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산소/질소 분리를 위한 다층구조 제올라이트 5A를 함유한 탄소분자체 분리막 제조

리 웬*,1 · 추 아 총 양**,1 · 배 태 현*,**,***,†

*싱가포르 난양이공대학교 화학생물공학부, **싱가포르 분리막 센터, ***한국과학기술원 생명화학공학과과
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Hierarchical 5A Zeolite-Containing Carbon Molecular Sieve Membranes for O_2/N_2 Separation

Wen Li*,1, Chong Yang Chuah,1, and Tae-Hyun Bae*,**,***,†**

*School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
**Singapore Membrane Technology Centre, Nanyang Technological University, Singapore 637141, Singapore
***Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea
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요 약: 다층 구조를 가진 5A 제올라이트를 탄소 분자체 분리막에 첨가한 복합막을 제조하고 질소/산소의 분리 특성을 평가하였다. 제올라이트의 첨가는 선택도에는 미세한 영향을 주지만 투과도를 크게 증가시키는 방법으로 전체적인 탄소막의 질소/산소의 분리 성능을 상승시켰다. 특히 메조포어를 함유한 다층구조의 제올라이트 첨가제는 분리막의 투과도를 보다 효율적으로 상승시켜 아주 우수한 분리 성능에 도달하였다. 이 연구의 결과는 저렴한 탄소막 전구체와 제올라이트 소재를 활용하고도 고성능의 질소/산소 분리막을 손쉽게 제조할 수 있다는 것을 제시한다.

Abstract: Mixed-matrix carbon molecular sieve membranes containing conventional and hierarchically structured 5A were synthesized for application in oxygen (O_2)/nitrogen (N_2) separation. In general, incorporating 5A fillers into porous carbon matrices dramatically increased the permeability of the membrane with a marginal decrease in selectivity, resulting in very attractive O_2/N_2 separation performances. Hierarchical zeolite 5A, which contains both microporous and mesoporous domains, improved the separation performance further, indicating that the mesopores in the zeolite can serve as an additional path for rapid gas diffusion without sacrificing O_2/N_2 selectivity substantially. This facile strategy successfully and cost-effectively pushed the performance close to the Robeson upper bound. It produced high performance membranes based on Matrimid® 5218 polyimide and zeolite 5A, which are inexpensive commercial products.

Keywords: *hierarchical zeolite, carbon molecular sieve membrane, O_2/N_2 separation, mixed-matrix membrane*

1. Introduction

In recent years, air separation processes have played a pivotal role in numerous industrial applications such as the production of primary metals (non-ferrous metals or steel), fuel combustion, gasification, petrochemical production, and glass and concrete production. For instance, high-purity oxygen (O_2) is preferred for oxy-fuel combustion, as it provides a higher energy efficiency than compressed air, as nitrogen (N_2) typically acts as a non-reactive gas that is not actively involved in the combustion process[1]. O_2 is also heavily used to lower the carbon content of iron-steel alloys, which leads to the formation of low-carbon steel[2]. The highly

†Corresponding author(e-mail: thbae@kaist.ac.kr, https://orcid.org/0000-0003-0033-2526)
[1]These authors contributed equally to this work.

inert properties of N_2 ensure its capability to act as a shielding gas during the degassing of molten metals, thus preventing any significant presence of oxidizing components (e.g., oxygen and moisture) that can lead to the oxidation of metals at elevated temperatures[3]. N_2 can also be used in food packing processes to preserve food for a long time[4].

In general, several methodologies have been developed to effectively conduct the air separation process. Distillation, the conventional cryogenic air separation process, has been actively used by major industrial gas companies due to its large-scale O_2 production capability[5-7]. Pressure swing adsorption or vacuum pressure swing adsorption can also be used to generate O_2 with high purity via the use of adsorbents that allow selective adsorption[8-10]. Nevertheless, these technologies have substantial limitations in terms of high capital and operating costs as well as high energy consumption. Hence, a membrane-based separation process has been considered a promising alterative due to its cost effectiveness, simplicity, and small plant footprint.

