

Review

Recent Advances on Carbon Molecular Sieve Membranes (CMSMs) and Reactors

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Abstract: Carbon molecular sieve membranes (CMSMs) are an important alternative for gas separation because of their ease of manufacture, high selectivity due to molecular sieve separation, and high permeance. The integration of separation by membranes and reaction in only one unit lead to a high degree of process integration/intensification, with associated benefits of increased energy, production efficiencies and reduced reactor or catalyst volume. This review focuses on recent advances in carbon molecular sieve membranes and their applications in membrane reactors.

Keywords: carbon molecular sieve membrane; carbon membrane reactor; gas separation

1. Introduction

Chemical separations account for about half of industrial energy use; the processes involved, such as distillation, account for 10%–15% of the world's energy consumption [1,2].

Compared to conventional separation processes such as distillation and adsorption, membrane separation processes have low energy requirement and low maintenance costs.

The majority of membranes currently used in industry are polymeric. The advantage of polymeric membranes is that they are easily processed into various forms, though they cannot be used in several industrial processes involving operation at high temperatures; moreover, they can suffer plasticization which decreases the permeation properties of the membrane. Two parameters characterize the separation performance of membranes: permeability and selectivity. For polymeric membranes, it was found that there is a trade-off between these parameters since an increase in the permeability for a given gas generally is accompanied with a decrease in the selectivity and vice versa. Robeson reported the separation upper limit of polymeric membranes for several binary mixtures of interest [3,4]. The objective in the development of new membranes is to surpass that limit, and carbon molecular sieve membranes (CMSM) are inorganic membranes that are able to overcome this upper limit.

On the other hand, researchers are continuously working on the development of better processes, catalysts and adsorbents to increase the efficiency of fuel and petrochemical productions which is highly dependent on the separation processes and their improvement [5–7]. A good alternative to solve this problem is to develop membrane reactors.

According to the IUPAC definition [8], a membrane reactor (MR) is a device for simultaneously performing a reaction (steam reforming, dry reforming, auto-thermal reforming, etc.) and a membrane-based separation in the same physical device. Therefore, the membrane not only plays the role of separator, but it can also take part in the reaction itself. The continuous extraction of one of the products can shift the equilibrium, enhancing yield and selectivity as compared with a traditional system [9].

Although CMSMs are still in the developmental phase, these membranes are believed to be promising candidates for gas separation and membrane reactors because: (i) they are relatively easy to manufacture; (ii) they have low production and raw material costs; (iii) they offer the molecular sieve

separation effect; (iv) they have high permeance; and (v) they can work in conditions where polymeric and palladium membranes are not stable [10–13].

In 1983, for the first time, Koresh and Sofer from the Atomic Energy Commission Nuclear Research Centre (Israel) reported the preparation of carbon membranes that contain pores no greater than those of the molecular dimensions of the gases by carbonization of thermosetting polymers. Moreover, they stated that the gas permeabilities and selectivities were significantly superior to the polymeric membranes [14].

Recently, Salleh and Ismail [15] published a review about CMSMs for gas separation; this review will focus on recent advances in CMSM development for gas separation; an overview of the most selective and permeable membranes is given together with commercial membranes; then, various applications of carbon-based membrane reactors with particular emphasis on hydrogen production will be presented.

2. Carbon Molecular Sieve Membranes

Carbon molecular sieve membranes have been considered the next generation of membrane technology [15,16]. They have been identified as very promising candidates for gas separation due to their high separation performance. They are composed of microporous and ultra-microporous, amorphous high carbon materials. They offer tunable pore structure for the separation targeted, and excellent thermal resistance and chemical stability in harsh environments [17–19]. They have high gas permeance and excellent selectivity compared to available polymeric membranes [20–22]. They have been proven to be very effective for various applications, such as purification of gaseous blend, dehydration of chemical products and natural gas processing in order to replace other traditional processes for the purpose of cost and energy saving [23–25]. CMSMs have the greatest potential among the inorganic membranes because of the relative ease of fabrication and their resulting low cost.

CMSM morphology consists of small graphene layers that are packed imperfectly; the resulting structure is called as turbostratic and the nano size openings within/between them are considered slit-like micro and ultramicropores [26]. Micropores allow high permeation while ultramicropores are responsible for the sieving ability of the structure [27]. Since the structure is amorphous, there is a pore size distribution instead of a single pore size.

Based on the pore size, CMSMs can separate gases by molecular sieving and selective surface diffusion mechanisms [28,29]. CMSMs contain constricted apertures close to the molecular dimensions of gas molecules allowing the transport of small molecules through the pores, avoiding the passage of larger molecules; therefore, molecules with only slight differences in size can be effectively separated by molecular sieving. In this case, a precise control of pore sizes is required. The molecules can be transported also by selective surface diffusion in which the more adsorbable gas in a feed stream on the high pressure side of the membrane selectively adsorbs onto the surface, diffuses across the surface of the membrane to the low pressure side and subsequently desorbs. By this mechanism, the membranes can separate non-adsorbable or weakly adsorbable gases (O_2 , N_2 , and CH_4) from adsorbable gases (CO_2 , NH_3 , and H_2S). Through adsorption and the molecular sieving mechanism, excellent separation can be achieved even between gases with almost similar molecular size [15,30,31].

CMSMs are obtained through the carbonization of polymeric precursors under an inert or vacuum atmosphere. In the carbonization process, the polymeric precursor is heated to pyrolysis temperature (773.15 K to 1273.15 K) under controlled atmosphere and heating rate before being held at the carbonization temperature for a sufficiently long thermal soaking time [10]. During the carbonization, gaseous decomposition products of the polymer are evolved, leaving micropores in the membrane; this process goes along with a considerable loss in weight and dimensional shrinkage.

A review regarding the development of CMSMs for gas separation as well as for membrane reactors was published by Saufi and Ismail [10]; among several aspects, some fundamental points were outlined: (i) the production of CMSMs currently has high cost (between one and three orders of magnitude greater than typical polymeric membrane) and therefore must achieve a superior

performance in order to compensate for their high cost; (ii) optimization of manufacture parameters during the carbonization process is perhaps the best way to increase the gas permeation performance because of the large number of parameters involved; and (iii) when a high performance CMSM is prepared, it is important to determine the effect of its exposure to water vapor; this is important for CMSM commercialization. The humidity found in the atmosphere can also have an adverse effect on CMSM performance. Therefore, the study of storage conditions for CMSMs is also an important aspect to be considered.

In order to prepare a high performance CMSM, it is important to select an appropriate polymeric precursor and to optimize the conditions for its carbonization. The most important parameters that would influence the final properties of CMSMs are: (i) the type of polymeric precursors, which must be thermosetting polymers (polymers should not flow before decomposing), such as polyimides, polyfurfuryl alcohols, phenolic resins, polyvinylidene chloride, polyacronitrile, cellulose derivatives and polyetherimide [10]; (ii) carbonization conditions, such as the heating rate, atmosphere and final temperature [32,33]; and (iii) modifications in the pre- or post-treatment, such as stabilization, activation or oxidation [34–36].

The carbonization temperature is generally above the decomposition of the polymer but below the graphitization temperature. In general, an increase in carbonization temperature will lower the permeability and increase the selectivity of the CMSM. Higher temperatures increase crystallinity and density and lower average interplanar spacing in the membranes [37,38].

