

Molecular sieve membranes for N₂/CH₄ separation

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Natural gas consumption has grown from 5.0 trillion cubic feet (TCF) in 1949 to 27.0 TCF in 2014 and is expected to be ~31.6 TCF in 2040. This large demand requires an effective technology to purify natural gas. Nitrogen is a significant impurity in natural gas and has to be removed since it decreases the natural gas energy content. The benchmark technology to remove nitrogen from natural gas is cryogenic distillation, which is costly and energy intensive. Membrane technology could play a key role in making this separation less energy intensive and therefore economically feasible. Molecular sieve membranes are ideal candidates to remove natural gas impurities because of their exceptional size-exclusion properties, high thermal and chemical resistance. In this review, the state of the art of molecular sieve membranes for N₂/CH₄ separation, separation mechanisms involved, and future directions of these emerging membranes for natural gas purification are critically discussed.



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I. NATURAL GAS GENERALITIES

The United States is the world's largest producer of natural gas.¹ As of 2015, the United States produces 28.8 trillion cubic feet (TCF) of natural gas per year.² The United States natural gas production has been increasing every year since 2010,³ and this increase in production can, in part, be contributed to the increasing use of fracking and other technologies that release previously untapped natural gases in shale.³ According to US Energy Information Administration, the natural gas consumption is expected to rise to 31.6 TCF in 2040.⁴ Processing of natural gas is by far the largest industrial gas separation application.⁵ Every year close to 100 trillion standard cubic feet of natural gas are used worldwide. This large demand requires an effective technology to process and purify natural gas.

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Natural gas consists primarily of methane, higher alkanes, carbon dioxide, nitrogen, and hydrogen sulfide as shown in Table I. In particular CO₂ and N₂ decrease the heat value of the natural gas. Therefore, it is highly desirable to remove CO₂ and N₂ from natural gas to improve its heat content, and to avoid the erosion of pipelines from CO₂ in the presence of moisture.

Approximately 14% of US natural gas contains >4% N₂.⁵ However, most pipeline standards require that natural gas contains less than 4% inert gases. N₂ dilutes the heating value of the gas, resulting in lower British thermal units. In the process of purification, it is highly desirable to maintain the gas at high pressure when explored to save recompression costs. In this respect, it is necessary to develop efficient processes to remove N₂ from natural gas.

II. NATURAL GAS NITROGEN REJECTION TECHNOLOGIES

Nitrogen rejection is a challenging technical separation because of the similar molecular size of N₂ (~0.36 nm)

and CH₄ (~0.38 nm). Several processes have been developed to treat natural gas to meet gas specifications.⁵ Many of these high-N₂ gas streams are diluted with low-N₂ gas to meet pipeline specifications. If this is not practical, an N₂ removal unit is required. This unit includes cryogenic distillation, pressure swing adsorption (PSA), lean oil absorption, or membrane separation.⁵

A. Cryogenic distillation

Most of the N₂ reject plants in the US apply a cryogenic distillation process.⁵ This process employs low-temperature thermodynamic distillation based on the boiling point difference between N₂ (−195 °C) and CH₄ (−162 °C). As the mixture cools, CH₄ condensates first, allowing the two gases to be separated. Cryogenic plants are suited to large gas fields that can deliver 50–500 million standard cubic feet per day of gas for 10–20 years.⁵ The major disadvantages of this process are (a) high-energy requirement, (b) high operation cost, and (c) high tendency for blockage of process equipment.

B. Pressure swing adsorption (PSA)

In addition to cryogenic distillation process, PSA has been used to adsorb N₂.⁷ PSA is known to be one of the most economic and widespread processes for gas purification. Typically, PSA employs a zeolite adsorbent or activated carbon to selectively adsorb CH₄ and higher hydrocarbons. The adsorbed gases are then regenerated from the adsorbent with a combination of pressure and thermal changes to give a gas free of N₂. However, there are drawbacks to this process, such as (a) limited gas stream adsorption, (b) discontinuous circulation, (c) complex design of the process, and (d) difficulty in scale up.

