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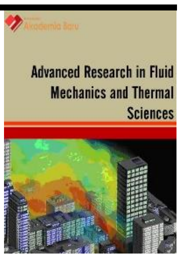
Akademia Baru

Journal of Advanced Research in Fluid
Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



A Short Review on Novel Membranes for Gas Separation

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ARTICLE INFO

Article history:
Received 5 October 2019
Received in revised form 31 December 2019
Accepted 25 January 2020
Available online 26 April 2020

ABSTRACT

The area is a membrane that works faster than any publicly accessible scheme. Membrane technology are more useful than other kinds of membranes for CO_2/CH_4 separation, which includes both carbon and zeolite molecular sieves and amorphous silica matrix. Besides, there are several related to the membrane system such as insufficient heat and chemical stability and plasticisation sensitivity. The further improve the transmitter system's position in the separation of gas and economic saving are the advantage of membrane technology to the world. Despite centuries of studies on the topic, fewer than ten polymer kinds are currently used for business gas separation, and no polymer specifically intended for this function. New membrane must deliver substantial rises in CO_2 permeance and selectivity of CO_2 / CH_4 relative to current technologies to contend internationally.

Keywords:
Hydrogen membrane separation; carbon membrane; polymeric membrane; zeolite molecular sieves; amorphous silica matrix

1. Introduction

The traditional gas separation methods are the advantages offered by the operation of a unit of necessary membrane gas separation [1,2]. Membranes created for hydrogen purification (H_2) and emphasises the removal of carbon dioxide (CO_2) from methane (CH_4). Separating CO_2 from natural gas streams is an important industrial process in which it is anticipated that the membrane structure will perform a more significant part in the future. The separation of CH_4 and CO_2 is vital to the industry especially for natural gas [3,4]. Twenty trillion cubic feet of standard natural gas was produced in the US each year, 20% of these gases require significant treatment [5,6]. Besides, there are 70% of the total gas can be found in CO_2 natural gas wells which can lead to erosion and reduce the calorific value of natural gas [7-9]. The US government has decided that the configuration of the tank must below 2%. The benefits of separating membrane gas from traditional methods include small energy

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https://doi.org/10.37934/arfmts.70.2.111

consumption, the convenience of use, and modest effect on the environment. Current business plastic cell fluxes and selectivity, however, are too low to handle significant quantities of gas and only small-scale amine factories working under 30 million standard cubes can be damaged by them every day [10,11]. Volume relaxation is defined in the form of a slowly increasing amount with time over specific pressures [12]. The membrane must also have outstanding heat and chemical stability, plastic strength (for polymeric membranes), shrinking strength, small price equipment and scale [13]. In the petroleum and chemical processing industries, hydrogen gas is used for various purposes, namely hydrodesulfurization, syngas and ammonia production, Fischer Tropsch synthesis, and for hydrogenation and hydrocracking reactions [14]. H_2 is produced worldwide of about 41 MM tons/year [10]. Hence the more efficient and economical H_2 separation method is needed for continuous use. The present H_2 separation method involves swing stress adsorption, cryogenic distillation, and extraction of membranes. The latter is usually more cost-effective and profitable [15-17].

The morphology of the membrane is characterised by electron microscopy screening (SEM). To evaluate the efficiency of membrane separation, gas permeance and selectivity are used. For each cross-membrane pressure, the amount of gas (in the mole) passing through the known membrane area per unit of time is used to represent membrane permeates. The gas permeance the proportion of any two species permeance the membrane and being used as a selectivity test of the removal effectiveness. Also, the literature permeates membrane in some of the systems used to demonstrate consensus and the outcomes recorded in both SI and Barrers branches. Barriers transformed into SI units when the author provides the density of the membrane. The median frequency is used for devices where the recorded density variety is used. Another common gas permeation device is the GPU (carbon permeation device) that can be transformed straight to SI units. Permeance of the value mentioned as Eq. (1):

$$1\,Barrer = 1\times10^{-10}\frac{cm^3(STP)\,cm}{cm^2\,s\,cmHg} = 3.35\times10^{-10}\frac{mol}{m^2\,s\,Pa}, \tag{1}$$

For a 1 μm thickness.

$$1\,GPU = 1\times10^{-6}\frac{cm^3(STP)}{cm^2\,s\,cmHg} = 3.35\times10^{-10}\frac{mol}{m^2\,s\,Pa} \tag{2}$$