Pore size distribution can also be tuned by short treatment with O₂ between 373.15 K and 723.15 K [39]. The phenomena called “oxygen doping” has been defined as a tool for the fine tuning of the selective ultramicropores [26,40]. Oxidation can increase pore distribution to such an extent that the diffusion mechanism could go from molecular sieving to adsorption selective. Therefore, when correct treatment is used, heavier hydrocarbons such as n-butane diffuse faster than non-adsorbing materials and therefore very good selectivities are obtained in olefin/paraffin separation [26].

Zhang and team members [41] investigated the membrane-casting parameters, solvents and drying methods in order to adjust the microstructure and gas permeation of CMSMs from poly(phthalazinone ether sulfone ketone) (PPESK). It was found that using a solvent with high boiling point is favorable for the reduction of membrane shrinkage and enhancement of thermal stability, and also that cold drying (including freeze-drying and refrigeration-drying) is preferable for elevating the thermal stability of the membrane; the O₂/N₂ selectivity of the membranes prepared by refrigeration-drying increases from 4.6 to 10.3 with pyrolysis temperature increasing from 923.15 K to 1123.15 K. The highest O₂ permeability of 270 Barrer (single gases) and 257 (O₂/N₂) (mixture) were obtained by CMSMs prepared by freeze-drying at 1023.15 K.

Polymers of intrinsic microporosity (PIMs) possess high BET surface area (up to 1000 m²·g^{−1}) with pores of less than 2 nm; Pinnau et al. [42] prepared CMSM from hydroxyl-functionalized PIM (PIM-6FDA-OH) film (80–100 μm thick) by carbonization under N₂. At 803.15 K, the membrane had very high permeability (4110 Barrer) for CO₂ with selectivity over CH₄ of 20. For treatments at 873.15 K, 903.15 K and 1073.15 K, the membranes approach a carbon molecular sieve structure by development of a larger fraction of size-sieving ultramicropores (<0.7 nm) and partial graphitization. The CMSM generated at 1073.15 K, reached ethylene permeability of about 10 Barrer and selectivity over ethane of 17.5, the most selective CMSM for ethylene/ethane separation reported to date [43].

3. Composite Carbon Molecular Sieve Membranes (c-CMSMs)

In order to improve the permeation and selectivity of the CMSMs, new composite materials have been developed (c-CMSM), where inorganic compounds are added to the carbon structure of the membrane. The permeability enhancement in c-CMSMs has been assigned to an increase of pore volume, pore size and surface area of the CMSM [44] and also on the interfacial gaps formed between carbon phase and the dopants (phase separation effect) [45]. Additionally, Foley et al. [46] reported that nanoparticles lead to thinner selective layers, thus allowing higher permeances. Barsema et al.

dispersed Ag nanoparticles into P84 and SPEEK precursors [47,48] and achieved higher O_2/N_2 selectivity values; the increase in gas-pair selectivity observed was attributed to the selective diffusion pathways that occur along the silver nanoparticles' surface. Xiao et al. [49] reported the preparation of c-CMSMs from Ag + SPAEK; they observed that the silver doped CMSMs exhibited higher CO_2/CH_4 selectivities (it was attributed to the greater interconnection among the ultramicropores formed by the migration of silver) and permeabilities. Composite alumina-CMSM using phenolic resins resol [40,50], novolac [37,51] and composite alumina-Ag CMSM [52] were for the first time reported by Pacheco Tanaka and Llosa Tanco et al.

Li et al. [53] prepared zeolite/carbon hybrid membranes by the combination of zeolites γ , β , or ZSM-5 with polyamic acid and carbonized it at elevated temperature. The gas permeability was enhanced and, though it was due to the ordered inner pore channels constructed in the zeolite, offering rapid and constant routes for diffusion of the gas molecules and the made pores, may create new channels for gas diffusion in CMSMs. Zhang et al. [54] produced a zeolite hybrid-supported CMSM, using polyimide and ZSM-5; the addition of zeolite increases greatly the gas permeability; the CMSM carbonized at 923.15 K surpassed the Robeson's upper bound for H_2/N_2 gas separation. Zhao et al. [55] have fabricated nickel-incorporated CMSMs, placing nickel nitrate into larch using liquefied larch sawdust as precursors and F127 as the template. The 10 nm nanoparticles of nickel integrated in the CMSM can improve the molecular sieve function of the membrane; Ni-CMSM with the largest pores possesses the highest gas permeation and gas separation.

Hydrophobic carbon-silica membranes were prepared by several dip coatings of supported γ -alumina membranes in a silica solution containing methyl-tri-ethoxy-silane (MTES) and tetra-ethyl-ortho-silicate (TEOS) and carbonization in an inert environment; these membranes are proposed for the separation of N_2 and O_2 in humid process streams [56]. Duke and team members prepared carbonized template molecular sieve silica (CTMSS) membranes for hydrogen purification from CO in the fuel cell system; these membranes were fabricated employing a novel surfactant templating procedure and revealed to be more stable than the regular non-templated molecular sieve silica (MSS) membranes when they are exposed to steam; showing that the hydrophobic template changes are important for the stable membrane process [57].

CMSMs can be divided according to their configuration into two categories: (i) unsupported and (ii) supported membranes.

4. Supported Carbon Molecular Sieve Membranes

Unsupported CMSMs are mostly prepared as flat films, capillary tubes or hollow fibers, while the supported CMSMs are produced generally in the form of flat sheets or are tubular. The most common configuration of supported CMSM is tubular; according to the outer diameter, they are classified in tube (more than 5 mm) and capillary (between 5 and 0.5 mm). Since permeation through membranes depends on the thickness and on the partial pressure difference, very thin membranes (selective layer less than 5 μm) are required. Very thin self-supported membranes are mechanically weak and are difficult to handle; therefore, supported membranes are preferred. In order to reduce the resistance to permeation by the support, asymmetric supports are used. In this configuration, the support consists of several layers with decreasing pore size. The pore size is controlled by the particle size, shape and their extent of aggregation. The surface properties of the support top layer are of critical importance for the membranes. In addition, the compatibility of this layer (reactivity, expansion coefficient, etc.) with the selective layer has to be considered. For large-scale applications, the capillary or hollow fiber membranes are more desired due to their high packing density.

Supported CMSMs are prepared by carbonizing thin polymer precursor deposited on a porous substrate. The most used techniques for depositing the polymer precursor are: dip coating, ultrasonic deposition, vapor deposition, spin coating, and spray coating [29].

The separation of NF_3 , CF_4 and SF_6 (F-gases) from nitrogen through thin CMSMs have been studied by S-J Kim et al. [58]. F-gases are strong greenhouse gases, and their emissions to the

atmosphere should be prevented. Matrimid 5218[®] was used as polymer precursor for supported CMSMs on alumina support; CMSMs carbonized at 923.15 K in high-pure He (99.9999%) exhibited the best performance for N₂/NF₃ separation (650 Barrer for N₂, and N₂/NF₃ = 26.6), in comparison with polymeric membranes. These CMSMs have high nitrogen permeance, due to the thin membrane with controlled micropores.