C. Lean oil absorption

Lean oil absorption technology absorbs the CH₄ away from the N₂ in a heavy hydrocarbon and then regenerates

the absorbed CH₄ either through staged pressure reduction or through thermally driven distillation.⁸ This technique uses the difference in liquid–vapor equilibrium constants between N₂ and hydrocarbons to selectively absorb the gaseous hydrocarbons in the condensate at room temperature and high pressure, leaving N₂ unabsorbed. The liquid fraction containing CH₄ is then treated to give away N₂-free gas as a product. However, this technique is a less competitive alternative with respect to cryogenic process because of its lower efficiency.⁹

For both PSA and lean adsorption, the resultant methane product would be at low pressure. However, typically the pipeline delivery for further use is at higher pressure and thus, the recompression could be cost prohibitive.

III. MEMBRANE TECHNOLOGY FOR MOLECULAR GAS SEPARATIONS

Separating gases through membranes offers the advantage of low-energy cost relative to the established gas separation processes, such as adsorption and distillation. During the last two decades, membrane technology has been widely used in several industrial separation applications.^{10,11} For membrane separation, the challenge is to develop continuous and reproducible membranes with the necessary separation characteristics. The two main parameters that are used to assess membrane performance for gas separations are: permeance or permeability and separation selectivity α . Figure 1 shows the two types of membranes that can be used for N₂ rejection: CH₄-selective and N₂-selective membranes.¹²

TABLE I. Typical natural gas composition.⁶

Gas	Formula	Mole fraction range
Methane	CH ₄	70–90%
Ethane	C ₂ H ₆	
Propane	C ₃ H ₈	0–20%
Butane	C ₄ H ₁₀	
Carbon dioxide	CO ₂	0–8%
Oxygen	O ₂	0–0.2%
Nitrogen	N ₂	0–5%
Hydrogen sulfide	H ₂ S	0–5%
Rare gases	Ar, He, Ne, Xe	Traces

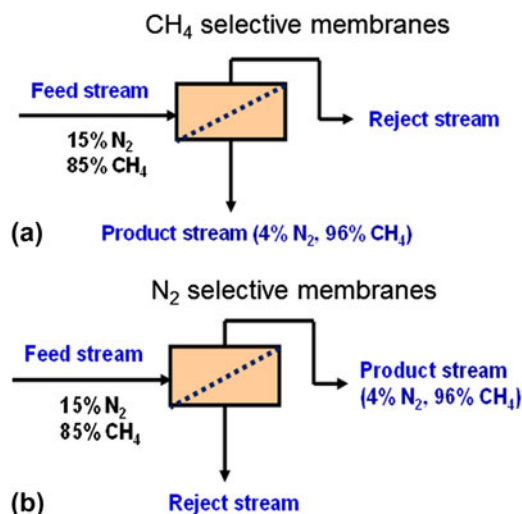


FIG. 1. Membrane configurations for N₂ rejection: (a) CH₄-selective membranes and (b) N₂-selective membranes. Modified from Ref. 12.

For CH₄-selective membranes [Fig. 1(a)], CH₄ is more permeable than N₂ so that it is concentrated in the low-pressure permeate side and needs to be recompressed before it is passed to the pipeline. Meyer and Henson¹³ evaluated the economics for CH₄-selective membranes. Single-, two-, and three-stage systems were analyzed in their study. The estimated costs were too high to be of commercial interest for the state-of-the-art CH₄-selective membranes unless the CH₄/N₂ selectivity could surpass 7. For N₂-selective membranes, CH₄ is rejected to the retentate [Fig. 1(b)], and thus there is a significant saving in recompression cost (by leaving CH₄ in the high pressure side) as compared to CH₄-selective membranes. However, the state-of-the-art N₂-selective polymeric membranes display low N₂ permeabilities, typically less than 10 barrers [1 barrer = 10⁻¹⁰ cm³ (STP) cm/(cm² s cmHg)] at a selectivity of approximately 3. Polymeric membranes including PDMS can achieve higher N₂ permeances but are CH₄ selective.¹⁴ Commercial processes design and economic considerations for the removal of nitrogen from methane employing polymeric membranes are discussed elsewhere.¹⁴

Industrial relevant gas separations are dominated by polymeric membranes. Recently, there has been great interest in the development and application of inorganic membranes displaying molecular sieving properties. In the next sections, we review and discuss the state of the art of these molecular sieve membranes that have demonstrated the ability to effectively separate N₂/CH₄ gas mixtures.

