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Review Paper

Carbon membranes for gas separation processes: Recent progress and future perspective

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HIGHLIGHTS

- Carbon membrane can be produced using a wide variety of polymer materials.
- Current carbon membranes for CO_2, N_2, and H_2 separation are reviewed.

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ABSTRACT

Carbon membrane can be produced using a wide variety of polymer precursor materials via heat treatment process. A general concept route of precursor selection-preparation-modification-performance analysis platform for the carbon membrane has been proposed to promote the development of carbon membrane material for a wide range of application. The current review considers the recent progress of carbon membrane preparation and the potential applications in gas separation and membrane reactor system. In particular, the current carbon membranes for CO_2, N_2, and H_2 separation are reviewed, along with special emphasis to their membrane precursor materials and the technique used to improve the membrane's performance. Issues affecting membrane performance such as the preparation method to produce supported carbon membrane are explored aligned with the future research to achieve commercially viable processes. For future perspective, carbon membranes hold significant potential and great promise for further investigation, development, and application.

1. Introduction

The increasing demand for high efficient operation has resulted in increased global willingness to embrace the membrane material as a potential long term solution to mitigate the emissions of gases that contribute to the greenhouse effects and global warming. With the global energy consumption predicted to nearly double by 2050 and our present fossil fuel reserves under the increasingly urgent environmental and economic pressures, we must unambiguously overcome many scientific and technological hurdles that exist between the present state of the membrane production, utilization, and potential applications. Nowadays, worldwide environmental concerns are triggering the search for environmental friendly materials to be used in the industries. Carbon membrane is one type of membrane materials that can provide an attractive solution to this issue. Tremendous progress has been made in the carbon membrane technology, especially for gas separation [1,2].

Carbon membranes, which composed of microporous, amorphous high-carbon materials, have emerged as promising materials for the gas separation applications because of their characteristics such as superior thermal resistance, chemical stability in corrosive environments, high gas permeance, and excellent selectivity compared to available polymeric membranes [2-4]. They have been proved to be very effective for various applications, such as purification of gaseous blend, dehydration of fine chemical products and natural gas processing in order to replace the other traditional processes for the purpose of cost and energy saving [1,5-7].

So far, polymer-based membranes are among the most popular material used in the industries, but in many cases, their poor temperature and chemical stabilities greatly limit their applications, and the demands for the inorganic gas-permselective membranes are increasing. Through adsorption and molecular sieving mechanism, the carbon membranes are particularly useful in gas separation, and the excellent separation may be achieved even between gases with almost similar molecular size [2,8-10]. However, they suffer greatly from low permeability and poor mechanical strength in industrial applications. Therefore, this review will discuss on the various new concepts and fabrication technique that has been introduced to improve the physo-chemical and gas separation properties of the carbon membrane.

Up to date, the utilization of carbon membranes in pilot plant and industrial scale are still unavailable due to the higher manufacturing cost as

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compared to the polymeric membranes. Thus, in order to compensate the high-cost, the research approaches in improving the gas separation performance for various types of gases have been explored worldwide [11,12]. The focus of this review concerns on the current advances in carbon membrane development including the improvement of available membrane, improvement of fabrication technique, development of new precursor membrane, and the application of carbon membrane in various type of gas separation. To the best knowledge of the authors, most of the carbon membrane studies are utilizing the gas separation and membrane reactor system designed in laboratory-scale.

2. Carbon membrane precursor materials

Some parameters such as heat treatment conditions and pre-/post-treatment conditions would determine the microstructure and gas permeance properties of the carbon membranes [13-17]. But above all, polymer precursor has a crucial function in determining the final structure of the carbon membranes since different polymer precursors carbonized in the same conditions lead to carbon membranes with different properties. The structure of the resultant carbon membrane will affect the transport mechanism of the molecules gases. Carbon membranes derived from the polymer precursors under controlled conditions have shown attractive separation performance for several gas pairs [11,12,18-23]. Carbon membranes have also been proved to be stable for high pressure feeds up to 1000 psi, without showing any plasticization that are commonly encountered in polymer membranes [24].

The usage of polymer material as a precursor membrane has been investigated by numerous researchers. For instance, polyimides [3,7,12,19,25-27], polyfurfuryl alcohol [14], polyetherimide [20,28-30], phenolic resin [31-33], polyphenylene oxide [34,35], polyacrylonitrile [23], and formaldehyde resin [10]. Among them, the aromatic polyimide-type polymer appears to be one of the most promising materials to yield the carbon membranes with superior separation properties. It is due to the high glass transition temperature, high melting point as well as great thermal and structural stability [2].

In the last two decades, CO_2 emission has caused a lot of environmental problems. To mitigate the concentration of CO_2 in the atmosphere, various strategies have been implemented, and one of it is the use of carbon membrane to capture the CO_2 effectively. Based on literature review, among all polyimide-based polymeric membrane, (4,4'-hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based polyimides have shown good separation performance, including high productivity, high selectivity (especially excellent intrinsic CO_2/CH_4 selectivity), thermal and chemical stability, and robust mechanical properties under high pressure of natural gas feeds. However, one drawback in using polyimides is that they are plasticized under high pressure or high CO_2 content operation, which causes separation efficiency loss [36-39].

Qiu's group [40] have found out a solution for this issue through the implementation of ester bond crosslinking of 3,5-diaminobenzoic acid (DABA)-based polyimide membranes by using a diol. The separation properties of CO_2 permeability and CO_2/CH_4 selectivity for the 6FDA-mPDA/DABA (3:2)-based polymer and carbon membranes are plotted against the upper bound limit as shown in Figure 1. It is showed that the separation performance of the carbon membranes based on cross-linked polyimide was significantly higher than the precursor polymeric membrane, including both uncross-linked and cross-linked. Both the CO_2 permeability and CO_2/CH_4 selectivity of the carbon membranes prepared from 550 to 800 ºC were attractive. These results confirmed that the carbon membranes derived from 6FDA-mPDA/DABA (3:2) showed higher permeability than most carbon membranes from other reported polymers [26,41]. Apparently, the high CO_2 permeability was the results from the DABA moieties in the precursor polymer. Previous studies on thermal crosslinking revealed that as the temperature approached the decarboxylation temperature, microvoids and packing disruptions were created in the space previously occupied by the -COOH groups, and moreover, the polymer chains may be locked in [42]. Such a microvoided cross-linked structure would maintain in the subsequent carbonization process, thus resulting carbon membrane with superior gas permeability. In order to provide more decarboxylation points, which refers to more cross-linkable sites, a higher DABA group concentration in the polymer precursor structure can be used. The combination of the new decarboxylation-induced crosslinking and the major increase in cross-linkable site density illustrate that this family of 6FDA-based materials forms a platform with many possible directions for the development of carbon membranes for gas separation [40].

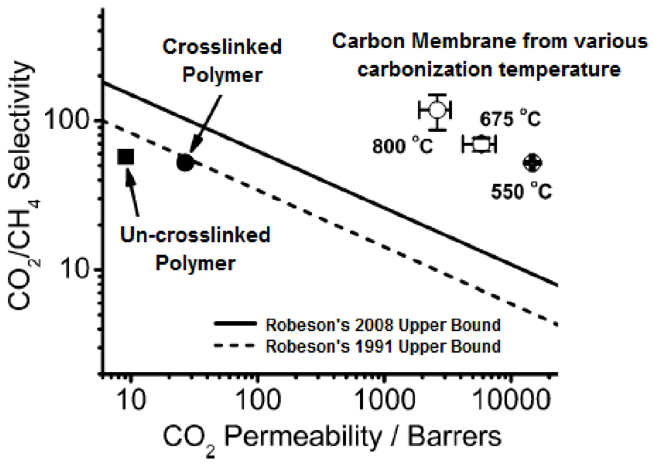

Fig. 1. Separation properties of CO_2/CH_4 for the 6FDA-mPDA/DABA (3:2)-based polymer and carbon membranes [40,43].

Besides that, N_2 removal from the natural gas is a difficult and expensive process. It is estimated that N2 removal is more challenging and costly than the corresponding CO_2 removal from coal bed methane [6]. Currently, cryogenic distillation process has been commercially used on a large scale due to the high CH_4 recovery. However, the complexity of pre-treatment and capital intensity makes it less attractive. Thus, N_2 removal using membrane technology has been studied by the researcher. So far, the report on N_2/CH_4 separation using carbon membrane is very limited. Previously, Steel and Koros [26] fabricated the carbon membrane from Matrimid at 800 ºC under vacuum and successfully obtained N_2/CH_4 selectivity of 5.89. Recently, Ning and Koros [6] proved that the N_2/CH_4 selectivity of Matrimid-based carbon membrane can be improved by treated under the Argon flow during the carbonization process. An attractive combination of N_2 permeability of 6.78 Barrer and N_2/CH_4 selectivity of 7.69 that exceeds the polymer-based membrane upper bound line was obtained for the carbon membrane treated at 800 ºC. The enhancement of N_2/CH_4 selectivity mainly results from the increase of diffusion selectivity. This is consistent with the unique structure of carbon membranes that contain a wide range of pore distribution [26]. Micropores will provide high sorption coefficients and high permeability, while ultramicropores function as the molecular sieving sites to give high diffusion selectivity and selectivity. Figure 2 indicates that the lower carbonization temperatures give poor separation performance for the N_2/CH_4. It is due to the structure of the carbon membrane that becomes more tightly packed, resulting in the ultra-micropore distribution shifting to the lower size as the carbonization temperature increased.