The effect of the gas used in the carbonization during the preparation of tubular-supported CMSMs from Matrimid as polymeric precursor was reported by Sazali et.al. [59]; the polymer film was carbonized to 1123.15 K, under either Ar or N₂ atmosphere. The results showed that membranes carbonized under Ar could produce higher selectivity and permeability compared to those carbonized under N₂. The authors concluded that CMSMs produced under high density environment gas (Ar ρ = 1.784 g/L) would have better skin integrity than CMSMs produced under low density environment (N₂ ρ = 1.251 g/L). Regardless of the carbonization temperatures, the heat treatment under Ar gas flow created more permeable pores as compared to N₂ environment. The highest CO₂/CH₄ and CO₂/N₂ selectivity of 87 and 80 were obtained for CMSM prepared under Ar atmosphere.

Lee and team members [60] have prepared ultrathin (<1 μ m) CMSMs using a metallic tube covered with an intermediate alumina layer as support (this know-how is licensed to Pall Corporation and commercially offered from Pall AccuSepTM Inorganic Membranes (New York, NY, USA)). A phenolic novolac resin (Kolon Industries, Gumi, Korea) was used as polymer precursor and dissolved in N-methyl-2-pyrrolidone (NMP) at 333.15 K. To maximize the performance of the CMSMs, the viscosity of the phenolic polymer solution was varied from 10 to 30 centipoises (cP), and the carbonization temperature was varied from 973.15 K to 1173.15 K. Multiple carbon layers were deposited to repair defects in the first carbon layer to achieve high separation factor. High performance CMSMs were obtained after a sequence of three coatings and carbonization at 973.15 K. When the polymeric solution has a viscosity of 20 cP, the highest separation of the membrane was found: for He/N₂ = 462, for CO₂/N₂ = 97 and for O₂/N₂ = 15.4.

Favvas et al. [61] prepared asymmetric carbon hollow fiber membranes and the gas permeation properties were investigated at high pressures (up to 6 MPa). The polymeric precursor selected was BTDA-TDI/MDI/ (P84) co-polyimide hollow fibers and the carbonization was carried out at 1323.15 K, for 4 h, under Ar. An increase in flux is apparent for all cases while a reduction at higher pressures was obtained in the cases of CO₂ and C₂H₆. Thus, for example, for CO₂ the permeance values change from 32 to 412 GPU at 27.5 and 22 bar, behavior being attributed to orientation correlations of the confined molecules mainly coming from quadrupole interactions between neighboring molecules. In general terms, the authors stated that low pressure measurements provide structural information about the pore size and network of the membranes, whereas high pressure permeance tests enable the determination of the optimum parameters in real industrial separation processes.

Recently, a paper was published by Song et al. [62] showing a new concept on the preparation of inorganic mixed matrix membrane. These authors incorporated phenolic resin into the pores of alumina substrate using a vacuum-assisted method. These membranes were tested for pervaporation desalination and gave very high water fluxes to 25 Kg·m⁻²·h⁻¹ for seawater (NaCl 3.5 wt.%) at 75 °C. Salt rejection was very high, varying between 93% and 99% depending on temperature and feed salt concentration.

5. Supported CMSMs Prepared by One Dip-Dry-Carbonization Cycle

Hennis and Tripodi [63] stated that is rather difficult to achieve an adequate thin selective layer without defects: several dipping-drying-carbonization cycles are required to obtain CMSMs without defects. In order to reduce cost, methods for preparing supported membranes in only one dip-dry-carbonization cycle should be developed. IKTS reported a one-step CMSM preparation using several commercially available polymeric precursors deposited on 5 nm asymmetric γ -alumina supports [64]. The best results regarding selectivity and permeances were acquired by carbonization of homemade epoxy resin at 1073.15 K [65]. The membranes were prepared inside an asymmetric coated

ceramic tube of 10 mm outer, 7 mm inner diameter and a length of 100 mm with a 5 nm asymmetric γ -alumina support [66]. An ultra-thin (0.7–1 μm) CMSM was formed [67].

D.A. Pacheco Tanaka, M. Llosa Tanco et al. reported for the first time the preparation of a 7 cm long, 1 cm diameter-supported composite alumina-CMSM from low cost polymer precursors phenolic resins (resol [40,50,52] and novolac [37,51]) on alumina tubes (200 nm pore size) in one dip-dry-carbonization cycle. When only phenolic resin was used during the preparation, the membranes were unselective (presence of defects) because the precursor penetrated excessively in the pores of the alumina support; consequently, additional dip-dry-carbonization cycles were necessary to obtain membranes without defects. However, upon loading with boehmite nanoparticles ($\gamma\text{-AlO}(\text{OH})$) in the precursor solution, a defect-free c-CMSM was prepared in a single dipping-drying-carbonization cycle. The selective layer obtained (with both novolac and resol phenolic resins) has a thickness of around 3 μm (Figure 1). During carbonization, the polymer decomposed, forming a carbon matrix with homogeneously distributed alumina nano fillers derived from the dehydration of the boehmite nanoparticles (Figure 1).

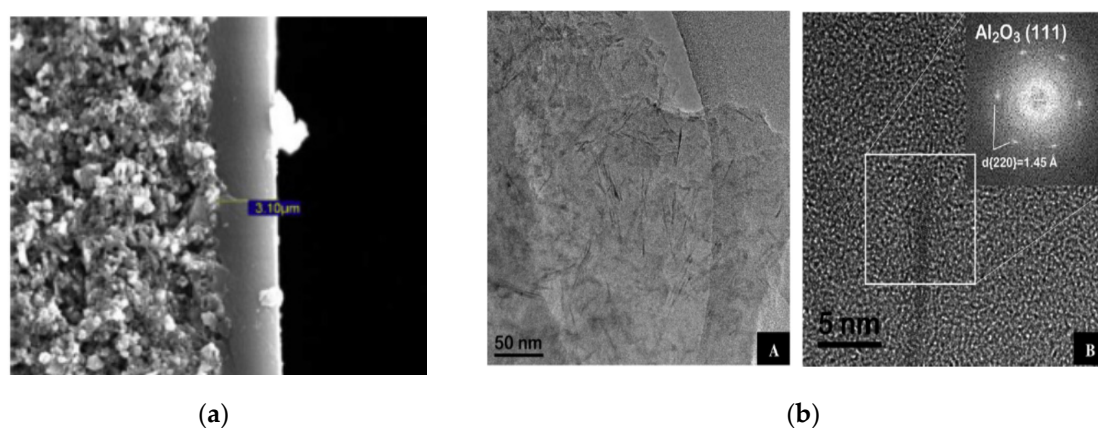


Figure 1. Alumina-composite-CMSM: (a) SEM picture showing the selective layer on the porous alumina support. Reproduced with permission from [51], Elsevier, 2014; (b) HRTEM pictures of the composite-unsupported membrane, the inset depicts digital diffractogram of the Al_2O_3 nanoparticles. Reproduced with permission from [40], Carbon, 2011.

Composite alumina-CMSMs using resol phenolic resins and boehmite were prepared with varying resin and boehmite compositions conducting to membranes with different C/alumina ratios (7.3, 4.4, and 3.7 wt.%) [50]. It was perceived that an increase in the C/alumina ratios led to c-CMSMs with greater volume of micropores and higher average length of the micropores. The permeabilities of the c-CMSMs for several gases are presented in Table 1 and Figure 2; it is observed that their permeation properties are above the Robeson upper bound for many gas pairs, especially $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$, thus making it promising for olefin purification. New c-CMSMs containing a polymer (phenolic resol resin) and two inorganic fillers—(i) alumina to increase the permeation and (ii) Ag nanoparticles to increase selectivity towards propene—were reported [52]. Alumina-Ag-CMSM performed better for all separations investigated and are particularly promising for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation, where their performance surpassed by far the best polymer membranes (Figure 2) [52].