Until now, polymeric membranes have been heavily used in the gas separation process, due to their high mechanical strength, high chemical resistance, and ease of fabrication. In addition, polymeric membranes can be fabricated into multiple membrane configurations such as flat sheets, spiral wounds, and hollow fiber modules. Nonetheless, the well-known permeability-selectivity trade-off, demonstrated in the Robeson plot [11,12], is the typical behavior of polymeric membranes, as the gas transport properties of membranes are governed by the solution-diffusion mechanism. Under this plot, an upper bound is constructed to demonstrate the limit of gas separation performance of polymeric membranes. Researchers have investigated several approaches that move the performance towards the upper bound limit. Among them, the carbonization of polymer precursors has been studied as a effective method for developing high-performance membranes[13-15]. However, the selection of an appropriate carbonization condition is generally dependent on several factors, such as type of inert flow gases (helium, nitrogen, argon), ramping rate, pyrolysis temperature, and soaking time[16,17]. In addition, it is well-known that the performance of such carbon molecular sieve membranes (CMSMs) is strongly dependent on the choice of polymer precursors. For instance, membranes that are derived from glassy polymers with high fractional free volume such as 6FDA (4,4'-(hexafluoro-isopropylidene) diphthalic anhydride) containing polyimides tend to give extraordinary gas separation performance. However, the harsh synthesis conditions and high costs generally limits the industrial applications of these polymers[17-19].

Therefore, we have adopted an approach that involves the carbonization of polymer precursors incorporating inorganic nanoporous fillers to form mixed-matrix CMSMs[20-24]. The polymer precursor selected for this study was Matrimid® 5218, as it is more readily availability than the other glassy polymers (e.g., 6FDA-based polymer[19]) that require sophisticated synthesis procedures. Meanwhile, zeolite 5A, which possesses a well-defined micropore 4.8 Å[25], was chosen as the filler materials. The pore structures of 5A zeolite fillers were systematically controlled to optimize the gas separation performance. It has been suggested that the creation of hierarchical microporous-mesoporous domains is an attractive alternative method, given the possibility that small micropore channels limit the accessibility of gas molecules, leading to a slow pore diffusion[26,27]. It should be noted that zeolite LTA can be readily synthesized in the form of hierarchically porous structure by using the soft templating method. In addition, instead of as-made LTA zeolite (Na-A) that can slow down the diffusions of O_2 and N_2 due to its small pore (3.8 Å), zeolite 5A possessing a larger pore can be deliberately used with an aim to improve the permeability of a CMSM which already has a good O_2/N_2 selectivity.

Based on the rationale mentioned above, we fabricated mixed-matrix CMSMs using Matrimid® 5218 carbon precursors and zeolite 5A fillers with a variety of physical properties (zeolite 5A and hierarchical zeolite 5A) for the application in O_2/N_2 separation. Then, the effect of zeolite 5A fillers on O_2/N_2 separation performance

was studied in a systematic manner, focusing on the impact of mesoporosity that was introduced into the zeolite particles. The membranes prepared with this facile method gave outstanding performances that were far better than the pure CMSM, indicating that the strategy tested in this study is highly suitable for industrial applications.

2. Experiment

2.1. Materials

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride solution (TPOAC, 42 wt% in methanol), sodium aluminate (Al: 50~56%, Na: 37~45%), aluminium isopropoxide (≥ 98.0%), sodium hydroxide (≥ 98.5%), sodium metasilicate pentahydrate (≥ 95.0%), Ludox® HS-40 colloidal silica (40 wt% suspension in H_2O), and tetramethylammonium hydroxide (TMAOH, 25 wt% in H_2O) were purchased from Sigma-Aldrich. Chloroform (≥ 99.8%) was purchased from VWR. The chemicals and solvents were used as received, without further purifications. Matrimid® 5218 was purchased from Huntsman Chemicals, and the polymer powder was dried at 180 °C under vacuum prior to use. Deionized (DI) water was produced in-house. Argon gas (Ar, ≥ 99.9995%), helium gas (He, ≥ 99.9995%), and O_2/N_2 (21/79 by volume) mixed gas were purchased from Airliquide.