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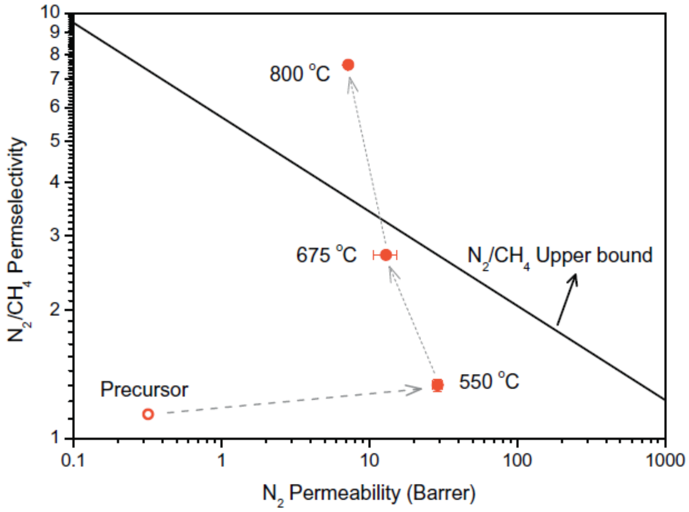

Fig. 2. Comparison of permeation results of Matrimid precursor and carbon membrane with upper bound line for N_2/CH_4 separations [6,44]..

Hosseini and Chung [41] have successfully improved the N_2/CH_4 selectivity of Matrimid-based carbon membrane by the addition of PBI polymer in the dope formulation. The PBI/Matrimid-based carbon membrane was prepared following a similar heat treatment conditions as Steel and Koros [26] studies and shows a high N_2/CH_4 selectivity approximately 8. Later, Hosseini's group [7] was explored the effects of the precursor molecular structures and the use of polymer blending to provide a guideline for the researchers in the field of designing and fabricating high performance carbon membrane for gas separation. In this comprehensive investigation, PBI was used as a principal polymer, while three engineering polyimides with different dianhydride (i.e., BPDA (Kapton), PMDA and BTDA (P84 HT)) were selected for the preparation of blends with PBI. The results show that carbon membrane derived from PBI (50%)/P84 HT (50%) offered the highest gas permeability compared to the other two blend samples. Meanwhile, carbon membrane derived from PBI (50%)/Kapton (50%) offered the least permeability for all gases.

Interestingly, although the gas selectivity of a PBI/Kapton-based polymeric membrane shows the lowest value, but it can offer the highest selectivity when it's converted into carbon membrane compared to its counterparts. This trend could be attributed to the reduction in pore size, formation of tighter and more compact structure, presence of less number of larger pores, or narrower pore size distribution upon the simultaneous application of higher degree of vacuum and increased carbonization temperature. The permeability of the carbon membrane could also be improved by increasing the Kapton content in the blend solution of PBI/Kapton up to 75 wt %. The highest gas selectivity for N_2/CH_4, CO_2/CH_4, O_2/N_2, and CO_2/N_2 of 2.47, 143.4, 12.17, and 58, respectively, was achieved. On the other hand, with the variation in the degrees of vacuum from 10^{-3} to 10^{-7} Torr, the ideal selectivity increases approximately 1.4 times accompanied by a reduction in the permeability [7]. This study has proved that the blending of suitably selected materials can enable the reconciling classes of polymers with different separation properties and physicochemical characteristics through a simple, but yet reproducible procedure. Also, the polymer blending not only can provide an opportunity for altering the properties of the constituent polymers for obtaining the synergistic properties, but also offers new features that may not be found in any of the constituents [45].

Previous works have also demonstrated an interesting advantage could be offered by employing the polymer blending technique for gas separation carbon membranes, such as PPO/PVP [46], PEI/PVP [20,47], PAN/PEG [48], PAN/PVP [48], PI/PEG [49], PI/PVP [50], PFNR/PEG [51], and PBI/PI [7,41]. Further study including the experimental, modelling and optimization of the gas selectivity and permeability on the carbon membrane derived from PBI-polyimides by applying the statistical technique has been conducted. During optimization, the key contributing factors such as polyimide precursor and blend component as well as final carbonization temperature and atmosphere was implemented as the effective response variables which could significantly enhance the efficiency of design, fabrication and performance of the carbon membrane. The findings of this research confirmed that the removal of various dianhydrides groups during carbonization would significantly affect the carbon structures and their gas permeation performance. As a result, this study shed the light on the factors of carbon membrane fabrication in the context of further exploitation of the blend membranes for gas separation and other applications [52].

Besides organic material such as polymer, carbon membrane can also be prepared by using inorganic material as their precursor membrane [53]. Metal-organic frameworks (MOFs) have emerged as a new family of gas molecular sieves, and they have attracted extensive research interest because of their highly diversified structures, tunable pore sizes and large range of porosity, and versatile functionalities. MOFs are porous crystalline materials consisting of metal ions or clusters interconnected by a variety of organic linkers. MOFs (ZIFs) are the excellent candidates for the preparation of nanoporous carbons [54,55]. Following the successful preparation of the MOF-based nanoporous carbons, Zhong and team [56] pursued the preparation of the MOF-based carbon composite membrane. In this work, a new leaf-shaped two dimensional (2D) zeolitic imidazolate framework (ZIF) (ZIF-L) was used. As illustrated in Figure 3, the preparation procedure of the carbon composite membrane comprised of three steps.

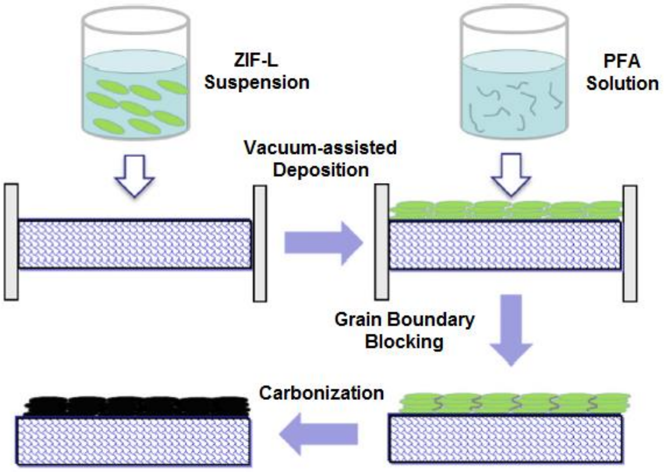

Fig. 3. The schematic illustration of the procedures for the preparation of ZIF-L derived carbon composite membrane on a porous alumina disk [56].

Gas separation results showed that the carbon composite membrane had a moderate H_2/N_2 and the H_2/CO_2 ideal selectivity of 6.2 and 4.9, respectively, with a very high H_2 permeance (~3.5 x 10^{-6}mol/m.s.Pa). As compared with the polymer-based carbon membranes, a much higher H_2 permeance was obtained from the ZIF-L-based carbon membrane. This is because small-molecule 2-methylimidazole coordinated with Zn^{2+} in ZIF-L structure decompose more easily than the organic polymers, thus a larger pores were created. This novel method was to synthesize the functional carbon composite membranes from ZIFs (or MOFs), providing an important platform for energy and environment-related applications [56].

Among polymeric precursors mentioned above, the aromatic polyimide type polymer appears to be one of the most promising materials to yield carbon membranes with superior separation properties. Although a substantial amount of article has been published on the gas separation performance of the carbon membrane prepared from various types of polymer precursor membranes (see Table 1), polyimide-based carbon membrane shows the most promising performances.

Table 1
Summary of polymer precursor selection.

Polymer precursor	Properties	Ref. (s)
Polyimide	• Limited (expensive and need to synthesize manually in the laboratory) • Good for H_2/CH_4, CO_2/N_2, O_2/N_2, CO_2/CH_4, N_2/CH_4, and C_3H_6/C_3H_8 separation • Gas transport through the membrane occurs according to the molecular sieving mechanism • Commercially available polyimide; Kapton, Matrimid, and P84 co-polymer (BTDA-TDI/MDI)	3,6, 7, 12, 19, 25-27, 36-39, 40, 41
Polyetherimide (PEI)	• Good chemical and thermal stability • Impressive separation factors • Give high carbon yield • Good for CO_2/CH_4 separation	20, 28-30
Polyacrylonitrile (PAN)	• Conquer nearly 90 % of all worldwide sales of carbon fibers • Low O_2/N_2 selectivity	23
Phenolic resin	• Inexpensive polymers • Good separation of hydrocarbon gas mixtures such as alkenes/alkanes and n-butane/iso-butane	31-33
Poly(furfuryl) alcohol (PFA)	• Simple molecular structure and formation mechanism • Only can be used for preparing supported membrane • Good for O_2/N_2 separation	14
Polymer blend	• Blending of two polymers with different thermal properties is preferably used (e.g.: PPO/PVP, PEI/PVP, PAN/PVP, polyimide/PVP) • Create a wide range of pore size distribution (ultra-micropore, micropore, macropore) • Enhanced the gas permeability	7, 41, 20, 46-51, 56

3. Carbon membrane configuration

In general, carbon membranes can be divided into two categorized: unsupported carbon membranes (flat, capillary or hollow fiber) and supported carbon membranes (flat or tube) [57]. Among them, the carbon hollow fiber membranes are preferable due to their low cost, high packing density, and high separation performance. However, the brittleness of carbon hollow fiber membranes makes them difficult to handle and limits their applications in the membrane separation [2,24,58]. In order to overcome this issue, recent research efforts have focused on the supported carbon membrane. Supported carbon membrane has been regarded as a favoured choice for commercial application due to their thin separation layer and high mechanical strength. Normally, the supported carbon membranes are fabricated by coating a polymeric precursor layer on a support membrane with high thermal resistance and high mechanical strength. It is then followed by the thermal treatment (carbonization) process of the supported polymeric membranes.