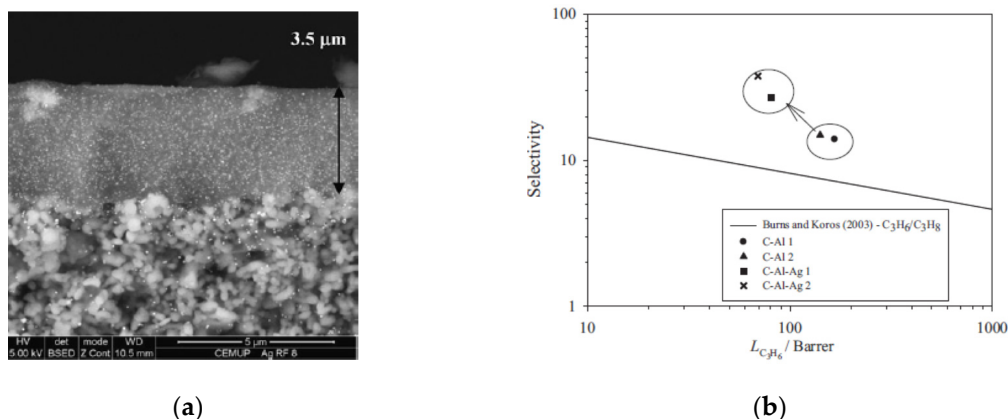


Figure 2. (a) SEM image of a supported composite Ag-alumina-CMSM, bright spots indicate the presence of Ag; (b) Gas permeation results for propene/propane and comparison with the respective upper bound plot. Reproduced with permission from [52], Elsevier, 2012.

Table 1. Gas permeabilities of c-CMSM at 293 K in function of C / Al ratio [50].

Membrane c/Alumina (wt.%)	Permeability (Barrer)						
	N ₂	O ₂	He	H ₂	CO ₂	C ₃ H ₈	C ₃ H ₆
7.3	32.7	153	971	2047	1148	1.96	36.2
4.4	58.2	256	1024	-	1499	28	420
3.7	83	284	1200	-	2017	78.5	776

Recently, D.A. Pacheco, M. Llosa Tanco et al. [51] reported the influence of carbonization temperature on pore size distribution and permeation properties of composite alumina-CMSMs prepared from in house synthesized novolac phenolic resin loaded with boehmite nanoparticles carbonized at temperatures from 723.15 K to 1273.15 K. Micropore size distribution studies showed that proportion of pores smaller than 0.45 nm (responsible of the sieving effect), increase as the temperature of carbonization increases; however, the proportion of intermediate-sized micropores (0.5–0.8 nm) increase for carbonization from 723.15 K to around 923.15 K and decrease for higher temperatures. Permeation of O₂ and N₂ of the membranes just after membrane carbonization (fresh membranes) was evaluated for N₂ (0.364 nm) and O₂ (0.346 nm) (see the results in Figure 3). For both gases, all membranes showed high permeances but small selectivities; from 723.15 K the permeation increases as the carbonization temperature increases peaking between 873.15 K and 973.15 K; these results are consistent with the pore size distribution of the membranes.

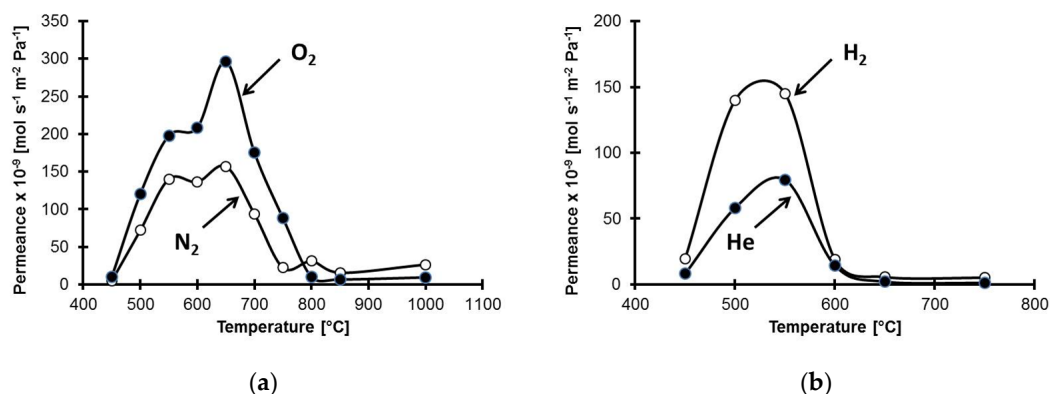


Figure 3. (a) O₂ and N₂ permeance of membranes just after carbonization, (b) H₂ and He permeance after 1 day aging. Reproduced with permission from [51], Elsevier, 2014.

The fresh membranes were left in the laboratory bench at room temperature for one day; after that time, the permeation of O₂ and N₂ decreased markedly (700 times for N₂ and 66 times for O₂); the samples carbonized at temperatures above 873.15 K showed permeances for N₂ and O₂ below the limit of detection of the equipment (Table 2). The decrease was attributed to the reduction of the pore size by oxygen chemisorption and water physical adsorption. The membranes show higher permeance for H₂ against He despite H₂ being larger than He (0.29 and 0.26 nm respectively). Permeation performance for H₂ against N₂ for membrane carbonized at 823.15 K is located above the upper limit of Robeson between the performances of palladium (Pd) pore-filled membranes at 373.15 K (Pd1) and 50 °C (Pd2) (Figure 4). For N₂ to H₂, the permeance increased as size of the gas decreased, an indication of the molecular sieve separation. However, the opposite is observed between H₂ and He: the smaller He has lower permeation than the bigger H₂. This fact is consistent with the gas transport through CMSMs that combines molecular sieving (small pores) and diffusion of the permeant gases (larger pores). The membrane carbonized at 823.15 K has a H₂/N₂ ideal selectivity of 725 and the permeance of $145 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at room temperature, values comparable to the best performing Pd membranes. These c-CMSMs can therefore be used instead of Pd for H₂ separation at low temperature where Pd membranes are not stable and have low H₂ permeation. Robeson plots for H₂/N₂, and H₂/CO₂ are shown in Figures 4 and 5.

Table 2. c-CMSM permeance to N₂, O₂, H₂ and He at 303.15 K and ideal permselectivities for c-CMSMs carbonized at different temperatures after 1 day aging [51].

Temperature K	mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹ × 10 ⁻⁹				Ideal Permselectivity		
	N ₂	O ₂	H ₂	He	O ₂ /N ₂	H ₂ /N ₂	He/N ₂
723.15	0.4	1.0	19.7	8.2	2.5	49	20.5
773.15	1.2	8.5	140.0	58.2	7.1	117	48.5
823.15	0.2	3.0	145.0	79.5	15	725	398
873.15	n.d.	n.d.	18.9	14.4	—	—	—
923.15	n.d.	n.d.	5.6	2.1	—	—	—
1023.15	n.d.	n.d.	5.1	1.2	—	—	—

n.d. below detection limit ($<8 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$).