IV. CARBON MOLECULAR SIEVE MEMBRANES FOR N₂/CH₄ SEPARATION

Carbon molecular sieve membranes (CMS) resulting from the high-temperature pyrolysis of some polymers at controlled conditions, represent a novel type of materials, which are highly appealing for molecular gas separations.^{15–19} CMS consist of highly disordered *sp*²-hybridized graphene-like carbon sheets, with very little long-range order (amorphous phases).²⁰ It has been suggested that these *sp*²-hybridized carbon sheets align into lamellar-like structures, yielding ordered microporous structures.²⁰ Specifically, these CMS phases display open micropores connected by rigid slit-like ultramicropores to provide high sorption and diffusion coefficients.²¹ Different from the well-defined microporous structures which characterize zeolites and metal organic frameworks, CMS exhibit distributions of micropores and ultramicropores.²¹

Koros group reported the synthesis of a CMS membrane obtained from a controlled pyrolysis of a commercial polyimide Matrimid® 5218.¹⁹ During the conversion process, (polymer to CMS) scission and reorganization of polymer main chains occur, with small gas molecules

released and free radicals formed.¹⁹ Those free radicals can form interchain or intrachain crosslinking leading to a conjugated aromatic 3D network with a graphene-like structure. With increasing temperature, these networks can form ordered structures. The packing imperfections between ordered regions can form a 'slit-like' pore structure, combined with a bimodal pore distribution. Therefore, the resultant CMS exhibit micropores with a size of ~0.7–2 nm connected by molecular sieving ultramicropores with a size <0.7 nm. The separation performance of these CMS membranes was evaluated for N₂/CH₄ gas mixtures. The membranes displayed N₂/CH₄ selectivities as high as 7.7 and N₂ permeability of 6.8 barrers at 24 °C, surpassing the polymer membrane upper bound line for N₂/CH₄.²² Authors suggested¹⁹ that the distinctive morphology of CMS as well as the presence of ultramicropores led to high observed N₂/CH₄ separation selectivity.

V. ZEOLITE MEMBRANES FOR N₂/CH₄ SEPARATION

Zeolites are hydrated crystalline aluminosilicate minerals made from interlinked tetrahedral of alumina (AlO₄) and silica (SiO₄). These tetrahedrally coordinated atoms (T-atoms) are coordinated to four oxygen atoms and linked to other T-atoms by sharing oxygen with a neighboring T-atom tetrahedron.²³ Zeolites are microporous crystalline solids with a relatively open, three-dimensional (3D) crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-earth metals plus water molecules trapped in the gaps between them.²³ Zeolites exhibit very uniform pore size distribution, high specific surface area, high porosity, and tunable variable chemical composition making them highly attractive for challenging gas molecular separations.

Two types of zeolite compositions in membrane form have been reported to separate N₂/CH₄ mixtures: zeolite SSZ-13 and zeolite SAPO-34. SSZ-13 zeolite displays chabazite topology. Its framework contains a tridimensional pore system made up of 0.38 nm, eight-membered oxygen rings. Its pore size close to the kinetic diameter of CH₄, makes zeolite SSZ-13 suitable for potential molecular sieving effect (for N₂/CH₄ gas mixtures). Wu et al. synthesized SSZ-13 zeolite membranes via secondary seeded growth on the outer surface of mullite porous tubes.²⁴ The resultant membranes displayed remarkably high N₂/CH₄ separation selectivities of 13 but relatively low N₂ permeances [2.2 × 10⁻⁸ mol/(m² s Pa) = 66 GPU] at 20 °C for a feed pressure of 270 kPa. Of all the reported molecular sieve membranes for N₂/CH₄ separation, SAPO-34 membranes have displayed the best overall separation performance for this binary gas mixture. Therefore, the rest of this section will center on SAPO-34 membranes for N₂/CH₄ separation.

SAPO-34, is a chabazite small pore zeolite silicoaluminophosphate displaying average pore size of 0.38 nm and having the composition Si_xAl_yP_zO₂, where $x = 0.01-0.98$, $y = 0.01-0.60$, and $z = 0.01-0.52$.²⁵ Fig. 2 shows a schematic of the framework structure of SAPO-34. SAPO-34 represents an ideal candidate in membrane form to molecular sieve N₂ from CH₄. Two decades ago, the first example of a continuous SAPO-34 membrane was documented.²⁶ Noble and Falconer groups have demonstrated the successful synthesis of high-performance SAPO-34 membranes being able to efficiently separate diverse gas mixtures including CO₂, H₂, CH₄, and other light hydrocarbons.^{24,27-35} The sharp molecular sieving properties of SAPO-34 membranes have been demonstrated for CO₂/CH₄,^{24,27-35} CO₂/N₂,^{36,37} CO₂/butane,³⁸ and Kr/Xe^{38,39} gas mixtures. In all these cases, the smaller molecules diffuse rapidly through the pores of SAPO-34, while the larger molecules at most diffuse slowly, resulting into high separation selectivities.