There are several coating techniques that can be used to fabricate the supported carbon membranes such as dip-coating [32,33,59,60], spray-coating [61,62], spin-coating [4,9,63,64], and vapour deposition polymerization [65]. Ideally, the top layer is a high performance layer that controls the selectivity, while the porous substrate improves the permeation rate and mechanical strength. Nevertheless, one of the challenges that were faced by the researchers during the fabrication of supported membrane is the interfacial adhesion. In order to improve the interfacial adhesion between the support material and the carbon layer, the support material can be modified prior to the polymer coating. The study on the modified support has been studied by Li and group [11]. In this study, a carbon interlayer between the thin separation layer and the support of carbon membrane has been implemented.

Generally, during the membrane fabrication, it is important to avoid the membrane defects (cracks and pinholes) to maintain the membrane selectivity. For this purpose, it is necessary to repeat the coating and carbonization procedure for several times [10,31,66-68]. The reports on the development of the defect-free supported carbon membrane by a single coating-carbonization step are very limited in the literature [11,31,32,69]. Teixeira and coworkers [32] proposed the incorporation of low cost ceramic nanoparticles of boehmite in the phenolic resin to produce a highly permeable composite carbon membrane with defect-free in a single coating-carbonization cycle. This membrane was prepared from dip-coating of the mixed solution (phenolic resin, boehmite, and NMP) over α-Al_2O_3 support tubes. The membrane consists of two layer which is substrate (supporter) and carbon layer. A carbon layer was formed from the decomposition of the resin and dehydroxylation of boehmite. It is found that, the studied carbon membrane is more suitable for separating bulk molecules such as C_3H_6 and C_3H_8 and less suitable for separating O_2 from N_2. Recently, this group [33] have prepared the supported carbon membrane with varying phenolic resin and boehmite compositions, leading to the formation of carbon membranes with different carbon/Al_2O_3 ratios. It was observed that an increment in the carbon/Al_2O_3 ratio led to the carbon membrane with higher volume of micropores and higher average length of these micropores.

Consequently, the membranes with higher carbon/Al_2O_3 ratio exhibited higher permeabilities toward the probe gases and lower selectivity. Results indicated that the high C_3H_6 permeability of 776 Barrer and considerable C_3H_6/C_3H_8 selectivity of 9.9 was obtained when the loading amount of boehmite used were increased. The gas permeability for CO_2 and O_2 is significantly increased approximately 76 and 86 %, respectively when the percentage of boehmite in the formulation increased from 0.5 to 1.2 wt %. Figure 4 illustrated the comparison of the permeation results of the resultant supported carbon membranes with the upper bound curves for C_3H_6/C_3H_8 separations [33]. Similar approach was also been used recently by Rodrigues and co-worker [10]. However, a good separation performance for O_2/N_2, H_2/N_2, and He/N_2 has been achieved when formaldehyde resin loaded with the boehmite nanoparticles is used as the precursor.

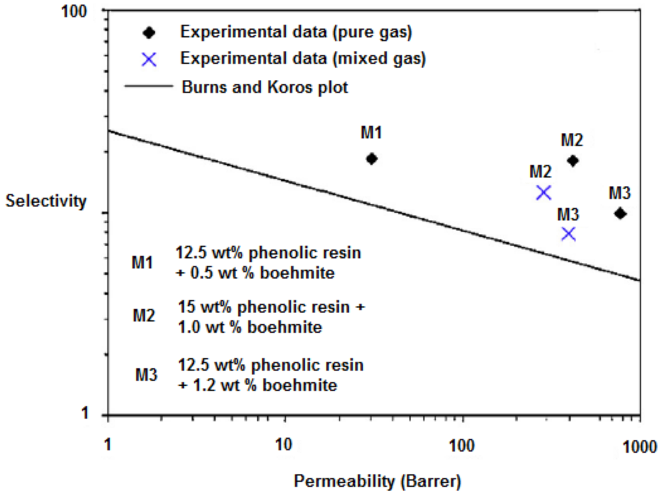

Fig. 4. Comparison of permeation results of the membranes with upper bound curves for C3H6/C3H8 separations [33,44,70].

Moreover, in order to fabricate the defect-free carbon membrane, not only the fabrication process but also the substrate material plays a key role. An ideal substrate should have a defect-free surface with low roughness, high porosity and small pore size apart from the other required properties such as physical strength, gas diffusivity and temperature stability. The porous ceramics are the most common substrate materials, so far, because of their outstanding stability and abundant market availability. In general, most of the micro-and nano-porous ceramics are manufactured by depositing one or more fine porous ceramic layers on a macroporous ceramic base through the sol-gel approach, forming an asymmetric structure [31,33]. Although the high quality of the substrate material helps to suppress the membrane defects and ease the membrane fabrication difficulty, their high cost will eventually hold back the perspectives of the membrane applications.

Such a situation motivates the development of the substrate materials that are low in cost but good enough for carbon membrane fabrication. For example, Wang and coworkers [71] have introduced an intermediate gel coating technique to reduce the surface roughness and pore-size as well as to repair the surface defects of the low-cost tubular macroporous α-Al_2O_3 substrate. In this study, the Al_2O_3 tubes were coated with the AlOOH (pseudo-boehmite) sol through an intermediate gel coating prior to the dip-coating of PFA polymer solution on the surface of the substrate. The membranes were then carbonized up to 700 ºC under the Ar atmosphere for 4 h with a ramp of 1 ºC/min, followed by a cooling process to room temperature under Ar. Normally, support membrane with a pore size below 1 µm might be directly used, while those with a larger pore size may have to be modified in advance, and the sol-gel process is the most popular technique.

The photographs and SEM micrographs of fresh Al_2O_3 and gel-Al_2O_3 are demonstrated in Figure 5. It can be seen that the surface of fresh Al2O3 is rough, which is composed of irregular Al_2O_3 particles whereas gel-Al_2O_3 showed highly smooth and defect-free structure. The SEM images of surface and cross-section view of the carbon membrane prepared on the gel-Al_2O_3 substrate are illustrated in Figure 6. A smooth surface as well as uniform and well anchored carbon layer on the Al_2O_3 substrate was obtained. This is because the gel film of AlOOH could prevent the penetration of PFA during the coating and heat treatment process. The gas permeation test data indicates that the gas permeation rates are in the following order of H_2 (44 x 10^{-9} mol/m^2.s.Pa) > CO_2 (20 x 10^{-9} mol/m^2.s.Pa) > O_2 (9.6 x 10^{-9} mol/m^2.s.Pa) > N2 (1.8 x 10^{-9} mol/m^2.s.Pa), which is in reverse order of their kinetic molecular diameters. This is in accordance with a typical characteristic of molecular sieving mechanism. The selectivity of 24, 11, and 5.3 was obtained for gas pairs H_2/N_2, CO_2/N_2, and O_2/N_2, respectively. It can be concluded that the AlOOH gel is highly effective in the modification of the substrate surface and facilitates the formation of high quality PFA film as the membrane precursor [71]. The resultant carbon membrane seems to be permeable and selective among the other supported carbon membranes reported in the literature [31,72-75].

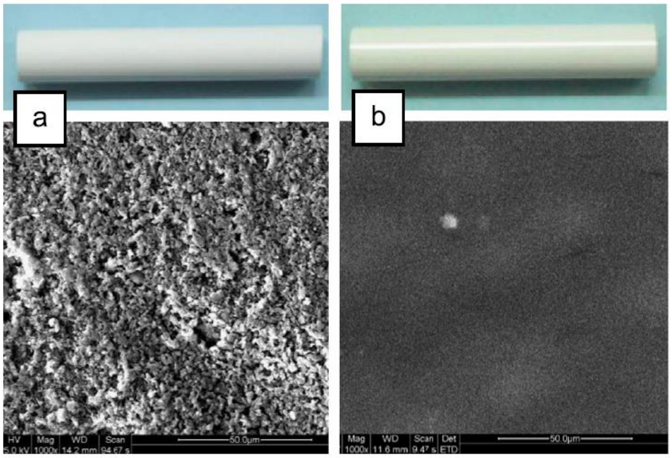

Fig. 5. Photographs and SEM micrographs of (a) fresh Al_2O_3 and (b) gel-Al_2O_3 [71].