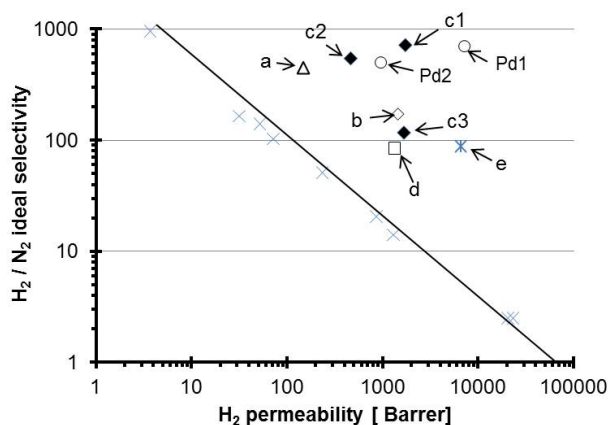


Figure 4. Robeson upper bound plot for H₂/N₂ for: (a) Campo [68], (b) Tseng [69], (c1) Llosa [51], (c2) Llosa [51], (c3) Llosa [51], (d) Hosseini [70], (e) Zhou [71], (Pd1) Pacheco, Pd pore-filled membranes at 100 °C [72], and (Pd2) Pacheco, Pd pore-filled membranes at 50 °C [72].

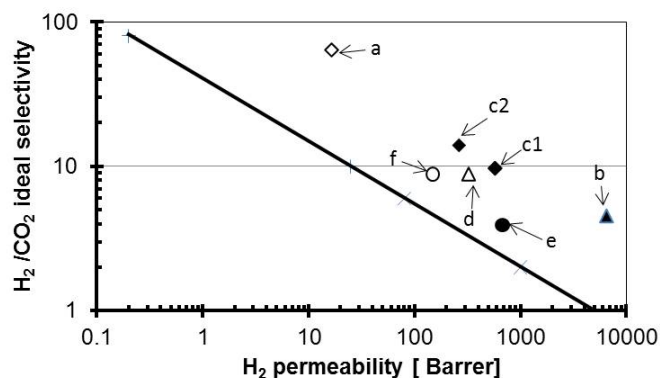


Figure 5. Robeson upper bound plot for H_2/CO_2 for: (a) Low [73], (b) Bux [74], (c1) Llosa [51], (c2) Llosa [51], (d) Hosseini [70], (e) McCarthy [75], and (f) Campo [68].

Tseng et al. [76] prepared supported CMSMs on titanium gel-modified alumina disks, using polyethyleneimine as precursor, and carbonized under vacuum at 873.15 K for 2 h. The CMSM supported on the unmodified Al_2O_3 support has a hydrogen permeability of 537.5 Barrer and H_2/CH_4 selectivity of 197.6. After modification of the CMSM supported on TiO_2/Al_2O_3 , the hydrogen permeability increased to 600.7 Barrer; the selectivity for H_2/CH_4 , H_2/CO_2 and CO_2/CH_4 are ~725, ~8 and ~90 respectively.

Ismail and co-workers [77] have prepared supported tubular CMSMs to study the effect of polymer composition (5 wt.%, 10 wt.%, 13 wt.%, 15 wt.% and 18 wt.% in NMP) in the dipping solution on CO_2/CH_4 separation using tubular TiO_2 supports where the inner surface was coated with ZrO_2 (2–3 nm pore size). Matrimid 5218 was used as polymer precursor. The carbonization was carried out under argon gas at 1123.15 K for 30 min. The experimental results showed that the supported tubular CMSMs prepared with 15 wt.% Matrimid performed the highest selectivity for CO_2/CH_4 (87.34%). According to the authors, this enhancement could be due to the increase in the packing density of the polymer chain as the concentration of the polymer increases the microporous formation.

Kruse and co-workers [78] (Fraunhofer IKTS/Hermsdorf), prepared supported CMSMs on Al_2O_3 tubes (inner diameter of 7 mm, outer diameter of 10 mm and a total length of 250 mm). The selectivity and permeance of CMSMs for binary mixtures (composed of He , N_2 , O_2 or carbon dioxide) at temperatures between 300.15 K and 450.15 K and high pressures (up to 20 MPa) were studied. The selective layer has a thickness of 2 μm and a pore size below 0.5 nm; with effective membrane area of $5.3 \times 10^{-3} m^2$. A maximum mechanical strength of 9.2 MPa transmembrane pressure difference was determined. They applied a Maxwell-Stefan diffusion approach to study the gas-to-gas and gas-to-membrane interactions. It was concluded that nitrogen transport is dominated by the interaction with CO_2 , while the transport of CO_2 itself is mostly determined by wall interactions. The variations in the results from experiment and modelling indicates that even after a one-time high pressure exposure, the carbon structure changes thereby influencing the transport coefficients.

In the supplementary information, Table S1 lists the gas permeation and selectivities of the recently developed CMSMs.

6. Carbon Molecular Sieve Membrane Modules

Small or laboratory-scale membrane modules have been built and their performance tested. Moreover, researchers have made attempts to improve the methodology for building large-scale CMSM modules. Kusuki and Tanihara et al. [79,80] invented an apparatus for the continuous carbonization, and the group of Zhou and Islam [81,82] improved the preparation method for flexible carbonized membranes. The selection and modification of porous stainless steel for supported CMSMs conducted by Acharya and Merrit [83,84] could lead to building a large module because welding can be used to seal between supports and module shells.

Yoshimune and Haraya et al. [85] stated that, until 2013, only two large-scale CMSM modules had been reported in the literature. Mendes and team members [86,87] characterized these two modules. The first module contained hollow fiber CMSMs and was commercialized for the first time by Carbon Membrane Ltd. (Dimona, Israel). The first step of the fabrication is the carbonization of dense hollow fibers of cellulose; in a second step, a selective layer was deposited by chemical vapor deposition (CVD) treatment (using propylene as the source) [28,86]; then, the hollow fibers were oxidized to create a pore structure of tailor-made dimensions within the CVD layer. The resulting membranes had an asymmetric structure and enhanced permeability and selectivity. The highest packing density reported for these modules was $2000 \text{ m}^2 \cdot \text{m}^{-3}$ (10,000 fibers, 4 m^2 per module). Commercialization started by the end of the 1990s, but the company closed in 2001.

Blue Membranes GmbH (Wiesbaden, Hessen, Germany) developed CMSMs with a honeycomb configuration with high packing density (up to $2500 \text{ m}^2 \cdot \text{m}^{-3}$, 10 m^2 per module) [88]. The flat support was an industrial-grade paper modified with ceramic fibers in order to limit the differential shrinking during carbonization. This support was then sheeted with a polymeric film (that constitutes the precursor of the selective layer) using an imprinting technique; the polymer system comprises a phenolic resin (Phenodur PR 515) and epoxy resin (Beckopox EP309). The final honeycomb module configuration was obtained from this flat precursor sheet. This membrane and the support were carbonized under nitrogen at 1053.15 K for 3 h with a heating rate inferior to $1 \text{ K} \cdot \text{min}^{-1}$. Subsequently, the selective was obtained by chemical vapor deposition (CVD) treatment ([88]). Finally, an activation step with oxygen was applied to tailor the pore structure. Blue Membranes GmbH shifted its business activities and stopped carbon manufacturing.

