon must be considered for real applications. Both the physical aging driven by thermodynamic instability and chemical aging caused by chemical adsorption would lead to declined gas permeability during long time usage. Haider et al. prevent the reacting between active sites and O_2 by online electrical regeneration, and the performance declination caused by aging is obviously slowed down[97]. Fig. 7c shows that O_2 permeability decreases for 20% after 135 days. For comparison, a fast and huge loss of permeability occurs after 30 days regardless storage in vacuum or air (Fig. 7d)[107]. Besides aging, the presence of water vapor (humidity) in feeding gas could commonly block the diffusive pores and lead to declined H_2 permeability and H_2/CO_2 selectivity. The reported data demonstrated that cellulose-based CMSMs were hydrophilic which leads to a long-time stable gas separation performance even at a high relative humidity (>75%) in Fig. 7e[88,89,94]. The reported gas permeation data of cellulose-based CMSMs are summarized in Table 3.

2.4　PEI-based CMSMs

PEI has a polyimide-like structure with stiff and thermally stable imide units combined with flexible ether segments[108–111]. As compared with PI, the price of PEI is much lower and the processibility is much better. The PEI-based CMSMs are commonly supported on ceramic matrix. The flexible ether segments strongly affect the structures and performances of the resulting CMSMs. The results show that both H_2 permeability (~ 50%) and H_2/N_2 selectivity (~ 10) are lower than control PI-based CMSM (H_2/N_2=230)[98]. Literatures suggest that the surface roughness, porosity and pore size of supports, and the interactions between PEI chains and supports are important for the gas separation performance of resulting CMSMs[99]. Fig. 8 summarizes the H_2/CH_4 and CO_2/CH_4 separation performances of PEI-based supported CMSMs. It is clear that different preparation and modification methods do affect the final gas separation performances. For example, a high H_2 permeability could be obtained by increasing the roughness of support surface, since the surface further affects the macro- and micro- structures of carbon sieving layer[99]. Tseng et al. introduced a TiO_2 intermediate layer between ceramic support and CMS layer to enhance their adhe-

Table 3 Gas separation performances of cellulose-based CMSMs.

Polymer		T (℃)	Permeability (Barrer)			Selectivity					Ref.
			H_2	CO_2	O_2	H_2/N_2	H_2/CO_2	H_2/CH_4	CO_2/N_2	CO_2/CH_4	
Cellulose	-	550	940	190	54	223		204	45	41	[86]
	5% Fe_2O_3	550	280	110	30	34		70	13	28	
	1.8% $Fe(NO_3)_2$	550	1000	310	86	122		476	38	148	
	3.8% $AgNO_3$	550	1500	180	53	294		1071	35	129	
	4% $Cu(NO_3)_2$	550	1100	81	25	478		1667	35	123	
Cellulose (CHFMs) at 130 ℃		550	1400				11				[87]
		700	773				50				
		850	445			829	84	5706			
Cellulose (CHFMs)	Drying at RT			900						100	[88]
	80 ℃			400						188	
	140 ℃			100						917	
Cellulose		550	206	13		1288	16		84		[89]
		600	121	4		1344	29		46		
Cellulose		500	19	8	1	316			137		[89]
		550	33	13	1	457		3259	186	1303	
		600	25	3	1						