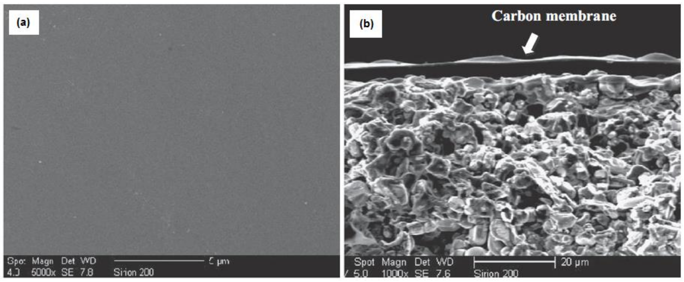

Fig. 6. SEM microphotographs of the (a) surface and (b) cross-section of carbon membrane prepared on gel- Al_2O_3 substrate [71].

In other study, the carbon membrane was used in the modification of disk of porous α-Al_2O_3 substrate (supporter) to improve the mechanical stability and separation performance of the composite membrane. A carbon matrix derived from PPO and carbonized up to 600 ºC is fabricated to form a gutter layer following the coating-carbonization procedures. The gutter layer is served as a channeling and adhesive medium between the selective layer (polymer membrane) and the supporting substrate. A smooth and continuous thin carbon layer is produced for porous substrate modified by the PPO even though the PPO has less weight remaining after the carbonization at temperature above 500 ºC. This is because the PPO solution is prepared with chloroform solvent, which has a low boiling point and high vaporization rate, with the result that the polymer-rich phase solidifies rapidly without penetrated into the porous substrate. The result shows that the pore volume of the carbon layer-modified substrate was increased compared with the original substrate. Based on gas permeation data, the composite membrane prepared from the carbon layer-modified substrate exhibits higher CO_2/CH_4 selectivity than those prepared without support. The CO_2 permeance is enhanced when the carbon layer-modified substrate is used [4]. Similar approach for H_2 separation has been reported by Weng et al., [76]. The carbon layer on the porous ceramic substrate was derived from poly (bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) (PBNPI) and carbonized up to 600 ºC. High selectivity of H_2/CH_4 and H_2/N_2 of 31.8 and 37.1, respectively were achieved for the composite membrane with the carbon layer between polymeric layer and porous ceramic substrate [76].

Recently, Cheng and coworkers [9] in 2014 have introduced an alternative method in the coating procedure using the plasma-enhanced chemical vapour deposition (PECVD). PECVD can be used to form a uniform ultrathin coating on a supported substrate [77-79]. In PECVD, gaseous molecules of the monomer precursor are ionized and then polymerized, during high-energy electrons released to break the monomer structure and free radicals are produced. In order to study the effectiveness of PECVD, two types of supported carbon membrane derived from PFA and FA monomer is fabricated using different techniques, including spin-coating and PECVD. The results show that the supported carbon membrane prepared from PECVD method exhibits much higher gas separation performance than those prepared from the spin-coating. The selectivity of CO_2/N_2 and O_2/N_2 increased about 60 % and 18 %, respectively when the PECVD is implemented. Besides that, the PECVD method only takes one-third of the time required for two cycles of spin-coating to form a defect-free and high performance supported carbon membrane. The deposition layer thickness for the supported membrane from PECVD is indicated to be decreasing from 0.7 to 0.12 µm when the carbonization temperature increased [9].

4. Methods for improving the performance of carbon membrane

Two key parameters that characterize the separation performance of membranes: the permeability and the selectivity. The permeability characterizes the ability of the membrane to be permeated by a solute while the selectivity characterizes the ability of this particular membrane to discriminate the permeation transport of a species compared to the mixture [80]. Recently, blending techniques of precursor formulation with inorganic materials have spawned research efforts across the globe, leading to thousands of publications that describe the compatibility and effectiveness of this method in the gas separation application. So far, the feasible inorganic materials used in carbon membrane preparation are silica [81], zeolite [82], ceramic nanoparticles (boehmite) [10,32], silver [83], and carbon nanotube (CNT) [20,84].

Nevertheless, the incorporation of inorganic materials would usually contribute to an inevitable embrittlement due to the formation of phase separation or micro-cracks along the interfacial boundary of dispersed materials in the host membrane matrix [12]. It is indicated that the selection of inorganic material also plays an important role in the preparation of carbon membrane with both outstanding gas permeability and selectivity. Therefore, an attempt to prepare the carbon membrane would be good when an inorganic material with better carbon-compatible property such as carbon molecular sieve (CMS) [85] and ordered mesoporous carbon (OMC) [12] is used. Intensive researches on the OMC materials have been made over the past decades. The most effective method used for the preparation of this material with well-defined pore structures and narrow pore size distribution are involving hard and soft-templates [86].

For instance, OMC synthesized by the hard-templating method that has been used by Zhang and co-worker [12] in the carbon membrane preparation. A defect-free flat sheet carbon membrane was produced by blending the OMC powder in the polyimide acid solution. The pyrolysis was performed at a heating rate of 1 ºC/min in N_2 flow up to 650 ºC. Results indicated that the thermal stability of polyimide is significantly enhanced by incorporating OMC in the membrane matrix. As compared to the carbon membranes derived from pure polyimide, the permeability of polyimide/OMC-based carbon membrane markedly increases by 3.4, 15, and 10.2 times for H2, CO_2, and O_2 gas, respectively. It is revealed that OMC would act as a pore forming agent which are beneficial for increasing the gas diffusivity through the carbon materials.

Shortly after that, an OMC synthesized by the soft-templating approach has successfully been executed to prepare a carbon interlayer between the thin separation layer and the support of carbon membrane. The one-step coating carbon membrane can be prepared on the support modified by the OMC interlayer. The results showed that the OMC interlayer can effectively reduce the surface defects of the support with large pore sizes. OMC interlayer can also improve the interfacial adhesion of the support to thin separation layer, which usually is the challenge in the supported membrane preparation. The first layer of OMC was coated on the disk-shape support and pyrolyzed at 800 ºC. The second layer of polyamic acid precursor was then coated and pyrolyzed at 700 ºC. The highest H_2 permeance of $545x10^{-10}$ mol m-2s-1Pa-1 was achieved together with high H_2/N_2 selectivity of 76. Results revealed that the gas permeance of the carbon membrane prepared with the OMC interlayer was higher than those carbon membrane prepared without the OMC interlayer [11].

On the other hand, OMC has also been developed as a self-standing membrane [87] and supported membranes on different substrates [88,89]. OMC membranes have attracted considerable attention over the last decades due to their ordered pore structure, narrow pore size distributions, and developed mesopores that are controllable in the size ranged 2-10 nm. It is reported that gas transport mechanism of these membranes is dominant by the Knudsen diffusion. Thus, the researcher has claimed that these types of carbon membrane hold a great promise regarding to the other application such as nanofiltration, membrane reactors, and chemical sensors [87,90] as well as bioseparations, and electrode materials for batteries [89]. A novel OMC membrane prepared by using the resorcinol and formaldehyde (RF) sol-gel method has showed a sharp pore size distribution in the mesopore region, which can be controlled within the range of 5.48-13.9 nm by adjusting the resorcinol (R) to catalyst (C) molar ratio. The prepared carbon membranes were found to be crack-free since there was no dependence of He and N_2 permeances on the feed pressure was observed according to the Knudsen diffusion mechanism. These membranes exhibited relatively high permeances for the gases with different molecular weights (H_2, He, CH_4, N_2, CO_2, and CF_4) due to their well-developed mesoporous structure [87].

Recently, a new method to prepare the OMC hollow fiber membranes through a confined soft templating route has been developed. In this case, the carbon membranes were prepared by the impregnation of precursor solution containing the phenolic resin and amphiphilic triblock copolymer (Pluronic F127) into the voids of commercially available PVDF ultrafiltration hollow fiber membranes. Upon solvent evaporation, the phenolic resin and surfactant self-assembled into ordered mesostructures within the polymeric membrane. After drying and carbonization, the mesoporous carbon hollow fiber membranes were obtained. Figure 7 shows the SEM images of the PVDF hollow fiber membrane, impregnated hollow fiber membrane, and OMC hollow fiber membrane. It is revealed that the thickness of the membrane wall is reduced due to the thermal shrinkage and the unfilled radical pore channels can be observed at the outer edge in the cross section of the OMC hollow fiber membrane. Based on the pure gas permeation tests, the results indicated that the diffusion of gases through the OMC hollow fiber membrane is governed by the Knudsen diffusion, which confirms the defect free characteristic of the prepared membrane [90].

In addition, carbon membrane derived from the resorcinol-formaldehyde resin, a low cost precursor, loaded with boehmite nanoparticles have been prepared by Rodrigues and coworkers [10]. The result found that the gas permeance increases as the temperature increases. This reveals that the gas transport through the prepared membrane is an activated diffusion process, as expected for a molecular sieve mechanism. As shown in Figure 8, the gas permeation data obtained were inserted into the trade-off plot devised by Robeson [44] to show the upper bound limits for O_2/N_2, He/N_2, H_2/N_2, and CO_2/N_2. The carbon membrane prepared at 500 ºC showed promising results for the separation of O_2/N_2 (permeability: 8.7 Barrer, ideal selectivity: >11.5), H_2/N_2 (permeability: 445.6 Barrer, ideal selectivity: >586), and He/N_2 (permeability: 413.8 Barrer, ideal selectivity: >544). This is because, a large number of micropores with larger dimensions were obtained for carbon membrane prepared at 500 ºC as compared to those prepared at 550 ºC (refer to Figure 9). It can be seen that the studied carbon membranes present ultramicropores (0.3-0.7 nm) and larger micropores (0.7-1.0 nm). However, carbon membrane prepared at 550 ºC has a large number of micropores and a larger volume of ultramicropores, which gives higher ideal selectivities and He permeance than those produced at 500 ºC.