2.2. Synthesis of zeolites

The zeolite LTA and hierarchical zeolite LTA were synthesized using the methods described in the literature[28]. For the preparation of hierarchical zeolite LTA (H-LTA), the precursor solution was prepared with a molar ratio of 10 Al_2O_3/40 Na_2O/15 SiO_2/2400 H_2O/1.25 TPOAC under ambient conditions. First, two separate solutions were prepared. One solution was a mixture of sodium metasilicate pentahydrate, sodium hydroxide, TPOAC, and deionized (DI) water, and the second solution was prepared by dissolving sodium aluminate in DI water. After the two solutions were completely homogeneous, the solutions were mixed together and heated at 100°C for 4 h via vigorous agitation. Once the reaction was completed, the product was collected using vacuum filtration, and it was washed with copious amounts of DI water to remove the undesired impurities. Then, the product was dried at 100°C overnight in a convection oven. Next, the sample was calcined in a furnace at 550°C for 3 h with a ramping rate of 1 °C/min. This step was required to remove the TPOAC that was present in the samples, thus creating hierarchical zeolite LTA. Similarly, zeolite LTA was synthesized using the same procedures as for hierarchical zeolite LTA, but without the addition of TPOAC. The molar ratio of the precursor solution was controlled to be 10 Al_2O_3/40 Na_2O/15 SiO_2/2400 H_2O.

Subsequently, ion exchange was conducted to convert the zeolite LTA (4A, with Na^+) to zeolite 5A (with Ca^{2+}). Specifically, 1 g of zeolite LTA was dispersed in 50 mL of 0.5 M $Ca(NO_3)_2$ solution and vigorously stirred at 60°C for 12 h. This ion-exchange procedure was repeated twice to ensure a higher degree of substitution to Ca^{2+}. Finally, the zeolite 5A and hierarchical zeolite 5A was collected using vacuum filtration, and the product was dried at 80°C overnight.

2.3. Synthesis of carbon molecular sieve membranes derived from polymeric and mixed-matrix membranes

Polymeric and mixed-matrix flat sheet precursor membranes were fabricated using a solution-casting technique that has been reported in previous studies[29,30]. For the synthesis of polymeric membranes, a dope solution was prepared by dissolving dry Matrimid® 5218 powder in chloroform, with the concentration of the polymer solution set at around 15 wt%. The dope solution for the mixed-matrix membranes was prepared using the following steps. The zeolites were first ground before being dispersed in a chloroform solution. To reduce the aggregation and improve the overall homogeneity of the zeolites in the dope solution, sonication horn (Qsonica, Q125) was used. Subsequently, dry Matrimid® 5218 powder was added to the solution, followed by vigorous stirring until it was completely

dissolved. Next, the dope solution was cast onto a glass plate with the aid of a casting knife. The casting process was conducted in a glove bag which is filled with chloroform vapor to slow down the solvent evaporation. The flat sheet precursor membranes were annealed at 180°C in a vacuum overnight to remove any residual solvents present in the sample. Subsequently, the membrane carbonization process was conducted to form carbon molecular sieve membranes in a tube furnace (Carbolite GERO, CTF 12/100/900). Prior to the carbonization process, Ar was purged into the quartz tube (> 1 h) to remove any residual air and moisture present inside the tube. Then, the membrane precursors were carbonized using a two-step ramping procedure (380°C for 0.5 h at a rate of 2 °C/min and 550°C for 2 h at a rate of 0.5 °C/min). The carbonized membranes were cooled to room temperature after the process was completed.