2. H_2 Membrane Separation for Porous Materials

CVD-prepared silica membranes for H_2 separation have been widely researched that provides an overview of the study conducted over the past several years [18-20]. Nearly all the studies reviewed using inorganic α-alumina supports that are coated by a single or multiple layer of γ-alumina [21,22]. The permeance of H_2 is generally in the order of 10^{-7} mol m^{-2} $s^{-1}Pa^{-1}$ also H_2 selectivity from 70 to 10,000. The silica precursor called TEOS is the most commonly utilized despite the successful use of another type of precursors, for example, phenyltrimethoxysilane (PTMS) and tetramethoxysilane (TMOS) [23,24]. O_2 is mostly used as an oxidizing agent to encourage decomposition of the silica precursor; however, it has been stated that the decomposition of the silica precursor occurs in an inert atmosphere [25,26]. Figure 1 shows membrane reactor for hydrogen production from natural gas at the Tokyo Gas Company [27].

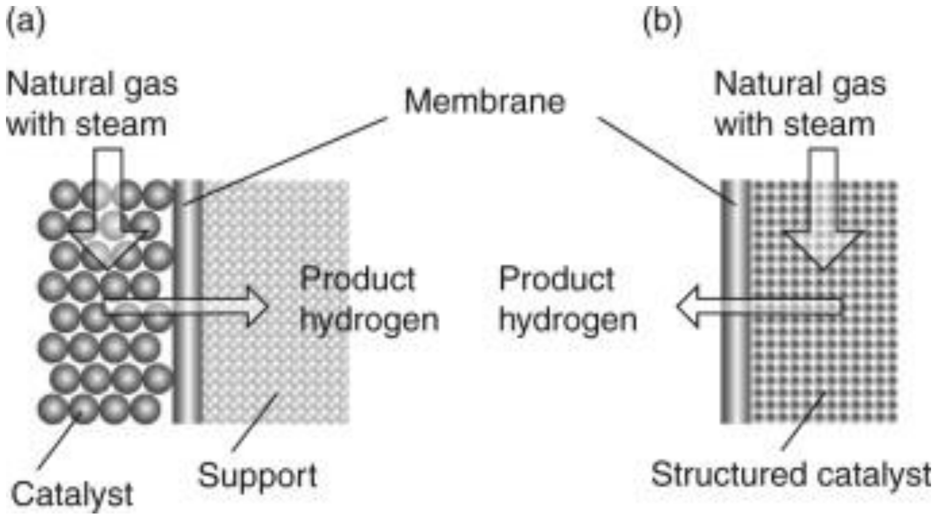

Fig. 1. Membrane reactor for hydrogen production from natural gas at the Tokyo Gas Company [27]

Hollow fibers are leading compared to the traditional ceramic tubular membranes due to the properties of high ratio of area to volume. Hollow fiber can be mounted into multi-tube reactors that will improve the use of volume. The silica separation layer has been discovered to be deposited on the outside of the fiber in all the report mentioned [28]. It is useful in separation but cannot be used in catalytic membrane reactors due to abrasion issues resulting from the contact between the permselective layers with the catalyst pellets. A more in-depth investigation of the outcomes stated in all but two research in the literature seems to have evacuated reactants through the pore walls during the CVD implementation [19]. Vacuum application is asserted to enhance the coverage of silica deposition defects [29]. Studies stated that, if an intermediate layer of γ-alumina is applied to the α-alumina substrate before CVD, the H_2 permeance is improved by an order of magnitude approximately [30]. The molar flow rate of silica precursor varied by more than two orders of magnitude but there was no evaluation of the impacts on H_2 permeance or selectivity. Three of the researches used O_2 or O_3, which functions as an oxidant to encourage decomposition in membrane pores of the silica precursor [31-33]. The implementation of the oxidant reagent gives a significant impact of increasing the final H_2 permeance than the research based on only the thermal decomposition of the silica precursor.