Media and Process Technology, Inc. (MPT, Pittsburgh, PA, USA) produce modules of CMSMs supported on porous alumina tubes. The CMSMs are prepared by the pyrolysis of a polyetherimide (PEI) placed onto a ceramic porous support [89]. These membranes perform hydrogen separation under an intermediate temperature i.e., 453.15 K to 573.15 K . Membrane hydrogen permeances ranging from 0.5 to $>2 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ at 473.15 K – 523.15 K have been measured depending upon the selectivity desired. Selectivities for H_2 to CH_4 are 50 to > 100 at temperatures from 473.15 K to 523.15 K . Characteristic performance of the carbon molecular sieve hydrogen-selective membranes is $1.5 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ at the H_2/CH_4 of 100 at 493.15 K . The membrane performance is stable at high temperatures in the existence of high concentrations of condensable organic vapors; the authors report that this membrane is ideal for hydrogen recovery from refinery off-gas.

MPT also fabricates CMSMs for dehydration via pervaporation applications at high temperature ($<523.15 \text{ K}$), making it possible to: (i) operate the condensers at (or close to) atmospheric pressure and ambient temperature, eliminating the necessity for vacuum and refrigeration; (ii) use heaters at a minimum or not at all; and (iii) increase the yield of the membranes with increasing temperature owing to the higher membrane permeance and the higher vapor pressures developed [90].

Very recently, T. Tsotsis et al. [89] (closely related to MPT) reported the preparation of CMSMs in “pilot scale” modules of 13 single tubes (38.1 mm diameter and 76.2 mm length) and 86 single tubes (76.2 mm diameter \times 762 mm length) (Figure 6). Porous alumina tubes were potted into a dense ceramic collar using a ceramic glass. The membranes were prepared by dip-coating the module in a polymeric precursor solution (a registered blend of phenol formaldehyde) and their subsequent carbonization under inert atmosphere at temperatures ranging from 673.15 K to 973.15 K ; details about the preparation were reported in other articles describing that more than one dip-dry-carbonization cycle was necessary to obtain defect-free membranes.



Figure 6. Alumina-supported CMSM tube pilot scale bundle and full-scale bundle produced by MPT. Reproduced with permission from [90], Elsevier, 2014.

7. Carbon Molecular Sieve Membrane for Water Separation

Inorganic membranes for water permeation, such as silica, zeolite and CMSM, have received much attention because of their excellent stability at high temperature and high permeation. Moreover, they do not swell at high feed of water concentrations and other organic compounds. However, silica is not stable against water and alkaline solutions, thus zeolite membranes without defects are very difficult to prepare. The selectivity of CMSMs towards water can be improved by the presence of hydrophilic groups on the pores of the membrane. The water molecules will adsorb on the surface and will pass through the membrane by adsorption diffusion mechanism; the pores will be blocked with water and the permeation of less absorbable molecules will be reduced. The structure of CMSMs prepared from polymers containing oxygen groups (such as phenol-formaldehyde [37,51,91], resorcinol-formaldehyde [92,93], sulfonated oxide (SPPO) [94]) carbonized at below 873.15 K still contains oxygen functional groups. In addition, during the carbonization process, the polymer precursor decomposes; gases are released leaving pores with highly reactive carbons. When fresh membranes (just after carbonization) are exposed to air, water reacts with the reactive places of the membrane (water chemisorption); as consequence, carbon-containing oxygen groups are formed in the pores.

Ritcher et al. [95] reported the high temperature water separation of a CMSM prepared on alumina tubes. The membranes were tested from 423.15 K to 553.15 K with a feed composition of $\text{H}_2\text{O}/\text{N}_2$ of 0.5/0.5 and feed pressure from 0.8 to 1.1 MPa; the membrane showed an infinite water/ N_2 selectivity. Infinite selectivity was also found with H_2 and CH_4 ; however, for CO_2 , the selectivity was 50 at 523.15 K.

Ueyama and team members [92] prepared a CMSM supported on flat alumina supports from resorcinol/formaldehyde/quaternary ammonium; the membrane showed high selectivity to water in the pervaporation of $\text{H}_2\text{O}/\text{EtOH}$ and $\text{H}_2\text{O}/\text{iso-propyl alcohol}$. The selectivity was explained by the hydrophilic nature of the pore and also molecular sieving effect. The membrane showed $\text{H}_2\text{O}/\text{iso-propyl alcohol}$ selectivity of 1155 at 303.15 K, but the separation factor decreased at an elevated temperature (343.15 K) due to the pore-blocking effect.

Tanaka et al. [93] prepared CMSMs supported on Al_2O_3 tubes by carbonization at low temperature (from 673.15 K to 873.15 K) of the resol/formaldehyde polymer. The permeation flux and separation factor were $0.23 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and 4150, respectively, for 10 wt.% water/iso-propanol mixture at 343.15 K. The membrane performance remains stable in dehydrating water/iso-propanol system. A sulfonation treatment was effective to increase the membrane stability in acid, whereas the CMSMs carbonized at moderately low temperatures have reduced stability against acetic acid due to dissolution of the carbonaceous component and/or the surface modification of membranes by acetyl groups. The permeation flux and separation factor were $0.12 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and 70, respectively, for 10 wt.% water/acetic acid mixture at 303.15 K for 196 h.

For membranes prepared from polymers with low content of oxygen such as polyimides (Matrimid Kapton), the pores are not hydrophilic [96]. For water-selective membranes, the CMSMs are carbonized at more than 923.15 K in order to obtain small pores to discriminate water through the molecular sieving mechanism. Tin et al. [96] prepared a CMSM on tubular alumina support by carbonization of Matrimid at 923.15 K for dehydration of ethanol; the membrane showed a great total flux of $4 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with a reasonably high separation factor of 50 at 333.15 K. Liao et al. [97] fabricated CMSM from Kapton; results of aqueous bioethanol sorption showed evident molecular sieving behavior of the CMSMs despite their hydrophobic surface. This behavior became significant at high pyrolysis temperature (973.15 K) at which the carbon content was high; the membrane delivered a high permeation flux of $1199 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and a high separation factor of 683.

Haraya and co-workers [94] prepared hollow fibers of SPPO carbonized at 873.15 K; in pervaporation dehydration of larger alcohols such as 2-propanol and 1-butanol; the CMSM displayed superior selectivity to water. The water permeance and ideal selectivity for the water/2-propanol system at 348.15 K were higher than $1.0 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ and 10,000 respectively.

Carbonized template silica membranes were manufactured and examined for water desalination [98]. The membranes were synthesized by a two-step base catalyzed sol-gel process using tetraethylorthosilicate (TEOS) as the silica precursor and triblock copolymer Pluronic P123 as the templating agent. The sol was placed by dip-coating on a porous alumina support and calcined under vacuum. The membranes were constant during testing of up to 250 h under various thermal and salt concentration solutions, always transporting very high salt rejections (>99.5%).

8. Carbon Molecular Sieve Membrane Reactors

The advantages of using MRs in comparison to the conventional configuration, in which a reactor is combined with a downstream separation unit, are: (i) reduced capital costs (due to the reduction in size of the process unit); (ii) improved production and selectivities (due to the equilibrium shift effect); and (iii) reduced downstream separation costs (separation is integrated) [99]. Membrane reactors, in which the continuous extraction of a product can shift the equilibrium, have a possibility of playing an important role in establishing an energy-efficient process in the future petrochemical and chemical industries [100]. Few studies with CMSMs for CMSM reactors have been reported. Table 3 shows the different studies reported in the literature along with the specific operating conditions.