2.4. Characterization

The morphologies of the zeolites and the cross-section morphologies of the carbon molecular sieve membranes were observed using field emission-scanning electron microscopy (FE-SEM, JSM6701 JOEL). X-ray diffraction (PXRD) patterns of the zeolites and carbon molecular sieve membranes were measured using a Bruker D2 phaser diffractometer with a Cu-Kα source (1.5418 Å) in the 2θ range of 5~50°. The thermal stabilities of the zeolites and membrane precursors were determined via a thermogravimetric/differential thermal analyzer (TG/DTA), (SDT Q600, TA Instrument) within a temperature range of 40 to 900°C. The measurements were conducted under pure N_2 purging at 100 ml/min, with a heating rate of 10 °C/min. N_2 physisorption measurement (Autosorb 6B, Quantachrome) of zeolites was conducted at -196°C (77 K) under the relative pressure (P/P^o) range of 0~1 bar to investigate the porosity properties of the zeolites. The zeolites were activated at 250°C for 24 h under a high vacuum prior to the measurement. The O_2 and N_2 adsorption isotherms of the zeolites were measured using a volumetric gas sorption analyzer (iSorb HP1, Quantachrome) at 35°C in the pressure range of 0~1 bar after the activation conducted under the same activation conditions mentioned above.

2.5. Mixture gas permeation

A gas permeation test was carried out using the constant pressure-variable volume system developed by GTR Tec Corporation. The membrane was first mounted onto the permeation cell with the temperature set to 35°C. Throughout the analysis, a binary O_2/N_2 mixture (21/79 by volume) and helium were flown continuously in the upstream and downstream, respectively, with the flow rate controlled by the mass flow controllers. At a periodic time interval, the gas in the downstream (a mixture of the permeated gas and He) was injected into the gas chromatography to analyze its composition. This process was repeated until the concentrations of O_2 and N_2 were no longer fluctuated. The measurement was repeated for at least three samples for each pure polymeric membrane and mixed-matrix membrane to ensure the reproducibility of the gas permeation results.

3. Results and Discussion

3.1. Properties of zeolites

The overall morphologies of the zeolite samples that are synthesized in this study are illustrated in Fig. 1(a) and (b). In general, zeolite 5A has a uniform structural topology; the typical cubic LTA crystals illustrated in Fig. 1(a) when TPOAC was not added to the precursor gel during the synthesis. In contrast, the overall shape of the particle was converted to a spherical shape (from a cubical shape) when TPOAC was incorporated into the reagent mixture. Based on the FE-SEM images, the particle sizes of the zeolites were estimated to be around 3 μm and 6 μm respectively. In addition, the successful formation of zeolites samples was verified using XRD, as shown in Fig. 1(c). The characteristic peaks and patterns of zeolite 5A were well-matched to those of the typical zeolite LTA framework reported in the literature[28]. In particular, the creation of hierarchical structures (containing both microporous

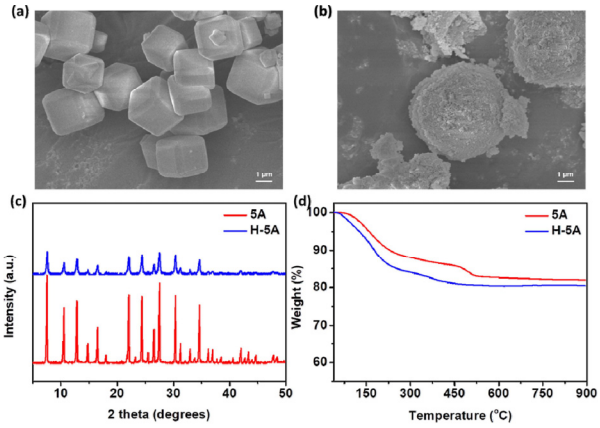

Fig. 1. Field emission-scanning electron microscope (FE-SEM) morphologies of (a) zeolite 5A and (b) hierarchical zeolite 5A; (c) X-ray diffraction (XRD) patterns of three zeolites; (d) Thermogravimetric analysis (TGA) curves of three zeolites in the 50~900°C range.

and mesoporous domains) generally resulted in a clear decrease in the peak intensity, as smaller fractions of zeolite domains can be expected. The feasibility of using zeolite 5A in membrane carbonization processes was assessed by evaluating its thermal stabilities from 50 to 900°C. A continuous weight loss which is attributed to the removal of water molecules that potentially resided in the samples was observed until 525°C was reached for all of the zeolite 5A materials. This result suggested that the integrity of zeolite frameworks can be maintained when these porous materials are heated to a carbonization temperature of Matrimid® 5218.