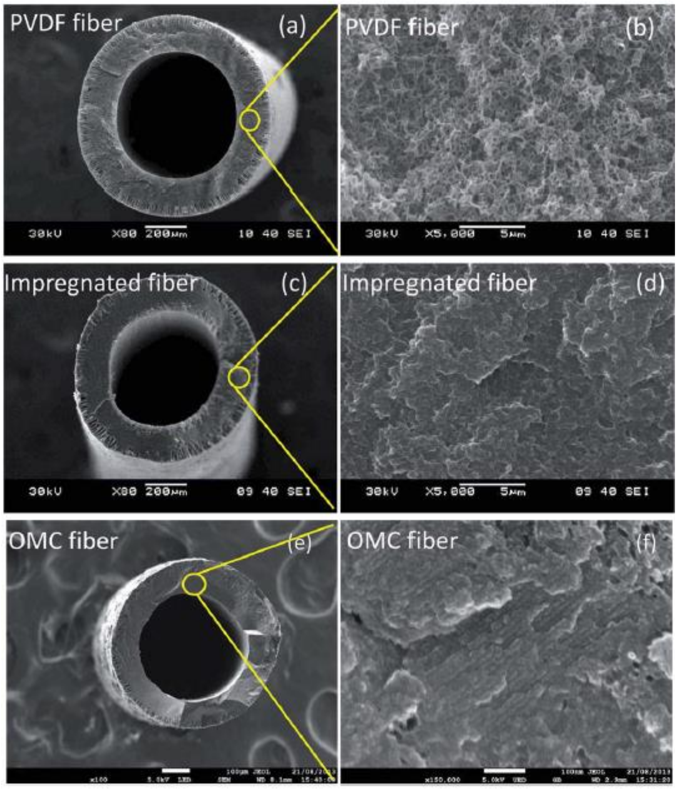

Fig. 7. SEM images of the (a, b) PVDF hollow fiber membrane, (c, d) impregnated hollow fiber membrane, and (e, f) OMC hollow fiber membrane [90].

5. Carbon membrane in membrane reactor

Traditionally, H_2 is produced via steam reforming of hydrocarbons such as methane, naphtha oil or methanol/ethanol. In industrial scale, most of the H_2 (more than 80%) is currently produced by the steam reforming of natural gases carried out in large multi-tubular fixed-bed reactors. The main drawbacks of steam reforming are that all reactions are equilibrium limited and produce a H_2 rich gas mixture containing carbon oxides and other by-products. Consequently, in order to produce pure H_2, these chemical processes were carried out in a number of the reaction units (typically high temperature reformer, high and low temperature shift reactors) followed by the separation units (mostly pressure swing adsorption). The large numbers of different process steps have made a decrement in the system efficiency and make it scaled-down to be uneconomical [91].

Among different technologies related to production, separation and purification of H_2, the innovative integrated system that is so-called the membrane reactor seems to be the most promising and the membrane technology nowadays is increasingly considered as a good candidate for the substituting conventional systems. Membrane reactor is an engineering system in which both reaction and separation are been carried out in the same device. This process can bring various potential advantages such as reduced capital costs (due to the reduction in size of the process unit), improved yields and selectivity (due to the equilibrium shift effect) and reduced downstream separation costs (separation is integrated). The success of membrane reactors for the H_2 production depends crucially on: (i) the advances in the membrane production methods for the production of thin membranes with high H_2 fluxes and high H_2 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 the membranes [91].

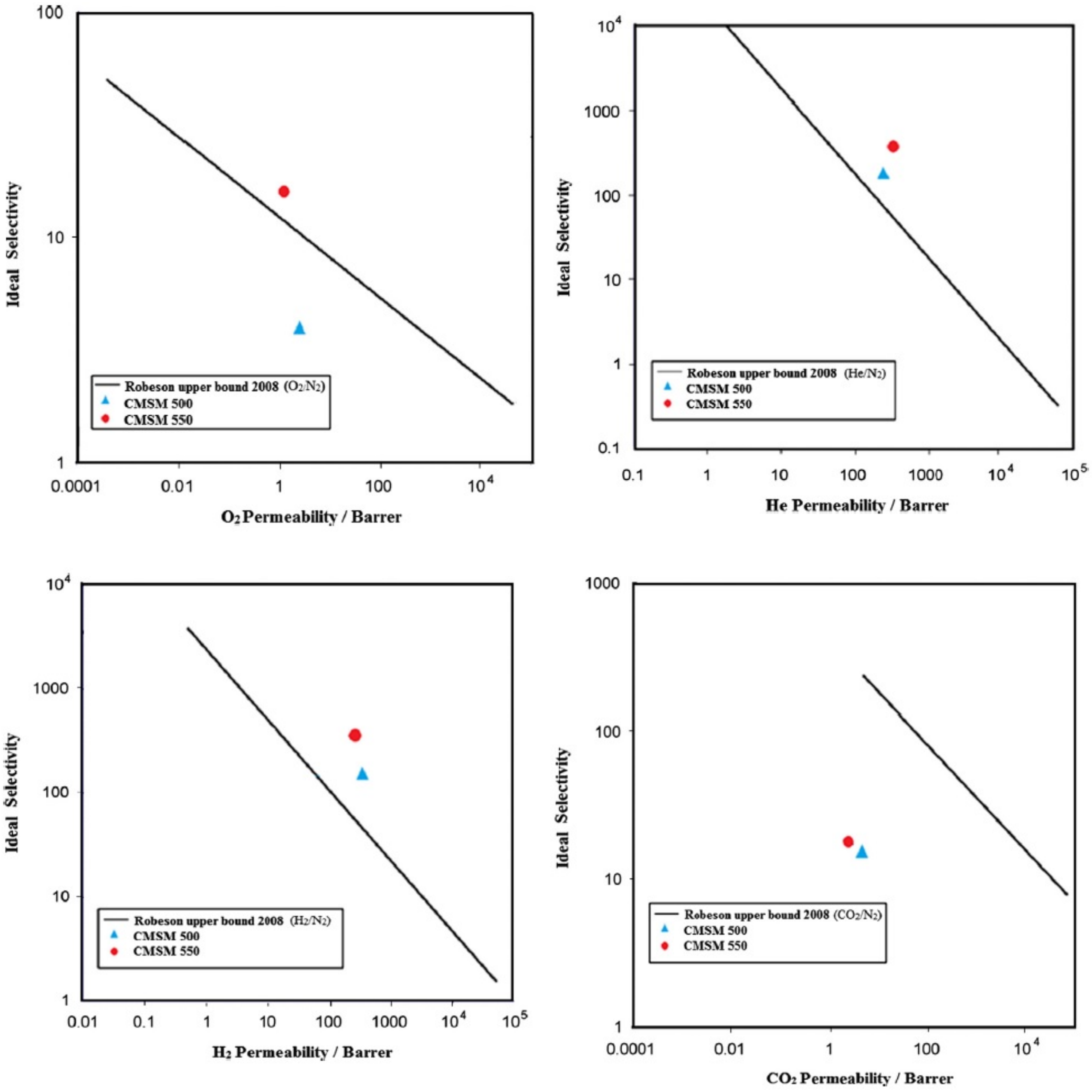

Fig. 8. Comparison of permeation results of the membranes with upper bound curves for O_2/N_2, He/N_2, H_2/N_2, and CO_2/N_2 separations [10,44].

There have been many applications of catalytic inorganic membrane reactors for reactions involving H_2, such as hydrogenation and dehydrogenation [92], methane steam reforming [93], and water gas shift (WGS) [94]. Nowadays, the researches on the use of carbon membrane in WGS have been extensively conducted [60,95-100]. Besides the carbon membrane, several different types of H_2-selective inorganic membranes have also been considered for this purpose, including Pd and its alloys [94,101], silica [102], and zeolite [103]. The WGS reaction is exothermic and its equilibrium conversion decreases with the temperature. Therefore, in order to overcome the equilibrium limitations and to increase the CO conversion at practical space velocities, two reactors were deployed, one operating at high temperature and the other at a lower temperature [60]. In overall, this process is complex and energy-intensive thus it is not very attractive, particularly in the context of carbon capture and storage. In order to optimize the WGS reactor design, the membrane reactors have been utilized. It is reported that the need of the dual WGS reactor system can be avoided when the membrane reactor is implemented due to the higher CO conversion along with the enhanced H_2 recovery and purity [91].

The use of a single carbon membrane in the laboratory-scale WGS-membrane reactor has successfully was verified by Liu's group [100] from USA to treat a synthetic stream containing substantial quantities of contaminants such as H_2S and NH_3, typically countered in coal and/or biomass gasifier off-gas. The carbon membrane reactor performance has been investigated for a range of pressures and sweep ratios, and showed higher CO conversions and H_2 purity compared with those traditional packed-bed reactor [100,97,98]. Figure 10 shows the experimental set-up and carbon membrane reactor module used in the carbon membrane reactor experiments [97]. In addition, the carbon membrane has demonstrated good stability in continuous reactor experiments that lasts over a month [100].