Table 3. List of carbon molecular sieve membrane reactors.

Precursor	Configuration	Catalyst	Reaction	Temperature K	Ref.
not disclosed USC and MPT * ¹	Tubular	Cu/ZnO/Al ₂ O ₃	Water gas shift	< 573.15	[104] [112]
Novolac MPT * ²	Module (13–86 tubes)	Cu/ZnO/Al ₂ O ₃	Syngas treatment	-	[89]
Novolac + PEG	Tubular	Cu/ZnO/Al ₂ O ₃	Methanol steam reforming	~523.15	[113]
Phenolic resin	Supported	Nanosize Cu	Methanol steam reforming	-	[107]
Cellulose CM Ltda * ³	Hollow fibers	Cu/ZnO/Al ₂ O ₃	Methanol steam reforming	473.15	[13] [108]
Matrimid 5218	Asymmetric tube	-	Methanol steam reforming	-	[115]
Carbon layer: Amorphous, turbostratic and crystalline	Supported	-	Ethanol steam reforming	-	[116]
FFA * ⁴ NGK * ⁵	Tubular Supported	Pt/Al ₂ O ₃	Dehydrogenation of methyl-cyclohexane	-	[117]

*¹ USC and MPT, University of Southern California and Media and Process Technology Inc; *² MPT, Media and Process Technology Inc; *³ CM Ltda., Carbon Membrane Ltd; *⁴ FFA, furfuryl alcohol; *⁵ NGK, NGK Insulators, Ltd. (-) Not reported.

8.1. CMSM Reactors for Production of Hydrogen

There are many applications of catalytic inorganic membrane reactors for reactions involving hydrogen, such as hydrogenation and dehydrogenation [109], methane steam reforming [110], and water gas shift (WGS) [101]. Several different types of H₂-selective inorganic membranes have been considered, such as palladium and its alloys [99,101,102], silica [111], and zeolite [103]. Itoh stated that the success of membrane reactors for the H₂ production depends crucially on: (i) the advances in the membrane production methods for the production of thin membranes with high H₂ fluxes and selectivity; (ii) the design of innovative reactor concepts which allow the integration of separation and energy exchange, the reduction of mass and heat transfer resistances and the simplification of the housing and sealing of the membranes [99].

Palladium membrane reactors [99] have demonstrated great performances for dehydrogenations, steam reforming reactions, etc., where only hydrogen is selectively separated from the reacting mixture. However, palladium membranes have some disadvantages in terms of costs; therefore, membrane materials alternative to palladium must be explored and developed. From this perspective, CMSMs are gaining interest to be used in membrane reactors.

Due to their molecular sieving effect, CMSMs show high H₂ selectivity from mixtures with gases with larger molecules such as CH₄. For this reason, CMSMs are considered good alternatives to Pd-based membranes for hydrogen production via dehydrogenation reactions in CMRs. In contrast with Pd-based membranes, CMSMs present resistance to sulfur-containing species. However, the drawbacks of CMSMs is that they are very fragile when they are not supported, they cannot be used in oxidizing atmospheres and the permeation and selectivity are much lower than Pd.

8.2. CMSM Reactors for Water Gas Shift Reaction

The reaction of water gas shift (WGS) is an important industrial reaction used for the production of hydrogen from synthesis gas which is then used in the production of ammonia (for the fertilizer industry), hydrocarbons, methanol, as well as a component of fuel processing for fuel cell applications. The use of gasification for power generation has also increased the use of water gas shift reactors. Harale and Tsotsis et al. [104,112] studied the performance of a novel reactor system, the hybrid adsorbent-membrane reactor (HAMR) for low temperature WGS reaction (<573.15 K). In HAMR, the reaction and the membrane separation steps are coupled with adsorption. CMSMs were used as hydrogen-selective membranes (supply by the University Southern of California and Media and Process Technology, Pittsburgh, PA, USA), layered double hydroxides (hydrotalcite) as adsorbents for CO₂ and CuO/ZnO/Al₂O₃ as catalyst. The CMSMs were 25.4 cm long and had an outside diameter of 0.57 cm and inner diameter of 0.35 cm. It was reported that membranes exhibited excellent permeation characteristics and hydrogen permeability competitive with metallic membranes, at temperatures lower than 573.15 K. Additionally, they remain unaffected by CO or H₂S. The CMSM was installed inside the reactor; the catalyst and adsorbent were loaded in the annular space between the membrane and the reactor body. Steam and CO were fed into the reactor and hydrogen-rich product is obtained on the permeate side. Once the adsorbent is saturated with CO₂, it can be regenerated using a pressure swing adsorption (PSA) process. The HAMR is cyclic; therefore, to produce a hydrogen-rich product, at least two reactors must be used, each undergoing repetitive reaction/regeneration steps. The ability of the membrane, catalyst and adsorbent to operate stably under a cyclic operation was tested experimentally in a four-cycle experiment: (i) adsorption-reaction-membrane separation; (ii) blow-down; (iii) purge; (iv) pressurization. In this four-bed operation, while one bed is undergoing reaction-separation, the other three beds are undergoing one of the regeneration steps. The experimental results agreed with the model predictions and HAMR system was shown capable of attaining high conversions, obtaining high purity hydrogen with reduced CO concentration.

Liu and Tsotsis et al. [105] developed a new membrane reactor system called the “one box” process, where the reaction and separation are joined in the same unit. This system was used for producing hydrogen from syngas made from coal and biomass; after removal of impurities, without additional

clean-up (the syngas contains contaminations such as H_2S and NH_3) using a CMSM for in situ hydrogen separation. The CMSM stability was also investigated in the presence of model tar and organic vapor compounds, and proved to be competitive with other reactive separation technologies for hydrogen production. Towards technology commercialization, the same team constructed an 86-tube CMSM module, characterizing it comprehensively [89]. Multiple field-tests under no reactive conditions were conducted at the US National Carbon Capture Center (North Wilsonville, AL, USA) coal gasification facility. The 86-module has been successfully tested with syngas, with feed rates maintained between 150 L/min and 250 L/min at pressures ~ 1.48 MPa and temperatures ~ 523.15 K. The experiments were carried out for more than 300 h of continuous testing and ~ 500 cumulative hours without degradation in the permeance. It was shown that, in the presence of H_2S and other syngas contaminants, no membrane degradation was observed during the tests, thus demonstrating that the CMSM exhibits a high chemical stability. From a hydrogen concentration of $\sim 5\%$ to 7% in the feed (in the feed as received from the gasifier), this was enriched to $\sim 50\%$ to 65% . The H_2S concentration in the feed (dry source) was 200 ppm and was reduced in the permeate stream to ~ 35 ppm. In order to mimic the feed hydrogen concentration to the “one box” process, the feed was artificially pointed with hydrogen to reach the range of 30% – 40% ; at the beginning of the process (2–50 h) and at the end of the process (~ 350 h), the hydrogen concentration was enriched to $\sim 95\%$. The stage-cut was $\sim 12\%$. The authors concluded that according to the field-testing results, this 86-full-scale CMSM module demonstrated to be both stable and highly effective for the removal of hydrogen from raw coal and biomass from syngas without any pre-treatment needed for the cumulative ~ 420 h of testing.