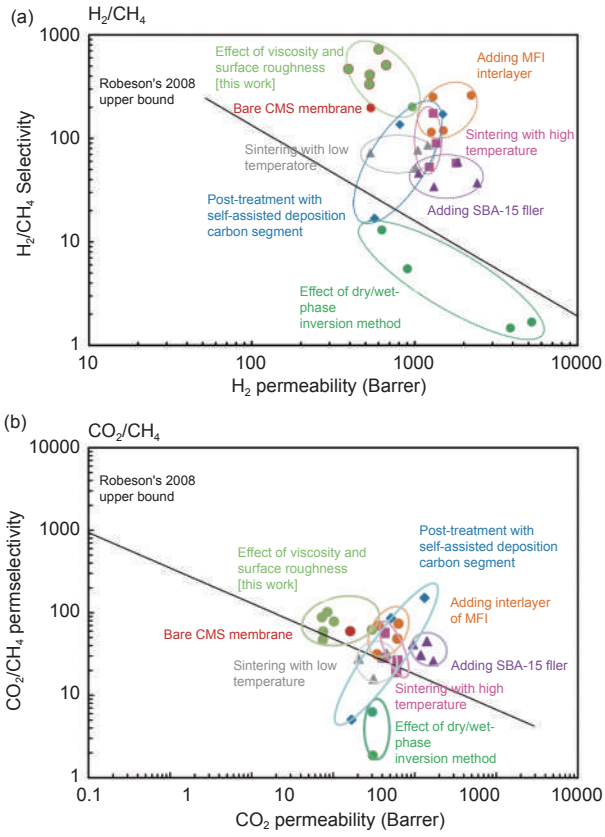

Fig. 8 Performance of PEI-derived CMS membranes with different preparation/modification methods for (a) H_2/CH_4, and (b) CO_2/CH_4 separation[99-101,105,112-115]. (Reprinted with permission).

sion. The defects in CMS layer were significantly reduced, and the resulting CMSM exhibited good separation performances for H_2/CO_2 and H_2/CH_4[100]. Wey et al. modified alumina support by TiO_2 and prepared PEI layer from its low viscosity solution, and the selectivity of the resulting CMSMs improves for 111% and 88% for H_2/CH_4 and CO_2/CH_4 separation, respectively[101]. Setnickova et al. achieved well balanced gas permeability and selectivity for CO_2/CH_4 separation by finely tuning the structures of intermediate TiO_2 layer[102]. It is clear that an appropriate intermediate layer is important for obtaining good gas separation performance of PEI-based CMSMs. The above discussions and the summarized data in Fig. 8 suggest that the intermediate layer is the most important factor for supported PEI-based CMSMs. Besides, support surface roughness, solution rheology, blends, filler, sintering condition, and phase separation method also play certain roles on the performances of PEI-based CMSMs. For example, mixing PEI with polymers, including PI[42], PVP[104,120,121] and Poly (p-phenylene oxide)[122] could achieve balanced cost and performances. The addition of inorganic materials, such as CNT, zeolite, in PEI matrix could concurrently increase the gas permeability and selectivity of the resulting CMSMs. The addition of multi-walled carbon nanotubes in PEI leads to ~29 times higher CO_2 permeability (~1 500 Barrer) and ~2 times higher CO_2/N_2 selectivity (~50)[103]. The addition of zeolite in PEI matrix increases the H_2/N_2 selectivity of the resulting CMSM from 24.2 to 85.8[106]. The gas separ-

ation data of PEI-based CMSMs are summarized at Table 4. It could be found that the PEI-based CMSMs have a high selectivity, although H_2 permeability is normally not higher than 1 000 Barrer. Considering the easy processibility and relatively low cost of PEI, it is possible that PEI-based CMSMs could be commercialized in future.

2.5 PIM-based CMSMs

The FFV in polymer is essential for its gas permeability. The intrinsically micropores (<2 nm) in PIMs lead to very high surface area (BET up to 1 000 $m^2\ g^{-1}$) which would dramatically improve gas diffusion. However, the PIM membrane normally has a low selectivity. To overcome the weakness of PIM, some researches tried to convert PIM into CMSMs to enhance molecular sieving. Swaidan et al. prepared CMSMs from PIM-6FDA-OH, and there are ~20 times increase in both H_2 and CO_2 permeability over PI membrane. Also, the developed ultra-micropores in CMSM exhibits excellent sieving ability. The H_2/CH_4 and CO_2/CH_4 selectivity increases from 28 to 40 and 38, respectively[123]. The CMSM is good for the separation of CO_2/CH_4 mixed gases[124]. For the chemical structures of PIMs, Hazazi et al. synthesized PIM-PI from spiro-bifluorene dianhydride and 3,3-dimethylnaphthidine, and the resulting CMSM shows unique high CO_2/CH_4 selectivity of 1 475 in Fig. 9e-f, respectively[119]. Li et al. synthesized PIM-PI from two triptycene-based diamine isomer monomers, and found that MTPI-based CMSMs exhibited two-fold higher in H_2 and CO_2 permeability than CPTI-based CMSM, even though MTPI is compacter and has less FFV than CPTI (Fig. 9a)[116]. The abnormal observation is ascribed to the dipole of MTA which further affects its pyrolysis. Spirobisindane-ladder prototype PIM-1 and embedding boron have also been used to enhance gas separation properties[125–127]. Other than chemical structures, Cosey et al. introduced the highly soluble metal-organic polyhedral-18 (MOP-18) into PIM-1. The resulting CMSM has an improved CO_2 permeability from 3 297 to 4 167 Barrer, and the gas separation performance is more stable than PIM-1-