3. CO_2/CH_4 Membrane Separation

The present CO_2 separation method on porous inorganic assistance, amorphous silica substrates, fiber substrates, blended medium substrates, and RTIL membranes includes zeolites and carbon molecular sieve. Literary reports published in recent years are used to review these systems [6,34,35]. Zeolite is a pore-structured aluminosilicate. In general, zeolite covers consist of a thin coating of several micrometres of zeolite placed on a covering such as tubular metal or porous α-alumina. Excellent heat and mechanical strength and chemical resistance are among the benefits that this membrane provides over traditional polymer gas separation membranes [36,37]. The separation of zeolite membranes is accomplished through molecular sieving with surface diffusion. The traps forming the zeolite's pore framework have the capacity to distinguish liquids depending on their kinetic diameter. Due to preferential adsorption in CO_2 instances, separation is increased at reduced temperatures [38]. Previous research showed the excellent results for both selectivity and permeance for the zeolite membrane [39]. Zeolite membranes supported by either stainless steel or α-alumina showed the highest values for both permeance CO_2 and selectivity of CO_2 / CH_4. Carreon and co-workers are able to synthesize SAPO-34 zeolite membranes on porous α-alumina support with permeance CO_2 1.0 - 2.0 x 10-6 mol m-2 s-1 Pa-1 and CO_2 / CH_4 selectivity 86-171 [40]. SAPO CO_2-permeance membranes 3.9 x 10-8 — 2.0 x 10-7 mol m-2 s-1 Pa-1 and CO_2 / CH_4 selectivity 32-118 described by two other accounts from the same study unit. The membrane is ready on the backing, a porous stainless-steel pipe, by crystallization in situ.

Furthermore, the DDR-type zeolite fibers constitute extremely hydrophobic assistance on α-alumina with 2.9 x 10-7 mol m-2 s-1 Pa-1 CO_2 permeable and more than 400 CO_2/CH_4 selectivities at house temperature [41]. Overall, in comparison with traditional polymer membranes, zeolite membranes demonstrate an enhancement in the design of gas separation. This can be ascribed to the present existence of transportation of zeolite gas. The zeolites have a transparent porous network, and if the membrane separation layer is thin, high gas dependency can be achieved. In gas zeolite membranes, size exclusion and selective adsorption are segregated, resulting in more excellent selectivity following the dispersion process than polymer membranes. Zeolite does not show plasticization until even at elevated concentrations, the selectivity of CO_2 / CH_4 is outstanding. Unlike polymeric membranes, zeolite fibers can resist comparatively high pressures in the existence of oxygen. It is essential that CO_2 / CH_4 choice with temperature declines owing to reduced specific CO_2 adsorption. Also, high cost, hard to process, and hard to manage, offsetting some of their appealing characteristics of separation. Commercial implementation cannot take place until the cost of the zeolite membrane is lowered by a percentage of 10 [42]. Figure 2 shows High-flux CHA zeolite membranes for H_2 separations [43].

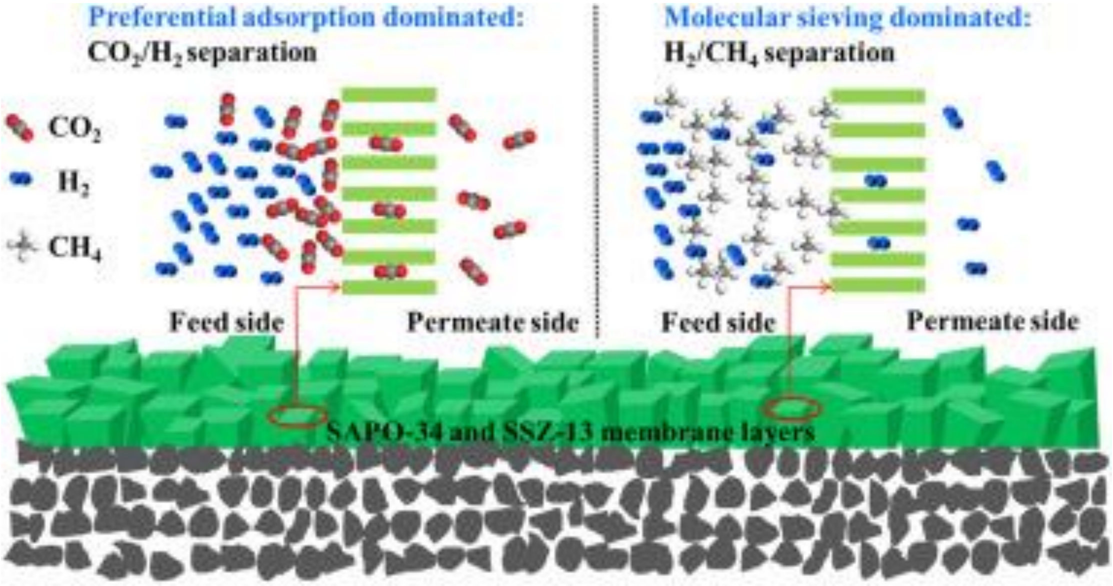

Fig. 2. High-flux CHA zeolite membranes for H_2 separations [43]