8.3. CMSM Reactors for Methanol Steam Reforming (MSR)

Methanol is an interesting hydrogen source because it is liquid at ambient conditions, possesses relatively high H/C ratio, has low reforming temperature (473.15 K– 573.15 K), and can also be produced from biomass.

Zhang et al [113] carried out the MSR reaction in a CMSM reactor system. For contrast reasons, this reaction was tested in a fixed bed reactor (FBR) and a CMSM reactor (CMR). The CMSM was set from a phenol formaldehyde novolac resin and poly(ethylene glycol) (PEG) solution that was sprayed onto a support tube (i.d. 6 mm) and then carbonized at 1073.15 K under an inert atmosphere; the supported CMSM layer was 20 – 30 μm thick. In both reactors, catalyst pellets of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ were packed in the reaction region. The results confirmed that both the methanol conversion and the H_2 selectivity in the CMR are superior to the FBR under all the studied experimental conditions; the methanol conversion at 523.15 K in the CMR was as high as 99.9% . The authors established that using CMR lower carbon monoxide was produced. In both cases, the CMR and FBR, methanol conversion improved with the increase in either the operational temperatures or the $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ feed ratio. In 2014, the same group studied MSR using a CMSM prepared from phenolic resin and resorcinol-formaldehyde as precursors [106]; the membrane displayed narrow pore size distribution with the mean pore diameter of 0.16 μm . For the hydrogen production reaction of MSR, the conversion rate of reactors coupled with both unsupported and supported CMSM increases by 1.6 and 1.9 times respectively in comparison with that of the traditional fixed bed.

By 2015, the same group of Zhang [107] prepared catalytic carbon molecular sieve membranes (CCMs) from a mixture of phenolic resin and nano-sized copper-based catalyst as precursors, through the process of blending, compressing, molding and carbonization. The CCMs were used to build reactors for the reaction of hydrogen production from MSR in a flow-through mode. In this mode, the reactants are forced to pass through the pores of the membrane in which the catalyst is present. The authors compared the performance of CCMs, traditional fixed bed and CMSM (without catalyst) reactors. The results showed that the carbon matrix is favorable for dispersing and improving the effective exposure of copper-based catalyst to reactant, and the distinct pore diffusion in CCMs is notable. Methanol conversion of 95% , and 92% for hydrogen yield when a CCM reactor is operated under the condition of space velocity of 9.6 h^{-1} and methanol/steam molar ratio of $1:1$ was observed.

In 2009, Mendes et al. [108] simulated the production of hydrogen by MSR in membrane reactors using a one-dimensional mathematical model. Two types of membrane reactors were studied: a CMSM reactor (CMR) and a 50 μm thick Pd/Ag membrane containing both carbon and Pd/Ag membranes, simulation studies revealed that the higher hydrogen recovery is obtained and the permeated has less than 10 ppm of CO. The same group of Sa et al. [13,114] studied the SRM in a CMR over a commercial CuO/ZnO/Al₂O₃ catalyst using a module containing 100 CMSM hollow fibers of 6.5 cm length, supplied by Carbon Membrane Ltd. (see Section 6). The results show that methanol conversion, H₂ recovery and H₂ yield are all enhanced by lower feed flow rates due to higher residence times, with the drawback of higher CO production (200 ppm). Simulation using water as sweep gas shows an increase in both methanol conversion and H₂ recovery, and also a dramatic decrease in the CO concentration (20 ppm).

Briceño and team members [115] prepared a CMSM supported on asymmetric tubular ceramic tubes with an external pore diameter of 2–3 nm using polyimide (Matrimid 5218) as a precursor to be used in a CMSM reactor for MSR. The gas permeation performance of the CMSM coated with PDMS (to cover the big defects) was comparable to porous inorganic membranes (H₂/N₂ selectivity of around 5.5). The experimental data demonstrates that higher conversions are achieved in the membrane reactor than in the traditional reactor.

8.4. CMSM Reactors for Ethanol Steam Reforming (ESR)

Caro et al. [116] investigated three different CMSMs for ESR with respect to their efficiency to selectively remove hydrogen from the binary and ternary reaction mixtures (H₂/CO₂, H₂/CO₂/H₂O and H₂/ethanol) as model systems for bio-ethanol steam reforming. The three studied CMSMs were: (i) an amorphous carbon layer prepared by physical vapor deposition (PVD) of carbon on a porous alumina support using a carbon fiber yarn; (ii) a turbostratic carbon layer obtained by pyrolysis of a supported polymer blend as precursor; and (iii) a crystalline carbon prepared by pressing graphite flakes forming a self-supported disc. For a H₂/CO₂ equimolar binary mixture, the three CMSMs were found to be hydrogen selective. For the ternary feed mixture (41 H₂/41 CO₂/18 H₂O vol.%), for the amorphous and crystalline CMSMs, the hydrogen selectivity is also maintained in the presence of steam, whereas the turbostratic CMSM separates preferentially steam (H₂O) from the ternary feed mixture (H₂/CO₂/H₂O).

8.5. CMSM Reactors for Dehydrogenation Reactions

In 2013, Hirota and co-workers [117] prepared CMSM by a vapor-phase method using furfuryl alcohol (FFA). The pore size of the carbon membranes was enlarged by activation using several gases and vapors such as H₂, CO₂, O₂ and steam. The membrane thickness was reduced by the CO₂ and O₂ activation, but the pore sizes did not change. In divergence, by the activation of H₂ and steam, the pore sizes of the FFA membranes are enlarged from 0.3 to 0.45 nm, causing an increase of H₂ permeance from 3.6×10^{-9} to 1.6×10^{-8} mol·m⁻²·s⁻¹·Pa⁻¹ with great permselectivities of H₂/CF₄ (41,500). The dehydrogenation of methyl cyclohexane was carried out in the membrane reactor using helium sweep gas between 473.15 K and 493.15 K. The methylcyclohexane conversion surpassed the equilibrium values due to the selective hydrogen permeation. This reaction can be used for chemical storage of hydrogen.

9. Conclusions and Future Trends

Carbon molecular sieve membranes (CMSMs) are useful for various applications including gas separation, dehydration and membrane reactors. CMSMs have better gas permeation properties than polymeric membranes and they can surpass the Robeson line; however, they are more expensive. CMSMs can be used in conditions where polymeric membranes are not stable, such as hydrogen separation at temperatures between 373.15 K and 473.15 K, and where valuable compounds are separated, such as propylene or ethylene from its saturated analog. In order to increase the flux,

recently very thin supported membranes on inorganic supports in one dip-carbonization process have been developed. The permeation properties (permeation and selectivity) of CMSMs have been improved by the addition of inorganic fillers in the carbon matrix (composite CMSM). Tubular CMSMs are suitable for integration in membrane reactors for hydrogen production, especially for methanol steam reforming where temperature of reaction is lower than 473.15 K. At different zeolite membranes, defect-free CMSMs can be prepared in one carbonization step and can be used in processes involving water separation such as pervaporation or removal of water in membrane reactors.

Even though promising results have been obtained in the field of CMSM reactors, more work needs to be done. Scaling up the production of membranes is an initial challenge to overcome; the membrane production should be reproducible, cost effective and easy to incorporate in membrane reactors. From an industrial point of view, there is a need to further scale up to pilot trials and perform long-term testing (2000 hours plus) as proof of concept.

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