The next paragraphs describe and discuss the state of the art work related to SAPO-34 membranes for N₂/CH₄ separation. Typically, a continuous polycrystalline SAPO-34 membrane can be grown on a porous support to ensure mechanical strength. These membranes are mainly prepared by the *in situ* synthesis or secondary seeded growth. For the *in situ* crystallization approach, the porous support is immersed into the gel synthesis solution, and then the membrane grows solvothermally by direct crystallization. In the secondary seeded growth approach, crystals or seeds are used to promote heterogeneous nucleation (rather than homogeneous nucleation in solution) at the support–membrane interface. In

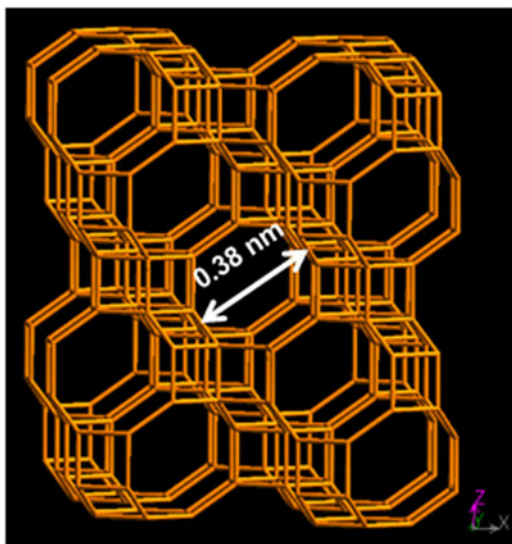


FIG. 2. General schematic of SAPO-34 structure (CHA topology). Modified from database of zeolite structures: <http://www.iza-structure.org/databases/>.

general, this method gives a better control over the membrane formation and quality. Therefore, for SAPO-34 membrane synthesis, typically secondary seeded growth is preferred. All reported SAPO-34 membranes for N₂/CH₄ separation have been successfully grown via secondary seeded growth on porous alumina supports.^{12,24,40-42} These porous tubes were typically 6 cm long with effective permeation areas between 6.5 and 7.5 cm².

Wu et al.²⁴ prepared SAPO-34 membranes by secondary seeded growth on the inside of seeded, porous Al₂O₃ tubes (1-cm O.D., 100 nm average pore size, 40–55% porosity). The membrane synthesis was carried out at 180 °C for 6 h using a gel composition of 0.85 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:2.0 TEAOH:155 H₂O. The template was removed by vacuum calcination at 450 °C for 6 h with heating and cooling rates of 1 °C/min. The authors reported a N₂/CH₄ selectivity of 5–7 for a feed pressure of 350 kPa and N₂ permeance of ~300 GPU. Although the separation selectivity was ~ half of that observed for SSZ-13 membranes,²⁴ the observed N₂ permeance was ~5 times higher. The higher N₂ permeance of SAPO-34 membranes as compared to SSZ-13 membranes was likely related to the membrane thicknesses (~3 μm for SAPO-34 membranes versus ~8 μm for SSZ-13 membranes).

With the hope of improving the separation performance of SAPO-34 membranes for N₂/CH₄ separation, we explored several synthesis parameters, including water content in the membrane gel, crystallization time, support pore size, and aluminum source.¹² We found that high-performance N₂-selective membranes were obtained on 100-nm-pore alumina tubes by using Al(i-C₃H₇O)₃ as aluminum source with a crystallization time of only 6 h. These membranes separated N₂ from CH₄ with N₂ permeance as high as 500 GPU and with N₂/CH₄ separation selectivity as high as 8 at 24 °C for a 50/50 N₂/CH₄ mixture.¹² We found that the heat of adsorption was higher for CH₄ (15 kJ/mol) than N₂ (11 kJ/mol), leading to a preferential adsorption of CH₄ over N₂ in the N₂/CH₄ mixture. On the other hand, the N₂ molecule diffused much faster than the CH₄ molecule suggesting that differences in diffusivity played a more critical role than the competitive adsorption. As such, the SAPO-34 membranes were selective for N₂ over CH₄ in the mixture.¹²