Table 4　Gas separation performances of PEI-based CMSMs.

Polymer		T (℃)	Permeability (Barrer)			Selectivity					Ref.
			H_2	CO_2	O_2	O_2/N_2	H_2/N_2	H_2/CH_4	CO_2/N_2	CO_2/CH_4	
PEI/Al_2O_3		600	280				10				[98]
		600	1100	205				138		26	[99]
		600	601	73	17	9	315	726	38	88	[100]
		600	669	102				510		78	
		600	601	73				726		88	[101]
PEI/TiO_2/Al_2O_3		600	479	63				333		47	
		600		1-7 (GPU)						47-97	
		600		1-45 (GPU)						19-56	[102]
		600		17-57 (GPU)						36-65	
	-	500		53	11	4			18		
PEI	PVP	500		64	21	5			14		[103]
	CNT	500		1463	724	24			49		
		550		2.6					12	22	
PEI	PVP	650		1.7					42	55	[104]
		800		0.7					35	69	
		650		2.2 (GPU)					10	12	
		650		1.7 (GPU)					21	24	
PEI		650		1.7 (GPU)					42	55	[14]
		650		1.0 (GPU)					26	52	
		650		1.9 (GPU)					12	15	
PEI	-	600	255	200			18	25	14	19	[105]
	PPO	600	812	513			136	136	86	86	
PEI	-	650	285	200	70	6	24		17		[106]
	zeolite	650	264	31	13	4	86		10		