Further evaluation of zeolite 5A was conducted using N_2 physisorption isotherms at -196°C (77 K) in the P/P^o range of 0~1, as demonstrated in Fig. 2(a). The analysis of the isotherms showed that all zeolites demonstrated high N_2 sorption at low partial pressure, which was a typical indication of a Type I isotherms (presence of large micropore volume). The presence of an hysteresis loop between the adsorption and desorption curves for the hierarchical zeolite 5A indicated the presence of mesopores, which were determined to be 8.3 nm according to the BJH algorithm[31] [Fig. 2(b)]. In comparison, the hierarchical zeolite 5A gave a comparatively lower N_2 sorption in comparison to zeolite 5A, which can be correlated with the surface areas and micropore volumes computed using the Brunauer-Emmett-Teller (BET) theory and t-plot method, respectively (Table 1). This analysis was generally consistent with the decrease in peak intensity of hierarchical zeolite 5A seen in the XRD patterns.

The O_2 and N_2 adsorption properties of zeolite 5A were also evaluated using pure component gas adsorption isotherms, which determined the affinities for these two gases. As shown in Fig. 2(c), the O_2 adsorption was generally lower than that of N_2 in all of the synthesized zeolites. This is probably attributed to the higher polarizability of N_2 compared to O_2 (17.4×10^{-25} cm^3 vs. 15.8×10^{-25} cm^3). Similar phenomena have been reported for other zeolite frameworks[32,33]. Based on the adsorbed amount, O_2 and N_2 adsorption can be generally correlated to the accessible surface areas evaluated by the N_2 physisorption measurement.

3.2. Properties of carbon molecular sieve membranes

After the successful preparation of zeolite 5A, membrane precursors were developed by incorporating the zeolites into mixed-matrix membranes. As shown in Fig. 1(d), the zeolites were thermally stable up to 900°C, as no signs of structural degradation were observed. Moreover, the thermal stability of the zeolites after the carbonization of the membrane precursors was also apparent from the XRD results. As described in Fig. 3, the characteristic peaks of the zeolite 5A were identified, suggesting that the crystallinity of the zeolite 5A remained intact after the carbonization process.

Next, the cross-section morphologies of the carbon molecular sieve membranes were verified using FE-SEM (Fig. 4). In general, the *sieve-in-a-cage* morphology is a typical interfacial defect that occurs when inorganic fillers (especially zeolites) are incorporated into mixed-matrix membranes. Surprisingly, this phenomenon was not observed in this study. In fact, the interfacial voids between the zeolite 5A and Matrimid® 5218 membrane seemed to narrow, perhaps because of the conversion of the glassy material into a rubbery polymer matrix at the glass transition temperature (319

Table 1. Surface Areas and Micropore Volumes of All of Zeolites Calculated from the N_2 Physisorption Isotherm at 77 K

Fillers	S_{BET}[a] (m^2/g)	S_{Lang}[b] (m^2/g)	S_{Micro}[c] (m^2/g)	V_{Micro}[d] (cc/g)
Zeolite 5A	779.0	810.4	750.7	0.3168
H-Zeolite 5A	476.7	561.9	398.7	0.1706

Notes: [a] Surface areas were computed using the BET theory at P/P^0 = 0.05~0.2, [b] Surface areas were calculated using the Langmuir equation at P/P^0 = 0.05~0.2, [c,d] Micropore areas and volumes were computed using the t-plot method at P/P^0 = 0.4~0.6.