In a very elegant work, Yu and Li's research groups used high-aspect-ratio-SAPO-34 seeds to synthesize via secondary seeded growth thin SAPO-34 membranes for N₂/CH₄ separation.⁴⁰ Figure 3 shows the remarkable control over seeds aspect ratio from ~1 to ~20. These thin seeds were used to synthesize high quality SAPO-34 membranes. Authors claimed that some of these seeds contain the thinnest SAPO-34 crystals reported thus far, which correspond to ~10 unit cells in thickness.⁴⁰ These

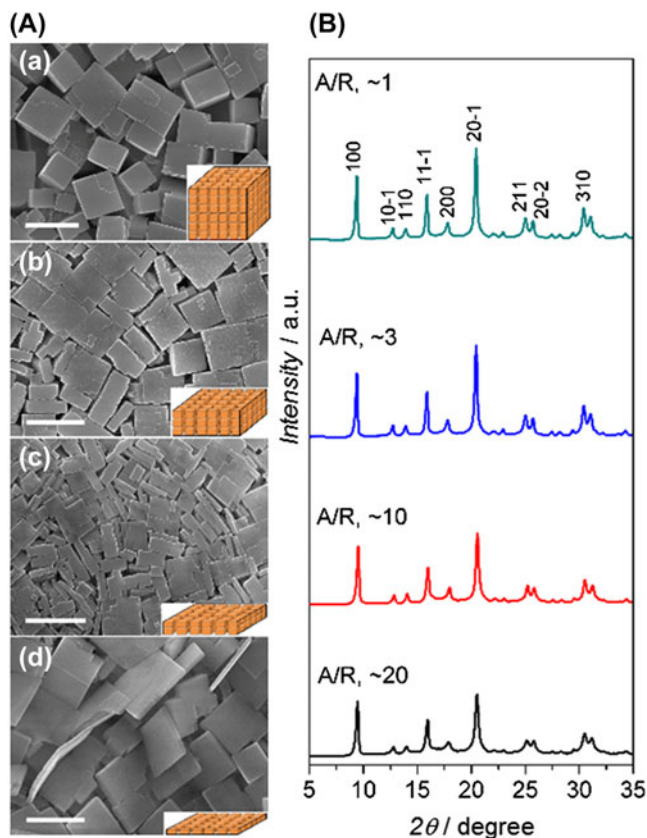


FIG. 3. SEM images (A) and XRD patterns (B) of SAPO-34 seeds with average aspect ratio (AR) of (a) 1, (b) 3, (c) 10, and (d) 20. The insets of each SEM images provided a schematic drawing of the typical morphology of a seed. Scale bars in (a), (b), and (c), 1 μm ; in (d), 0.5 μm . Reprinted from Ref. 40 with permission of Wiley-VCH.

seeds were used to grow SAPO-34 membranes with thicknesses up to ~ 2.3 μm . Interestingly, the authors found that the seed aspect ratio (AR) not only affected the thickness of membranes but also played a crucial role on the control of defect formation. High-aspect-ratio crystals packed much better and formed a much thinner seeding layer than cubic regular crystals. In principle, this helped to minimize the concentration of nonzeolite pores/defects while maintaining a thin membrane thickness. The resultant membranes were tested for separation of equimolar N₂/CH₄ mixtures at 22 $^{\circ}\text{C}$ and at a fixed feed and permeate pressure of 275 kPa and 101 kPa, respectively. These SAPO-34 membranes displayed N₂/CH₄ selectivities as high as 11.2 with N₂ permeance of ~ 860 GPU.

In another report, we optimized synthesis conditions for SAPO-34 membranes toward N₂/CH₄ separation by diluting the membrane gels.⁴¹ Specifically, we used the gel composition of 1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 TEAOH:1.6 DPA:*x* H₂O (where *x* varied from 150 to 400). In Figure 4 representative scanning electron microscope (SEM) images of the membrane surfaces [Fig. 4(A)] show well-intergrown micron range zeolite crystals for SAPO-34 membranes prepared with different

water contents. Cross-sectional SEM images of the membranes [Fig. 4(B)] show zeolite layers. The thickness of the membranes decreased from ~ 6.8 to ~ 2.7 μm as the water content increases from 150 to 400; indicating that diluted gel forms a thinner membrane layer.