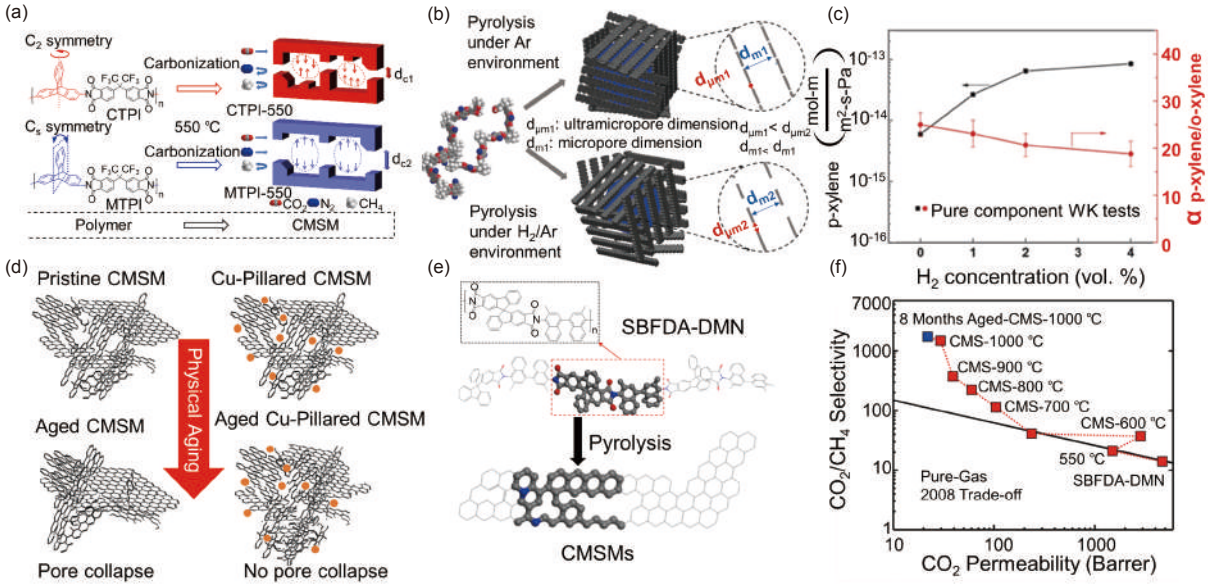

Fig. 9 (a) Chemical structure of CTPI and MTPI and pore structure scheme of CMSMs derived from two precursors[116]; (b) Change of ultramicorpores by introdudtion of H_2 during pyrolysis, (c) Permeability of p-xylene and permselectivity of p-xylene/o-xylene as H_2 concentration[117]; (d) Aging mechanism scheme of PIM-1 based CMSMs and mixed CMSMs doping MOP-18 after 550 ℃ carbonization[118]; (e) Scheme of structural evolution about SBFDA-DMN; (f) CO_2/CH_4 Separation performance of the SBFDA-DMN polyimide and its heat-treated CMSMs[119]. (Reprinted with permission).

based CMSMs after 21-day aging[118] (Fig. 9d). Above results suggest that a material with a stable porosity structure could effectively weaken the adverse aging effect of CMSMs. Furthermore, other modification methods, such as vapor phase infiltration and water vapor selectively oxidation, have been adopted to improve molecular sieving ability[128].

The PIM-based CMSMs normally have relatively larger pores than PR- and cellulose-based CMSMs, which make them possible to separate molecules with larger sizes, such as olefins and alkanes. Recently, more and more attentions have been paid on the separation of ethylene/ethane or propylene/propane. It is found that PIM-6FAD-OH-based CMSM has a C_2H_4 permeability of 70 Barrer and a C_2H_4/C_2H_6 selectivity of 10-20[129]. The same membrane could also be used for the separation of C_3H_6/C_3H_8 (45 Barrer C_3H_6 flux, 33 selectivity)[130]. Ma et al. prepared PIM-1-based CMSMs for the separation of xylene isomers of benzene derivatives[131], which is one of the most important and challenging organic mixture separations practiced in industry. The diffusion selectivity could be decoupled into enthalpic and entropic contributions. Ma's research suggested that *p*-xylene had a higher permeability than *o*-xylene, and the entropic factors dominated the xylene selection. Ma et al. also strengthened the formation of mid-range (0.5-0.9 nm) microstructures by an introduction of low concentration of H_2 into pyrolysis to promote the transport of p-xylene (Fig. 9b, c)[117]. Table 5 illustrates the gas separation properties of PIM-based CMSMs.

2.6 Other precursors

PVDC could be used for making CMSMs. In 1990s, Air Products and Chemical, Inc. prepared alumina supported PVDC-based carbon membrane with 0.6-0.7 nm nano-pores, and the selectivity was ascribed to selective surface flow (SSF)[132]. Compared with other CMSMs, PVDC-based SSF carbon membrane exhibited high gas permeability (10^{-6}-10^{-7} mol m^{-2} s^{-1} Pa^{-1}). The SSF carbon membranes were successfully applied to gas separation of H_2S/H_2, CO_2/H_2, and H_2S/CH_4[132–136]. The corresponding preparation conditions have been systematically explored to obtain optimal performances. The studies also show that PVDC-based CMS fibers with most 0.3-0.7 nm pores could be used for propylene/propane separation, and their excellent performances exceed commercial adsorbents including MSC-4K and zeolite 4A[137,138]. Centeno et al. reported the copoly-

Table 5　Gas separation performances of PIM-based CMSMs.