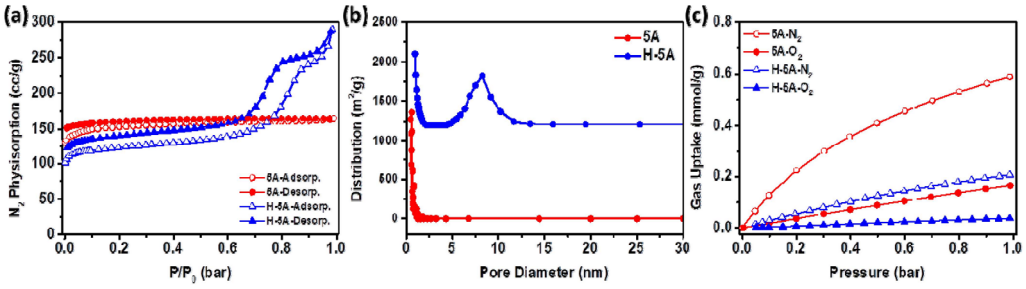

Fig. 2. (a) N_2 physisorption isotherms of zeolites measured at -196°C (77 K) under the P/P^0 range of 0 to 1. (b) Pore size distribution of zeolites, which were determined via a BJH method. (c) O_2 and N_2 adsorption isotherms of zeolites at 35°C.

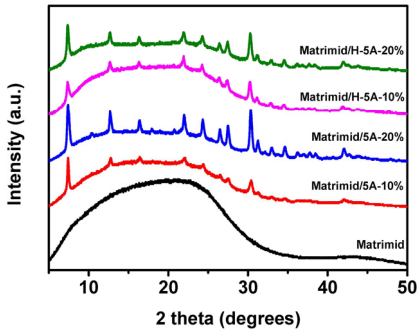

Fig. 3. XRD patterns of carbon molecular sieve membranes derived from pure Matrimid® 5218 and mixed-matrix membranes.

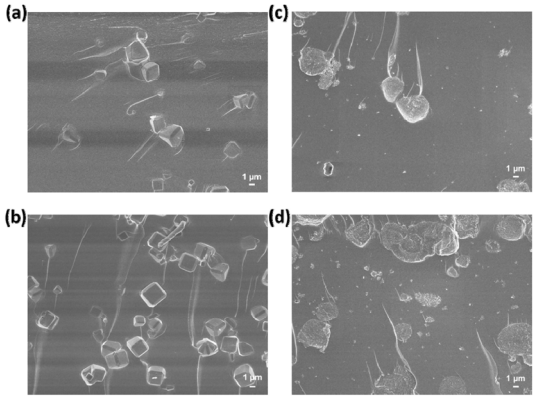

Fig. 4. FE-SEM images of cross-sections of CMSMs; zeolite 5A (a) 10 wt%, (b) 20 wt%; H-zeolite 5A (c) 10 wt%, (d) 20 wt%.

°C), prior to the carbonization process[34]. During this process, the polymer chains had sufficient flexibility to undergo thermal rearrangement to heal the interfacial voids that occurred at a higher temperature (550°C). Nonetheless, it is still difficult to completely seal the interfacial voids, such that microscopically invisible nanogaps at the carbon/zeolite 5A interfaces may still be present.

3.3. O_2/N_2 separation performance of carbon molecular sieve membranes

The O_2/N_2 separation performance of the carbon molecular sieve membranes was evaluated at 35°C and 1 bar by the mixture gas permeation testing (Table 2). As compared to pure Matrimid® 5218 precursor membrane (before carbonization)[35], pure Matrimid® 5218 CMSM showed an enhanced O_2 permeability (4.8 barrer) with marginal dip in O_2/N_2 selectivity (5.64). In addition, the O_2/N_2 separation results for the pure Matrimid® 5218 CMSM were comparable with the data in the literature which reports the O_2 permeability of 5 barrer and the O_2/N_2 selectivity of 6[36]. Meanwhile, it was observed that the incorporation of either zeolites 5A or H-zeolite 5A into the carbon molecular sieve membranes dramatically improved the O_2 permeability.