These SAPO-34 membranes separated N₂ from CH₄ with N₂ permeance as high as 1300 GPU and selectivity of 7.4 at 23 $^{\circ}\text{C}$ for a 50/50 N₂/CH₄ mixture.⁴¹ Furthermore, membranes were reproducible and effectively separated gas mixtures having low N₂ content which are relevant compositions of natural gas.

Recently our group reported SAPO-34 membranes synthesized in stainless steel autoclaves and Teflon autoclaves with water bath, ice/water bath, and flowing water cooling for N₂/CH₄ separation.⁴² Interestingly, we found that the synthesis in the stainless steel autoclaves cooled with a water bath, ice/water bath, and flowing water cooling resulted in thinner SAPO-34 membranes (as compared to the Teflon liners) and thus into higher permeances for N₂/CH₄ separation and slightly improved N₂/CH₄ selectivities. Specifically, the best membrane displayed N₂ permeance of ~ 2600 GPUs and N₂/CH₄ separation selectivity of 7.4. This membrane was synthesized in the stainless steel autoclave with a water bath cooling. A more selective membrane with a N₂/CH₄ selectivity of 8.6 and N₂ permeance of ~ 2150 GPUs was also prepared in the stainless steel autoclave but with an ice/water bath cooling. These N₂ permeances are the highest reported for any SAPO-34 membrane for this particular binary gas mixture.

Comparing the separation performance of the membranes prepared in the stainless steel autoclaves versus the Teflon liners, we found that the stainless steel autoclaves promoted better membrane performance than those in the Teflon liners, especially for N₂ permeance.⁴² The enhanced N₂ permeance was explained by a simple one-dimensional Fourier heat law analysis.⁴²

In particular, we found that the heat flux rate of the stainless steel autoclaves during membrane preparation was \sim two orders of magnitude higher than that of the membranes prepared in conventional Teflon liners. The higher heat flux rate slowed down the kinetics of crystal growth, translating into thinner and more N₂ permeable membranes.

VI. ALUMINO PHOSPHATE MEMBRANES FOR N₂/CH₄ SEPARATION

AlPO-18 is a microporous aluminophosphate (AIPO), consisting of AlPO₄⁻ and PO₄-tetrahedral units.⁴³ AlPO-18 with AEI topology, possesses a three-dimensional framework with a crystallographic pore size of ~ 0.38 nm.⁴³ Based on the kinetic diameter of N₂ (~ 0.36 nm) and CH₄ (~ 0.38 nm) and the micropore size of AlPO-18, this aluminophosphate could potentially