Polymer		T (℃)	Permeability (Barrer)		Selectivity				Ref.
			H_2	CO_2	H_2/N_2	H_2/CH_4	CO_2/N_2	CO_2/CH_4	
PIM-6FDA-OH		530	2860	4110		14		20	[123]
		600	5248	5040		30		38	
		800	2177	556		363		93	
PIM-6FDA-OH		800	512					88	[124]
		800	471					59	
SBFDA-DMN		550		1500				21	[119]
		600		2853				37	
		700		236				41	
CTPI		550	6444	4633	54	54	39	39	[116]
MTPI		550	10601	9878	36	48	34	45	
PIM-1/Poly(dimethysiloxane)		500	800	1000		<30		30	[128]
		550	1000	1050		20		35	
		600	600	800		25		30	
PIM-1		550		3297				52	[118]
Aged 6 days				1902				70	
PIM-1	40%MOP-18	550		4167				19	
Aged 6days				4187				21	
			C_2H_4	C_3H_6	C_2H_4/C_2H_6	C_3H_6/C_3H_8			
PIM-6FDA-OH		600	70		7				[129]
		800			17				
PIM-6FDA-OH		600		45		33			[130]
PIM-6FDA		500	328		2				[125]
		600	77		4				
		800	3		25				
PIM-1	Boron	700	14		10				[126]
PIM-1		600	44		6				[127]
		800	1		13				
PIM-1			p-xylene (10^{-10} mol m^{-2} s^{-1} Pa^{-1})			p-/o-xylene			
		550	3			27.5			[131]
PIM-1	0%H_2	550	1.4			1.4			[117]
	4%H_2	550	52.3			8.9			

merized PVDC with vinyl chloride. The resulting CMSMs exhibited high selectivity of CO_2/CH_4 (65), CO_2/N_2 (24), and O_2/N_2 (14)[139]. PVDC could be melt processed into self-standing CMSM, which has a 46% larger microporosity, 54% higher modulus, and 6-20 times higher H_2 and CO_2 permeability than Matrimid-based CMSMs[137]. The low cost, easy processibility, and good gas separation performances are the major advantages of PVDC-based CMSMs.

PBI membrane has been used for separating H_2/CO_2, and the cross-linked PBI exhibits better separation selectivity[140,141]. However, their H_2 permeability is low[142,143]. PBI-based CMSM has a "hourglass" pore structure composed of rapidly diffusive microcavities and ultra-micropores. The carbonization temperature of PBI is important for its gas separation performances. The H_2 permeability increases and the selectivity of H_2/CO_2 remains almost same when the temperature increases from 500 to 700 °C[144]. At a temperature above 700 °C, the H_2 permeability decreases, while the selectivity increases. PBI could also be added into other polymer precursor to adjust the pore structures in the resulting CMSMs[145–147].

PAN is the most dominant precursors for making carbon fiber, and could also be used for making CHFMs or porous fiber-type support[148,149]. PAN-based CHFM shows a high O_2 permeance (180 GPU), but a low selectivity of O_2/N_2 (1.9)[152]. The asymmetric PAN-based hollow fiber membrane could withstand high pressure, which is a great advantage for in-

dustrial applications. Recently, PAN-based CMSMs exhibited an ethylene/ethane separation performance (7.62 selectivity)[153].

Ether ketone is also a promising precursor for making CMSMs due to their low cost, good solubility, high char yield, good thermal resistance, good strength and high glass transition temperature. Wang et al. prepared poly(phthalazinone ether sulfone ketone) (PPESK) based CMSM which had comparable gas separation performance as Matrimid-based CMSMs[154]. The sulfone/ketone ratio, stabilization condition, and carbonization temperature affect the structure, morphology and performance of the resulting CMSMs[154–156]. In addition, cardo poly(arylene ether ketone) based CMSMs also show a high H_2 permeability of 5 260 Barrer and high selectivity (H_2/CH_4=311, H_2/N_2=142)[157].