Recently, an 86-tube carbon membrane bundle has been developed and successfully tested at multiple field tests, which focused on demonstrating the H_2 separation and contaminants removal from the coal-derived and/or biomass-derived raw syngas without gas pre-treatment. The findings show that the high gas separation efficiency of the membranes and the successful ceramic potting offer a viable solution for the commercialization of tubular carbon membranes for high-temperature and high-pressure gas separations. There is no membrane degradation is observed in the presence of H_2S and the other syngas contaminants during the tests. This confirmed that the carbon membrane exhibits a high chemical stability. Both H_2 concentration in the permeate and reject sides during the test with a single and bundle carbon membrane tube are shown in Figures 11 and 12, respectively [60].

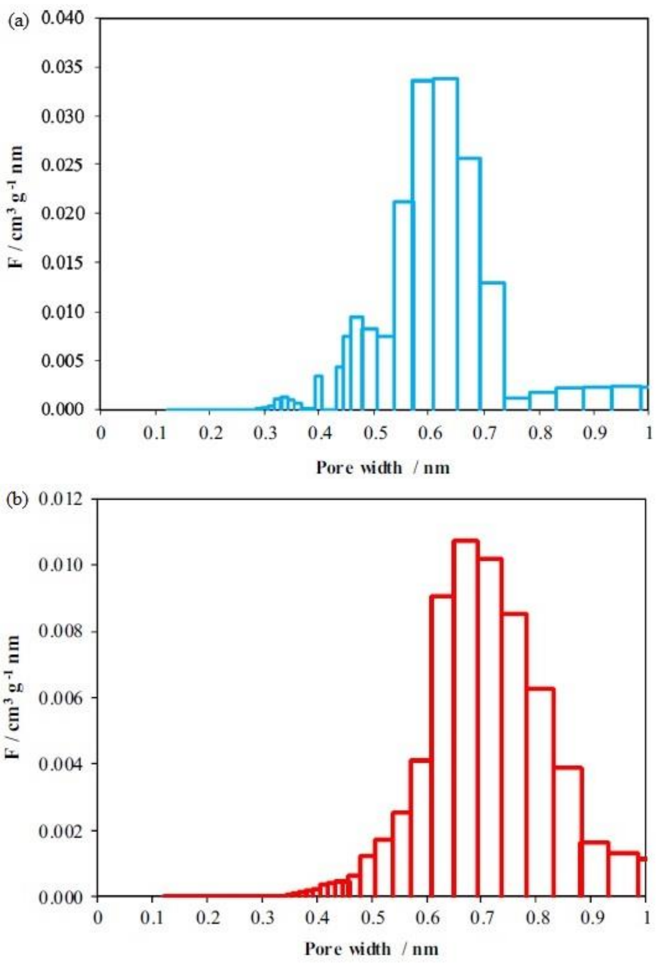

Fig. 9. Pore size distribution for carbon membrane prepared at (a) 550 ºC (b) 500 ºC [10].

It is indicated that the H_2 purity in the permeate stream (from the 2 h testing point onwards) was consistently higher than 95 % when the single tube carbon membrane was used. The stage-cut for most of the run fluctuates between 10 % and 20 %. The calculated H_2 recovery in the ranges of 18 to 36 % was obtained. In the case of carbon membrane bundle, for most of the run, the H_2 concentration in the permeate stream was consistently enriched to ~ 50 to 65 % from a H_2 concentration of ~ 5 to 7 % in the feed as received from the gasifier without any artificial enhancement. The H_2S concentration in the feed (after being spiked with H2) was typically ~ 200 ppm (dry-basis), and was reduced in the permeate stream to ~ 35 ppm. Near the end of the run, the H_2 concentration in the retentate and permeate streams for the carbon membrane bundle is shown in Figure 13. It is observed that for the feed concentration ranged from 36 to 43 %, while the H_2 concentration in the permeate ranged from 95.0 to 95.4 % was obtained [60].

In the case of methane steam reforming reactors, the comparison between traditional reactors with a carbon membrane reactor has been studied by Zhang and coworkers [62]. The schematic view of the carbon membrane reactor together with the experimental system is illustrated in Figure 14. The results indicated that a higher methanol conversion (~99.9 %) and lower CO yield has been achieved by the carbon membrane reactor. Regarding the permeation selectivity, the H_2 selectivity is quite high (~ 97%) in the carbon membrane reactor. These promising results justify the need of a detailed study of the potential advantages of carbon membranes over the other types of inorganic membrane especially, the Pd membrane. In accordance to this matter, the analysis and comparison study of both Pd and carbon membrane reactors for the methanol steam reforming was conducted. The comparison was focused on the analysis of the methanol conversion, H_2/CO reaction selectivity, CO concentration at the permeate side, and H_2 recovery. Based on the results, the carbon membranes present higher permeability, higher H_2 recovery, and lower selectivity [62].

In terms of production cost, the Pd membranes are more expensive than the carbon membrane but in terms of performance, the Pd membranes exhibit much higher selectivity towards H_2 compared to the carbon membrane. A comparison study of the performance of both Pd and carbon membrane reactors are shown in Figure 15. It is clearly observed that for an intermediate relative permeate pressure region, the carbon membrane reactor presents better performance than the Pd membrane reactor, concerning the methanol conversion. In fact, the permeate pressure in the carbon membrane reactor does not have to be as low as the one in the Pd membrane reactor to achieve the same conversion. In addition, a combination of carbon and Pd membrane reactor has revealed some advantages towards the carbon membrane reactor, specifically higher H_2 recovery and keeping the CO concentration at the permeate side below 10 ppm. In comparison to the Pd membrane reactor, this membrane combination allows the use of smaller membranes and higher feed flow rates, without prejudice of the membrane reactor's performance [99].

Furthermore, the catalytic carbon membrane reactors for the dehydrogenation reactions of cycloalkanes and methylcyclohexane have been applied by previous works [59,104,105]. The dehydrogenation reactions of organic chemical hydrides are endothermic and equilibrium reactions. In this process, the equilibrium conversion is also limited by the thermodynamics and increases with temperature. Dong et al., [104] have prepared H_2-permeable carbon membranes on a porous alumina plate support from furfuryl alcohol (FFA) by a vapor-phase synthesis. A uniform pores with a size of 0.3 nm was achieved from the membrane carbonized at 800 ºC. The prepared carbon membranes have showed very high separation factors for H_2/CO_2, H_2/N_2, and H_2/CO binary gas mixtures. On the other hand, for the separation of H_2/methylcyclohexane and H_2/toluene from the dehydrogenated chemical of methylcyclohexane, larger pore sizes (< 0.6 nm) are favourable for improving a H_2 permeance since the kinetic diameters of the methylcyclohexane and toluene are about 0.60 nm. Recently, FFA-based carbon supported membrane has been implemented in the membrane reactor for the dehydrogenation of the organic chemical hydrides (methylcyclohexane) application, for the first time by Hirota and team members [59]. A schematic diagram of the membrane reactor used is shown in Figure 16.

During the experiment, methylcyclohexane (feed material) was sent to a vaporizer and carried to the membrane. The purity of H_2 obtained from the permeation side was measured by the gas chromatograph and the conversion of methylcyclohexane was determined from the concentration ratios of unreacted methylcyclohexane. Prior to the performance test, the prepared carbon membrane was activated under the H_2, CO_2, O_2, and steam to improve the H_2 permeance. The pore sizes of the carbon membrane are increased from 0.3 to 0.45 nm, resulting in an increase of H_2 permeance from 3.6 x 10^{-9} to 1.6 x 10^{-8} mol/m^2.s.Pa with high permselectivity of H_2/CF_4 (>1500), when the activation by H_2 and steam was performed. In contrast, the pore sizes of the carbon membrane were not changed for the activation under the CO_2 and O_2. These results had proved that the microporous carbon membranes are one of the promising membranes for the dehydrogenation of chemical hydrides in membrane reactors [59].