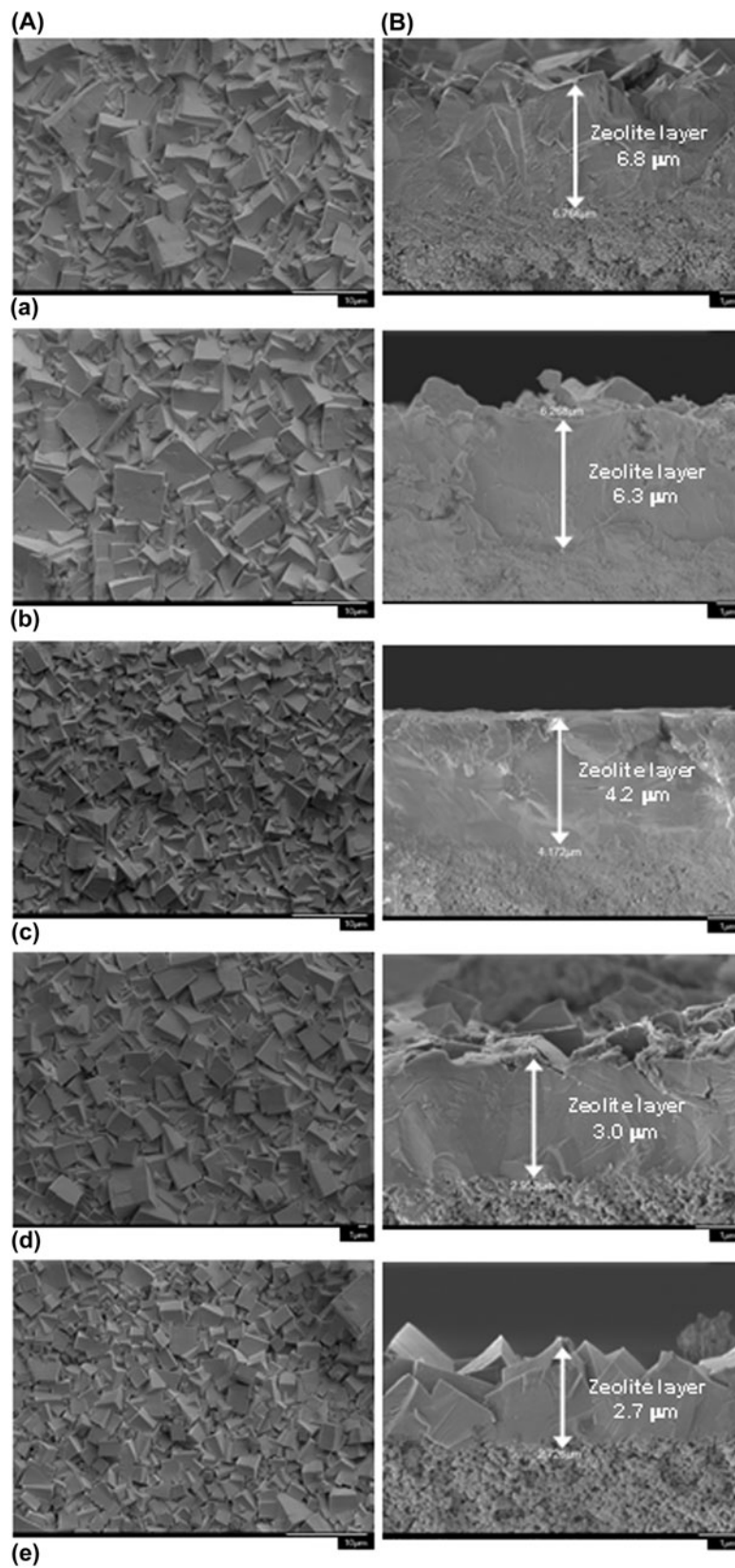


FIG. 4. Top (A) and cross-sectional view SEM (B) images of SAPO-34 membranes prepared with gel compositions of 1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 TEAOH:1.6 DPA:*x* H₂O: (a) *x* = 150, (b) *x* = 200, (c) *x* = 250, (d) *x* = 300, and (e) *x* = 400. Reprinted from Ref. 41 with permission of Elsevier.

molecular sieve N₂ over CH₄ or at least make that N₂ molecules diffuse rapidly through the pores, while CH₄ at most will diffuse slowly meaning that high separation N₂ selectivities could be potentially achieved based on molecular diffusion differences. Our group reported the first example of continuous AIPO-18 membranes exhibiting molecular sieving properties for CO₂/CH₄ gas mixtures.⁴⁴ Later reports by Zhou group confirmed the molecular sieving properties of AIPO-18 membranes for CO₂/CH₄, CO₂/N₂, and H₂/CH₄ binary gas mixtures.^{45,46}

Inspired by the molecular sieving ability of AIPO-18 membranes for these binary gas mixtures, our group recently reported the separation performance of this AIPO for N₂/CH₄ mixtures.⁴⁷ These AIPO-18 membranes were grown via secondary seeded growth on alumina porous tubes. Figure 5 shows representative top and cross-section view SEM images of AIPO-18 membranes. The top view SEM shows well-intergrown rectangular AIPO-18 crystals on the surface of the alumina support [Fig. 5(a)]. The size of the surface crystals of the membrane was larger than that of the seeds, suggesting that secondary seed growth led to a recrystallization process. Cross-sectional SEM image showed a ~2.4 μm thick dense aluminophosphate layer [Fig. 5(b)].

These AIPO-18 membranes were used to separate premixed equimolar N₂/CH₄ mixtures.⁴⁷ The separation results for these membranes are shown in Table II. AIPO-18 membranes displayed N₂ permeances as high as 3076 GPU, with N₂/CH₄ separation selectivities as high as 4.7. To the best of our knowledge, this is the highest N₂ permeance reported for any membrane for this particular binary mixture. Although the separation selectivity is moderate, preliminary economic evaluation for N₂/CH₄ separation¹² suggests that high N₂ permeances are essential to reduce the N₂ rejection cost employing membrane technology. In Table II, separation index³¹ is defined as [$\pi = N_2$ permeance \times (selectivity - 1) \times permeate pressure]. This index has been used as a reliable parameter to predict porous crystalline membrane reproducibility.^{31,38,42,47,48}

AIPO-18 membranes displayed separation indexes π in the 0.11–0.25 mol/m² s range, indicating good membrane reproducibility.