2.7 Aging

The fresh CMSM commonly experiences aging phenomena during application. Normally, aging of CMSMs leads to a great decline of gas permeability but improve selectivity. The decrease of gas permeability could be ascribed to either chemical adsorption or physical aging. During chemical adsorption, gas molecules could be adsorbed in the micro-pores of CMSMs and restrict the diffusion of other gas molecules. Water is a widespread component in most gas mixtures. When CMSM is exposed at high humidity, water vapor could easily permeate into the gas sieving channels and block the transportation of other gas molecules. Literatures suggest that cellulose-based CMSM has a good anti-humidity due to their hydrophilic feature, which allows water vapor permeate membrane easily[89]. Additionally, a hydrophobic layers and oxygen doping could weaken the pore-blockage effect of water vapor[122,158]. If CMSMs could work at relatively high temperature, the detrimental adsorption effects of humidity or chemicals would be strongly weakened due to the reversible chemical adsorption[159].

The physical aging is normally referred to pore collapse in CMSMs. When gas molecules diffuse through pores, the interactions between gas molecules and surrounding carbon surface could cause the pore shrinkage or collapse. Also, if the surrounding carbon structures are not very stable, the pores could collapse by themselves simply during storage. Therefore, how to prevent or weaken the aging phenomenon of CMSM is vital to its application. So far, some results suggest that the physical aging could be weakened by introducing crosslinking[31] and molecule doping[46,160]. Also, the gas permeability of fresh CMSM was also found to be well maintained while the inert gas continuously flowed through the membrane[107]. Whereas, a hyper-aging treatment could strongly accelerate the aging process[161]. Normally, a higher temperature would lead to a faster aging to reach a stable structure[162]. In summary, there are lots of unknown knowledge for the aging phenomenon and corresponding reasons.

3 Simulation

Making CMSMs involves multiple fabrication procedures and complex structural evolutions, which make it extremely time consuming to obtain valid experimental data and establish the correlation between precursor and the performances of the resulting CMSMs. Simulation might be a great benefit for the development of novel CMSMs in the following ways: (1) better understanding the sieving mechanism, (2) better understanding the complex structural evolution from precursor to carbon. Hither to now, most simulation works focus on understanding the correlation between pores and molecule sieving. Fig. 10d shows typical atomic models for pores, and the corresponding molecule transportation behaviors could be obtained[151]. Based on simulation the permeability of various molecules could be calculated. In this work, it is concluded that defect-free model has the most stable selectivity of CO_2/CH_4 (Fig. 10e), and the pores with a diameter of 0.67 nm are most effective for separating CO_2 and CH_4 (Fig. 10f). To better understanding the structural evolution during pyrolysis, reactive molecular dynamics simulation is a powerful tool. Fig. 10a shows that PEI chains degrade and evolve into various structures. The simulation results suggest that the PEI-based CMSM consist of an amorphous