6. Conclusions

The recent progress of carbon membrane from materials to application is illustrated in details. An appropriate combination of material and engineering practice determines the achievement of good performance membrane operations. While tremendous progress has been made in the production of carbon membrane, exciting opportunities remain for adapting new materials and methods to optimize their separation properties particularly for the gas separation. Despite the outstanding development in the material science, polymer membranes, already widely utilized at the industrial level and remain to be the best option. However, as a function of aggressive environment operations and purity level requested, the choice of membrane material has changed to carbon membrane materials. According to the previous researches, carbon membranes have shown a remarkable accomplishments in terms of gas separation performance and robustness in high-temperature and high-pressure operation to mitigate the gas emission crisis. The whole knowledge

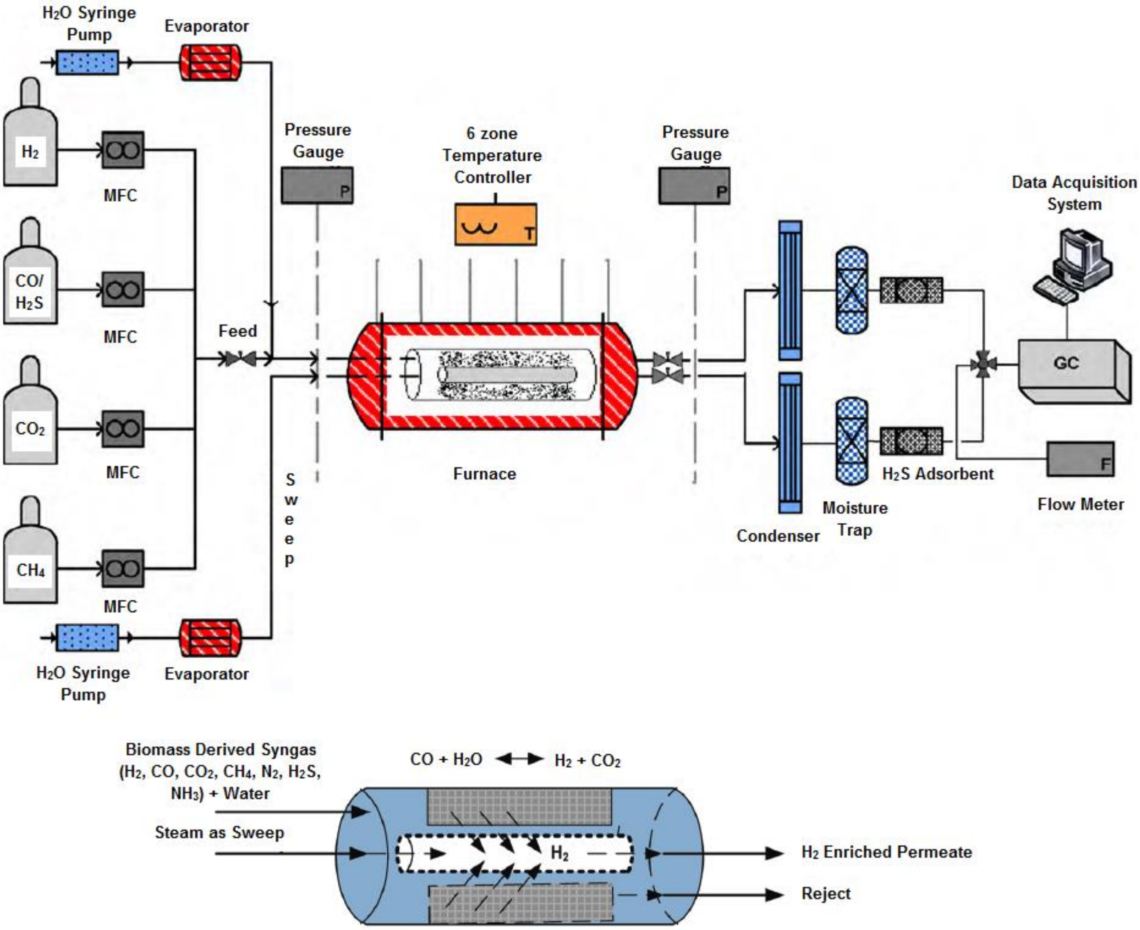

Fig. 10. Experimental set-up and carbon membrane reactor module used in the membrane reactor experiments [97,98].

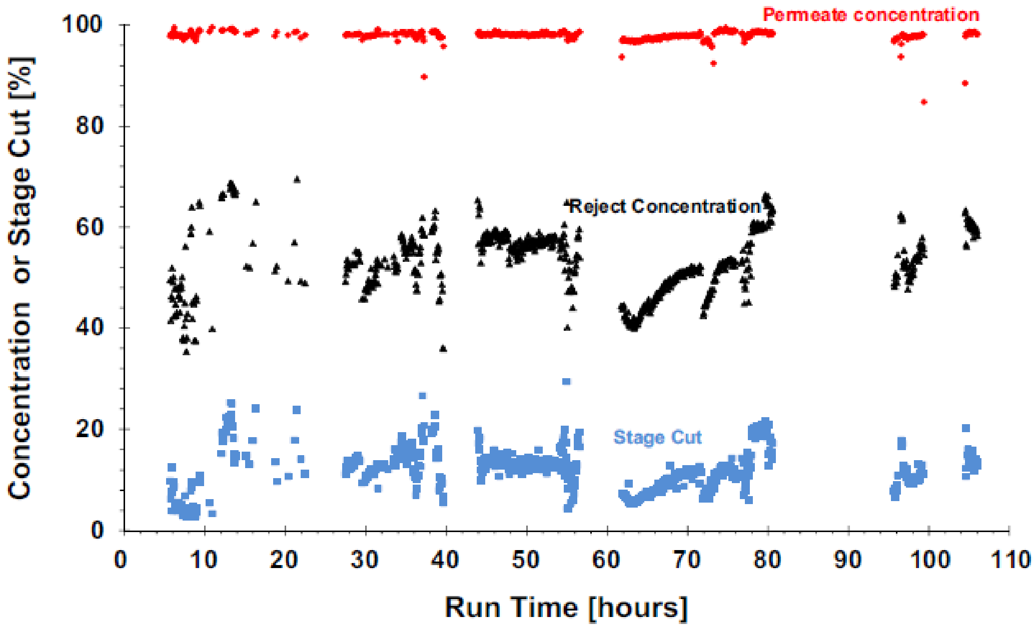

Fig. 11. H_2 concentration (dry-basis) in the permeate and reject sides and stage-cut during the test with a single carbon membrane tube [60].

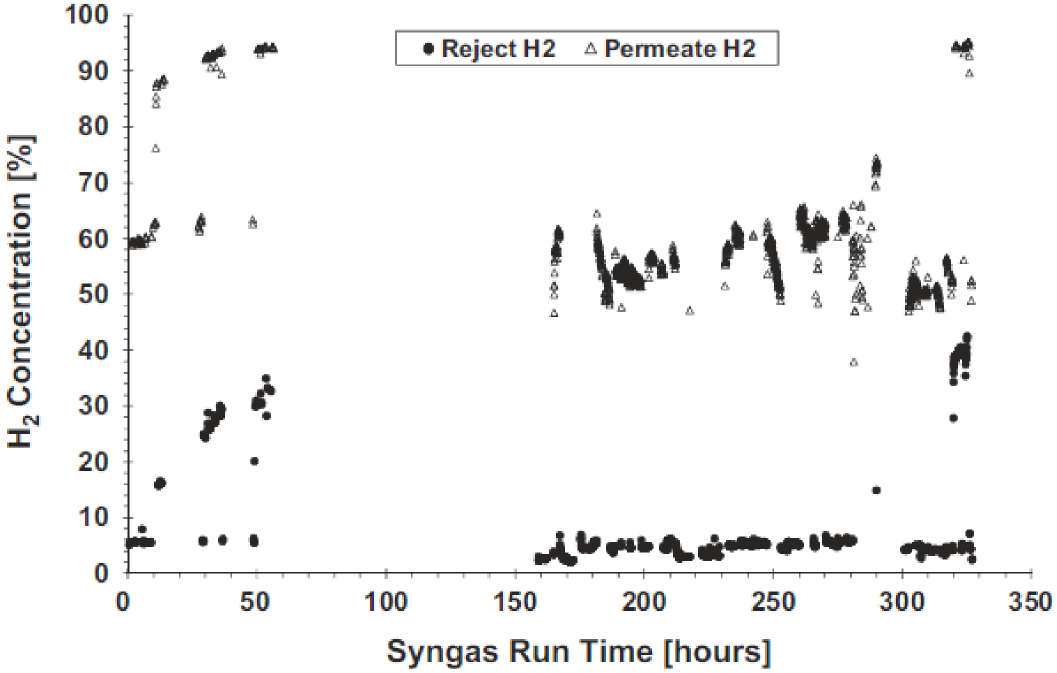

Fig. 12. H_2 concentration (dry-basis) in the permeate and reject sides during the testing of the carbon membrane bundle (250 C, 14.8 bar, 150-250 l/min, feed composition; 6.49% H_2, 74.03% N_2, 9% CO, 9% CO_2, 0.9% CH_4, and 312 ppm H_2S) [60].