Table 2. Mixture Gas Permeation Data Measured at 35°C and 1 bar Upstream Pressure (O_2/N_2 = 21/79) for CMSMs derived from Pure Matrimid® 5218 and Mixed-Matrix Precursors

Membrane	O_2 permeabilitya (barrer)	O_2/N_2 selectivity
Matrimid® 5218	4.8 ± 0.2	5.64 ± 0.13
Matrimid® 5218/Zeolite 5A-10%	84 ± 4	4.38 ± 0.16
Matrimid® 5218/Zeolite 5A-20%	142 ± 3	4.22 ± 0.08
Matrimid® 5218/H-zeolite 5A-10%	151 ± 9	4.36 ± 0.16
Matrimid® 5218/H-zeolite 5A-20%	185 ± 6	3.96 ± 0.04

[a] 1 barrer = $10^{-10}\ cm^3_{STP} \cdot cm/cm^2 \cdot s \cdot cmHg$

On the other hand, incorporation of H-zeolite 5A achieved an exceptional enhancement in O_2 permeability, reaching a high O_2 permeability of 185 barrers with only a slight decrease in O_2/N_2 selectivity. It should be noted that the overall accessible surface area for H-zeolite 5A was the lowest among the three zeolites (Table 1). Accordingly, the mesopores were the most probable transport pathways for rapid O_2 diffusion, supplementary to the presence of intrinsic micropores in the zeolite 5A. This is demonstrated by the exceptional enhancement in O_2 permeability (37.5-fold) for Matrimid® 5218/H-zeolite 5A-20% compared with its nascent membrane. It gives a better performance than zeolite 5A under the same particle loading (20%), with 28.6-fold of enhancement has been reported. Although O_2/N_2 selectivity was slightly decreased with the Matrimid® 5218/H-zeolite 5A, the overall O_2/N_2 selectivity was still comparable across zeolites with different particle sizes.

To investigate the success of our optimal design of the filler properties (particle size and pore size) in carbon molecular sieve membranes, the gas permeation results were compared and plotted against the upper bound limit for O_2/N_2 separation. The comparison clearly showed that it was generally challenging for current CMSM to surpass the 2008 upper bound limit[12], as demonstrated in Fig. 5, probably because of the low performance of the porous carbon matrix derived from Matrimid® 5218. In addition, considering the fact that zeolites preferentially absorb N_2 over O_2, there is a possibility of decreased in O_2/N_2 selectivity in mixed-matrix CMSM. In this regard, it is important to emphasize that although our strategy was unable to completely reverse the trade-off phenomenon, the extraordinary enhancement in O_2 permeability by the incorporation of H-zeolite 5A into CMSM alleviated the shortcoming of the trade-off relationship, as demonstrated by a gentler decrease in selectivity. Clearly, this approach drastically improved the overall O_2/N_2 separation performance relative to the pure CMSM. This implies that a performance beyond the upper bound can potentially be realized by using a different polymer precursor that gives higher O_2/N_2 selectivity instead of the inexpensive commercial polymer used in this study. However, using such precursor would inevitably increase the cost of membrane production.

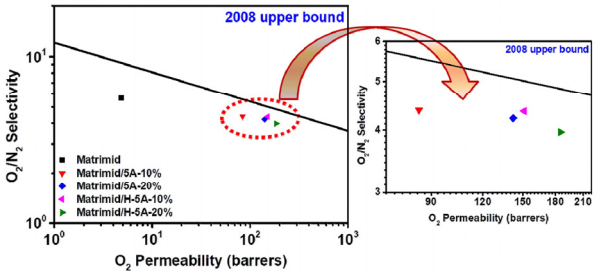

Fig. 5. Robeson plot comparing the O_2 permeabilities and O_2/N_2 selectivities of carbon molecular sieve membranes.

4. Conclusion

Mixed-matrix CMSM containing zeolite 5A with various structural properties were synthesized for enhanced O_2/N_2 separation. In general, incorporating 5A fillers into CMSM dramatically increased the permeability of the membrane with marginal sacrifices in selectivity.

Thus, the study of the investigation of hierarchical porous structure were conducted in a systematic manner. Interestingly, hierarchical zeolite 5A, which contains both microporous and mesoporous domains, improved the performance even further, indicating that the mesopores in the zeolite can serve as an additional pathway for rapid gas diffusion. This strategy is facile yet effective in improving the gas permeability in a cost-effective way and producing high performance membranes based on readily available, inexpensive membrane materials such as commercial polymer and zeolites.

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