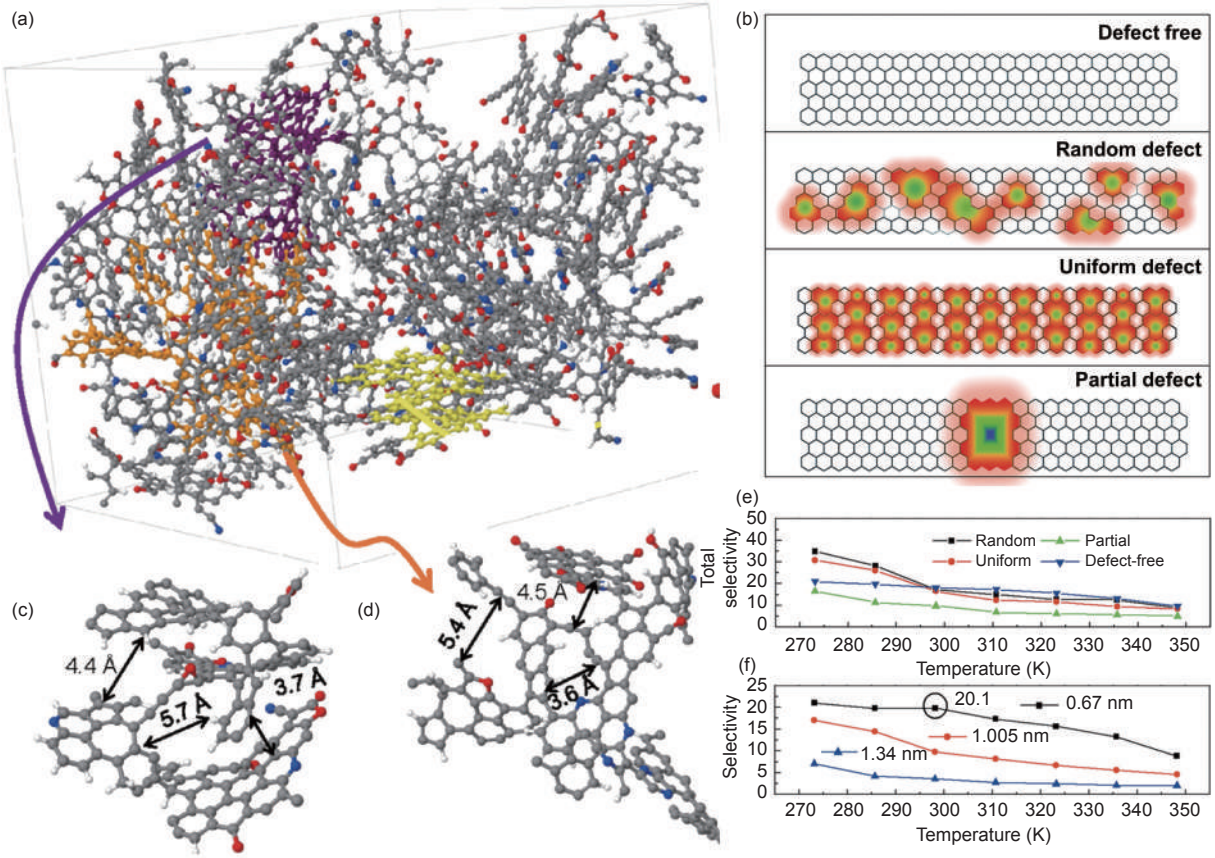

Fig. 10　(a) Model of carbonaceous structure formed form the PEI pyrolysis; (b-c) Crystalline graphite-like local structures[150]; (d-f) Pore models and total selectivity with temperature for different pore sizes and each defect type at 100 kPa, respectively[151].(Reprinted with permission).

carbon matrix with stacked graphitic domains, and the pores have a diameter in the range of 0.2-1.5 nm (Fig. 10b, c)[150]. Now, the simulation is only a beneficial supplement for the research of CMSMs. With the development of simulation theory and tools, it would become a powerful tool for designing CMSMs with desired performances.

4　Summary and perspective

Many polymer precursors could be used for making CMSMs. It is well known that the chemical structures of precursors are critical for the gas separation performances of the resulting CMSMs. Since most papers report the gas permeability of CO_2, N_2 and CH_4, the gas separation performances of CO_2/N_2 and CO_2/CH_4 are plotted in Fig. 11 to better understand the correlation between precursor types and the gas separation performances of the resulting CMSM. It is clear that CMSMs made from different precursors do have distinctly different gas separation performances. For the permeability of CO_2 in CMSM, PIM ≈ 6FDA-PI > PI ≈ PF > PEI > cellulose ≈ PFA. For CO_2/CH_4 selectivity, cellulose > PEI ≈ PI ≈ PFA > PIM, whereas for CO_2/N_2 selectivity, cellulose ≈ PI > PF ≈ PFA ≈ PEI. The selectivity mainly depends on the pore size and distribution. The different chemical structures of precursor determine pyrolysis routes and mechanisms, which are the essential factors for the structural feactures of resulting carbon materials.

Similar to other carbon materials, the structural correlation between polymer precursor and the resultant CMSM is essential for the development of high performance CMSMs. However, due to intensive chemical and physical structural evolutions during thermal treatment, there is still no well developed theory. With the development of computer simulation, machine learning, and genome method, the major factors are possible to be quantitively identified in the future, and the criterions for judging the quality of precursor membrane could be possibly established.