Carbon membranes are random porous networks that are generated under regulated circumstances by thermosensitive polymer thermosets and have excellent heat and chemical stability [44]. Pyrolysis produces layers with a molecular aspect (molecular sieve) allocation of the small pore volume. Depending on the preparation circumstance, the pore magnitude in carbon fibers used to separate the gas ranges from 0.35 to 1 nm [45]. Pore construct can be defined as a comparatively big gap comparable in volume to the gas molecules in the "tight" throat. The primary mechanism of gas transport is the diffusion of molecules where smaller dimensional particles are absorbed by choice compared to larger dimensional particles [46]. More substantial molecule permeability is strictly sterically restricted while permeation of smaller molecules of a specific size occurs faster. The interaction of the gas molecules with the walls of the carbon molecular sieve made up of two teams that repulsive and attractive. The gas molecule is required to overcome the activation energy barrier that results from the rejection force passing through the pore opening. The significant changes in permeance caused by small changes in the size of the molecule can be explained by the diffusion activated through the membrane. The second mechanism of transport in the carbon membrane is associated with surface diffusion with selective adsorption. Carbon membrane, which depends on the particular surface diffusion mechanism, generally has a larger pore size and is capable of separating highly adsorbent gas (NH_3, CO_2, H_2S) from the adsorbent gas (CH_4, O_2, N_2) and can either be supported (on tube or flat) or not supported [47]. Unsupported carbon membranes (flat or tubular) are fragile and difficult to maintain, and, moreover, thicker than supported membranes and thus exhibit lower gas permeability. Carbon membrane supported permeates better showcase for decreasing the thickness of the active layer, which reduces the resistance to gas flow — carbon molecular sieve membranes displaying excellent properties of separation CO_2 / CH_4.

Yoshimune and Kenji [48] synthesized unsupported carbon membranes. The results show that the selectivity of CO_2 / CH_4 are very high 100-130 but low permeance (2.8x10-9 - 7.5x10-9 mol m-2 s-1 Pa-1). This phenomenon is due to the high membrane thickness (23-25 m) [48]. Jiang *et al.,* [49] synthesized double-layer hollow membranes on Matrimid support. The emission of CO_2 on this membrane was relatively low (4.2x10-9 mol m-2 s-1 Pa-1) due to the collapse of micropores in the support layer, but CO_2 / CH_4 selectivity was high [49]. Membrane selectivity is impaired in the thin layer of carbon separation (1μm) supported on α-alumina, but nonetheless, the results are promising. The thin layer of active carbon separation must be defect-free if the membrane selectivity is significantly reduced. The carbon membrane has many of the same problems as the zeolite membrane. Instead, they are costly, hard to process, and hard to manage. Other disadvantages include the susceptibility of carbon membranes to oxidizing agents and the degradation of water vapour over time [50,51]. The synthesized stable carbon membranes, required to have technology accessible first to create excellent polymeric membranes. Under very narrow circumstances, polymeric substrates must be pyrolyzed, which can be hard to enhance. The amorphous and mesoporous membranes are the two types of silica membrane that can be split by membrane morphology. In cases of amorphous silica, or claims of mesoporous silica, these membranes are usually generated by CVD or sol-gel synthesis from silica precursors or by sol-gel or hydrothermal synthesis. CVD-prepared membrane using conventional silica precursors like TEOS or tetramethyl orthosilicate (TMOS) usually produces a small silica microporous or nonporous film appropriate for H_2 or He separation [29]. In relatively small gas molecules, these membranes are very soluble, but the permeability of bigger gas molecules such as CO_2 is very low. It is essential to use silica precursors comprising significant organic components, such as phenyl clusters, to attain greater CO_2 absorption levels through the CVD process. Two types of research investigated here using phenyl-containing precursors that form a tight silica-packed porous framework relative to normal CVD [52]. The mesoporous membrane provided by the sol-gel technique has a clear pore structure and acts as a molecular sieve. Sol-gel pathways are an easy way to produce silica layers, but the final morphology of the membrane is highly dependent on the synthesis parameters. This enables monitoring of the exact pore morphology and composition, but also makes the ultimate membrane susceptible to synthesis circumstances and thus hard to replicate. In particular, more significant emissions in sol-gel-prepared membranes are much greater in the CVD membrane relative to CVD, but membrane stabilization and film durability [18].