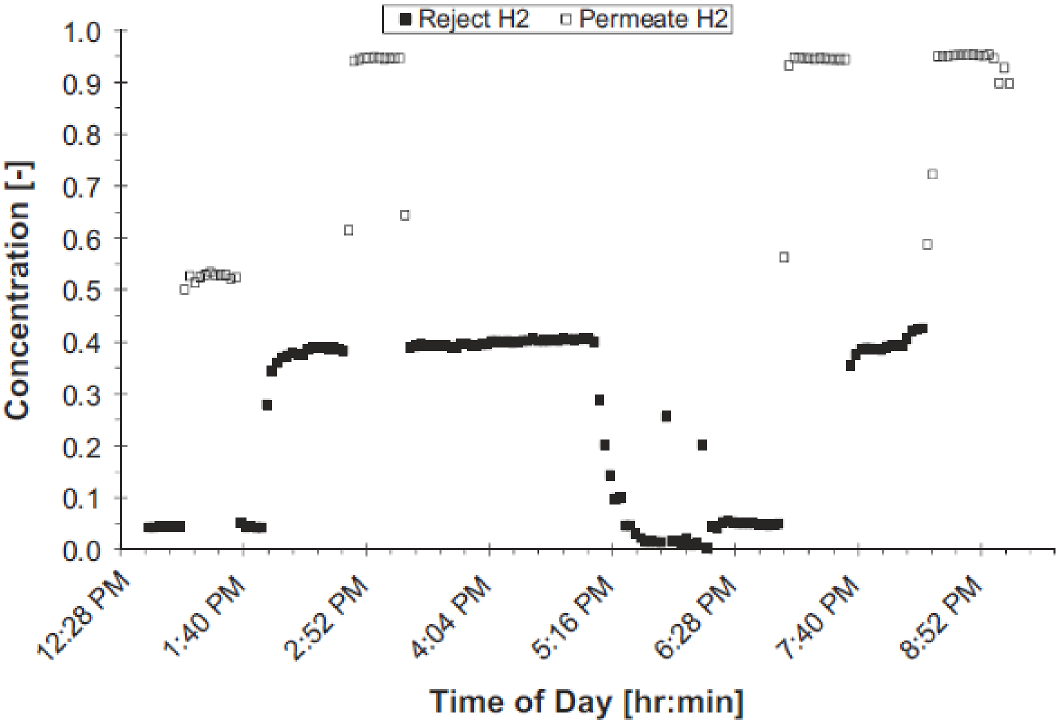

Fig. 13. H_2 concentration in the permeate and reject sides near the end of the test [60].

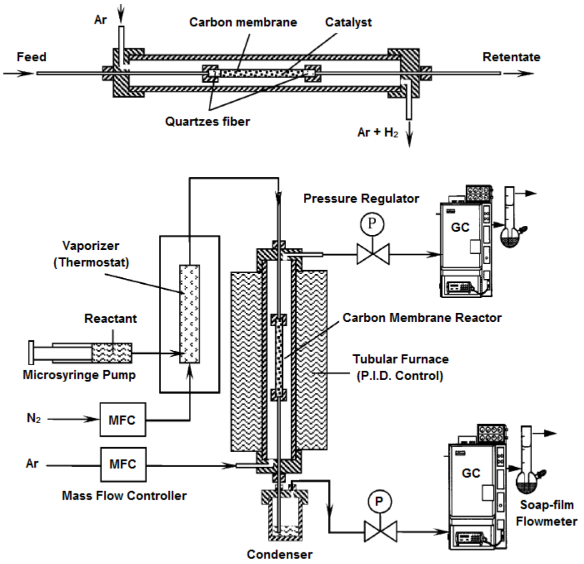

Fig. 14. Schematic view of the carbon membrane reactor and experiment system [62].

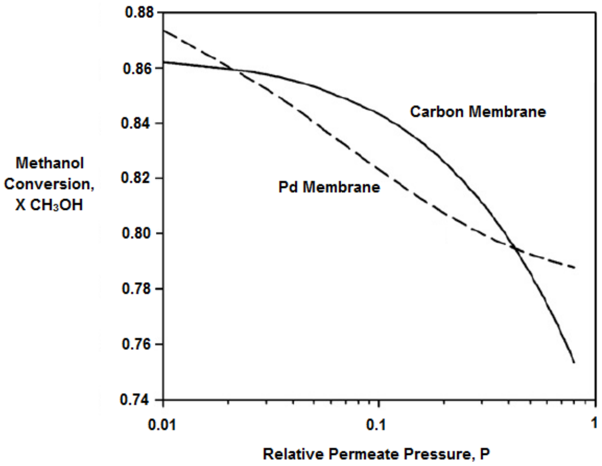

Fig. 15. Methanol conversion as a function of the total relative permeate pressure for a Pd membrane reactor and a carbon membrane reactor [99].

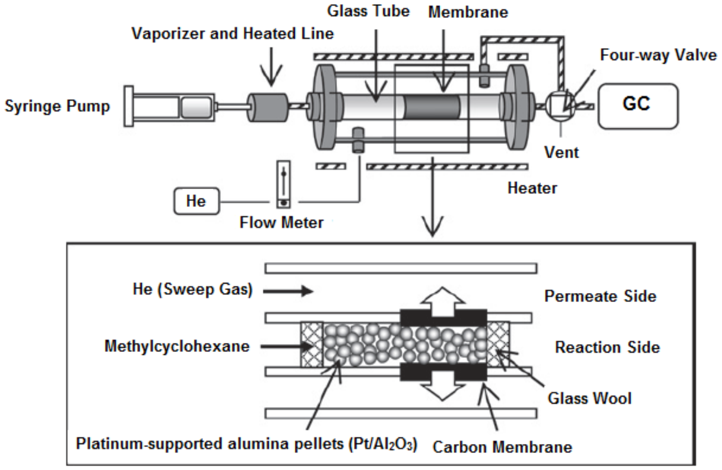

Fig. 16. Schematic diagram of the membrane reactor apparatus used for dehydrogenation reactions of methylcyclohexane [59].

of the main limits of carbon membranes such as brittleness allowed the efforts on finding the appropriate strategies in the fabrication techniques. The rapid development of recent advances in the fabrication techniques has enabled the promising properties of carbon membrane to be easily harnessed and assessed. The opportunity to apply carbon membrane in gas separation and membrane reactor system has opened a bright scenario in the separation process technology and development.

Overall, it is difficult to draw definite conclusions about the improved properties from the results published in the open literature due to the challenges in ensuring the reproducibility of wide range of approaches. Also, there are lot of works to be done before such membranes become a commercial reality. For the time being, the modification of available materials and the effort to seek for new fabrication techniques in carbon membrane for gas separation application has extensively explored by the global research community. This is because further improvements are still necessary to meet the requirements of the industrial application in gas separation fields. It is anticipated that with the continuing advances in the development of carbon membrane, the application range of this materials can be enormously promoted and expanded.

7. Future perspectives

The fundamental study in the carbon membrane fabrication is the precursor membrane selection. The utilization of pure polymer and polymer blend as a precursor membrane in the carbon membrane fabrication has shown a great promise for the increasing gas separation performance particularly for the CO_2, N_2, and H_2 removal. Carbon membrane produced from the crosslinked-6FDA-mPDA/DABA membrane exhibit higher CO_2 permeability than those produced from the Matrimid, 6FDA/BPDA-DAM, Torlon, and P84. However, a higher selective of carbon membrane for CO_2/CH_4 separation could be achieved when the polymer blends of PBI/Kapton was utilized as a precursor membrane. In the case of N_2 removal from the natural gas, consisting primarily of methane, an attractive combination of N_2 permeability and N_2/CH_4 selectivity that exceeds the polymer-based membrane upper bound line could be obtained by using the Matrimid-based carbon membrane through the implementation of Ar as a carbonization environment. Also, the addition of PBI as a second polymer in the polymer solution would improve the selectivity of the carbon membrane. In addition, the carbon membrane can also be prepared by using pure inorganic material or polymer blends of polymer and inorganic materials as their precursor membrane. This is due to their highly diversified structures, tunable pore sizes, large range of porosity, and versatile functionalities. However, the effective and homogeneous polymer/inorganic-based carbon membrane synthesis is still at a premature stage and need for further improvements.

Extensive research on a supported carbon membrane is underway to overcome the current barriers and obstacles. During supported carbon membrane fabrication, the production of membrane with defect-free in a single coating-carbonization cycle is the main challenge. This issue could be overcome by the incorporation of low cost ceramic nanoparticles of boehmite in the polymer solution or utilized a high quality defect-free support. Besides that, the modification of support material via the intermediate gel coating technique has been introduced to avoid the high cost of high quality support. This technique is not only improving the separation performance of the composite carbon membrane but also the mechanical stability of the composite polymeric membrane. The carbon layer between the selective layer of polymeric membrane and the supporting material can serve as a channelling and adhesive medium for the composite membrane fabrication. The result shows that the pore volume of the carbon layer-modified substrate was increased compared with the original substrate and high selectivity of H_2/CH_4 and H_2/N_2 was achieved. In addition, an alternative technique using the plasma-enhanced chemical vapour deposition (PECVD) to prepare the supported carbon membrane has been explored.

Furthermore, the application of carbon membrane in the membrane reactor is expected to attract the increasing interest of researchers in future. A number of carbon membrane reactor used in the reactions involving H_2 such as hydrogenation and dehydrogenation, methane steam reforming, and water gas shift (WGS) have been documented in the past few years. This process can reduced the capital costs and improved yields since both reaction and separation are performed in the same system. The success of the membrane reactors mainly depends on the H_2 permeability and selectivity. Carbon membrane produced from the FFA has showed a high H_2 permeability in the membrane reactor for the dehydrogenation of chemical hydrides. The need of the dual WGS reactor system can be avoided by the implementation of carbon membrane reactor. It is due to the higher CO conversion along with enhanced H_2 recovery and purity. On the other hand, the findings indicated that higher H_2 selectivity and methanol conversion, as well as lower CO yield has been achieved for the carbon membrane reactors as compared to the traditional methanol steam reforming reactors. It is expected that the carbon membrane reactor will gain continuous attention from the material scientists and engineers across the world, where the future is believed to be prolific.

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