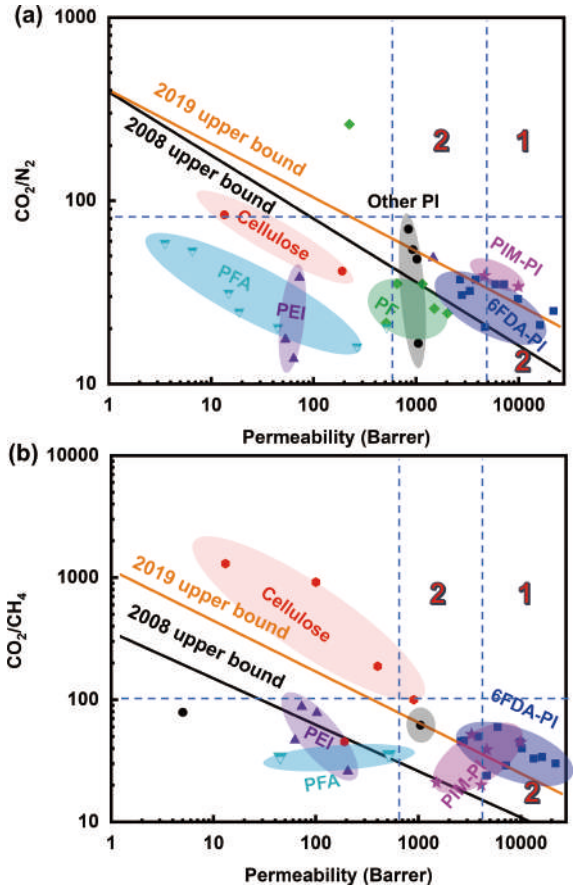

Fig. 11 Reported gas separation performances of (a) CO_2/N_2 and (b) CO_2/CH_4 of various CMSMs.

So far, major studies focus on tuning the chemical structures of precursors. The physical structures of precursor membrane, such as chain aggregation and orientation, also affect the resulting carbon structures, and need more attentions. Furthermore, the pyrolysis conditions of precursor membrane mostly focuses on carbonization temperature, and little attentions have been paid to other processing factors, such as tension, pressure, and stabilization conditions. Last, the processing of CMSMs have not fully investigated. The hollow fiber membrane is preferred for its high interfacial area and packing density. The fiber spinning conditions determine chain packing, orientation and morphologies. These physical factors of precursor chains are expected to affect the resulting carbon structures and gas separation performances, but have not been systematically investigated or even carefully considered. For the performances of CMSM, one of the major weaknesses is the brittleness of CMSMs, which strongly restricts module assembling, separation pressure, and long-time structural integrity. The improvement of CMSM strength is highly desired, and an alternate way is to develop high strength porous hollow fiber support.

The long-time performance of CMSMs is another issue for its commercial applications. The adverse aging effect of CMSMs normally leads to a lower gas permeability during usage. Furthermore, the humidity resistance of CMSMs also need to be addressed. For the cost of CMSMs, PI and PIM are relatively high because of raw materials. By comparison, PF, PFA, PEI and cellulose are relatively low cost, and are promising to be used in large scale in future. For the commercial applications of CMSMs, both performance and cost are important issues. PI-based CMSMs are most widely investigated and exhibit very good gas separation performances. Also, considering the low cost, good fiber spinnability, and relatively good gas separation performances of cellulose-based CMSMs, both PI and cellulose based CMSMs are promising to be commercialized at the earliest. In order to overcome the high cost issue of high-performance precursors, such as PI and PIM, the development of suitable and low-cost porous hollow fiber support is another possible way to reach a balance of manufacturing cost and gas separation performances. A well balance between performance and cost is the key for CMSM commercialization. Recently, some studies focus on practical application of CMSMs by evaluating cost and performance using proper software (Aspen HYSYS, etc).

Overall, the gas separation performances of CMSMs are mostly superior compared with polymer membrane. Especially, CMSMs are promising for separating organic molecules which are extremely difficult for polymer membranes. Although CMSMs have not been successfully commercialized, there is no doubt that CMSMs would be a major part for membrane separation in the future. So far, the CMSMs exhibit excellent purification ability for H_2 and CO_2, and could potentially play important roles in hydrogen energy and carbon neutralization.

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