4. Polymeric Membranes

The organic polymer is the material most commonly used in gas separation membranes [53]. The polymer can be split into two groups, i.e. running above crystal transfer temperature (a plastic polymer) and working below crystal transfer rate (crystal polymer). Polymer glasses can efficiently distinguish molecules depending on tiny variations in molecule dimensions [54]. In the magnitude and structure of the rubber polymer, they are more competitive and therefore, more appropriate for CO_2 separation. According to Henry's law of gas absorption in rubber polymer; the absorption in glass polymers can be described by the complicated absorption isotherms connected with the unabsorbed size of the matrix when discharged under the glass transition temperature. Complete details of solubility can be discovered elsewhere in glass polymers [55]. Commercial polymer membranes have asymmetric constructions that are usually backed by porous materials with tiny specific strands. The thicker backing layer guarantees the structure's stability while the thinner protective coating enables higher flux of gas through the membrane. Recently papers on technologies that mix various polymers. In the case of mixed membranes, glass polymers are covered with high diffusivity in a matrix of rubber polymer to incorporate high selectivity from the latter [56]. Besides, the glassy polymer provides mechanical support to the matrix structure and rubber [57]. The polymer membranes are not porous and gas permeation mechanism administered by the deployment of the solution. Therefore, the mechanism was by the solubility in the polymer matrix [58]. The gas molecules absorb from the portion of the feed into the gas membrane interface, dissolving and absorbing the molecules through the membrane with random dispersion. Dissemination happens between polymer chains in free-volume components (0.2 and 0.5 nm in length) that occur and continually vanish owing to thermal motion.

The dispersion of gases through the naturally non-porous polymeric structure is slow, and thus the polymer membrane exhibits low CO_2 permeance with moderate CO_2 / CH_4 selectivity. Polymer membranes now monopolize the market due to low material cost and processing facilities [54]. Compared with other membrane systems described above, the polymer membrane is more comfortable to handle more than the critical current scale. The polymer membrane systems studied in this chapter generally exhibit permeances below 1x10-8 mol m-2 s-1 Pa-1. The reduced gas permeability of the polymer membrane can be understood from the gas diffusion mechanism. Permeance is naturally low because gas must dissolve in and absorb through non-porous solids. Also, there is a well-known trade-off between the selectivity and permeance for polymer membranes. Despite intense research on membrane gas separation in recent years, polymer membranes have not been able to progress beyond the "line of death" called the Robeson plot which describes the precision selections in polymer membranes.

5. Mixed Matrix Membranes

Organic-inorganic membrane consisting of a mixture of inorganic particles. Mixed matrix membranes attempt to mix the handling of polymeric materials with outstanding molecular sieve vapour separation properties [59]. Gas transferred through the inorganic and polymer stage. Inorganic ions may behave as molecular sieves. Transportation happens primarily through the inorganic stage at very elevated inorganic load. There are also blended matrix membranes that depend on inorganic fillers, selectively absorbing various gases [36]. According to Suzuki and Yasuharu [60] the suitable option for CO_2 / CH_4 of 54-95 was 6FDA-TAPOB modified hyperbranched polyimide – silica hybrid with tetramethoxysilane as a precursor. The mixed matrix membrane regime CO_2 permeance investigated in this section usually drops below 1x10-8 mol m-2 s-1 Pa-1. There was no vital rise in CO_2 / CH_4 selectivity over a polymer membrane in the general composite membrane of organic-inorganic.

6. Conclusions

Some of membrane systems have CO_2 permeability above 1x 10^{-6} mol m-2 s-1Pa^{-1} with an ideal CO_2 / CH_4 choice above 100. The findings achieved with PTES thermal decomposition binary organic-inorganic silica membranes show that these membranes function well in comparison with other kinds of membranes. For comparison, low CO_2 permeances in the range of 1x 10-11 to 1x 10-8 mol m-2 s-1Pa-1 and CO_2 / CH_4 selectivity between 15 and 100 were shown by organic membranes (polymeric). Mixed matrix membranes showed no significant increase in CO_2 separation compared to polymeric membranes. The CO_2 surface is usually less than 1x 10-9 mol m-2 s-1Pa-1, and the ideal CO_2 / CH_4 choice is less than 100. Compared to other membrane separation technologies, supported ionic liquid substrates demonstrate lower CO_2 / CH_4 separation efficiency. Overall, the CO_2 permeance backed by ionic liquid filters is more significant than polymer matrix or blended, but the selectivity of CO_2 / CH_4 is low.

Acknowledgment

The authors would like to acknowledge the financial support from the Ministry of Higher Education and Universiti Malaysia Pahang (UMP) with grant number RDU192315.

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