Table III compares N₂ permeances and N₂/CH₄ selectivities for the reported molecular sieve membranes. All these membrane compositions surpass the polymer membrane upper bound line for N₂/CH₄.²² SSZ-13 membranes display the highest reported N₂/CH₄ selectivities, but only moderate N₂ permeances.²⁴ On the other hand, AIPO-18 membranes show the highest reported N₂ permeances, at moderate N₂/CH₄ selectivities.⁴⁷ SAPO-34 membranes show the best overall separation performance, with N₂ permeances as high as 2591 GPU⁴² and N₂/CH₄ separation selectivities as high as 11.3⁴⁰. In the next paragraphs, the separation mechanisms involved in these molecular sieve membranes for N₂/CH₄ gas mixtures are discussed and correlated with their observed separation performance.

VII. MEMBRANE SEPARATION MECHANISMS

A. Carbon molecular sieve (CMS) membrane separation mechanisms

The idealized pore structure of CMS membranes has a bimodal pore size distribution consisting of micropores and ultramicropores.¹⁹ The rigid window pore aperture of the ultramicropores lies between the kinetic diameter of nitrogen and methane, and therefore high diffusion separation selectivity (due to effective size and shape diffusion) has been observed for N₂/CH₄ mixtures over CMS membranes.¹⁸ Furthermore, the rigid pore size nature of CMS membranes introduced an additional factor contributing to the separation mechanism: entropic diffusion selectivity. This factor provides additional diffusion selectivity.^{15,49}

B. Zeolite and AIPO-18 membrane separation mechanisms

It has been proposed that N₂/CH₄ gas mixtures can be separated over SAPO-34^{12,41,42} and AIPO-18⁴⁷ membranes

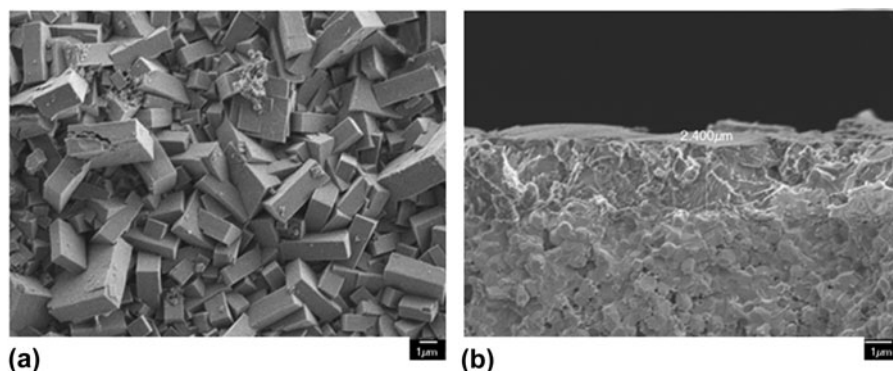


FIG. 5. Representative SEM images of AIPO-18 membranes: (a) top and (b) cross-sectional views. Reprinted from Ref. 47 with permission of American Chemical Society.

by at least one of the following separation mechanisms: (a) *molecular sieving*, in which larger molecules cannot fit into the pores, and therefore the smaller molecules preferentially permeate; (b) *competitive adsorption*, in which one type of molecule is more strongly adsorbed on the microporous structure and thus can dramatically inhibit permeation of the second molecule; and (c) *differences in diffusivity*, in which the smaller, less hindered type of molecule in a mixture diffuses faster than the larger ones. In the case of SSZ-13 membranes, (although not reported) it is expected that at least one of these separation mechanisms is present. In principle, all these three membrane compositions (based on its crystallographic pore size and the kinetic diameter of nitrogen and methane) could display some degree of molecular sieving. However, competitive adsorption and differences in diffusivities have been identified as the most dominant separation mechanisms for N₂/CH₄ gas mixtures.

Nitrogen and methane adsorption isotherms have been used to learn about the competitive adsorption between these two gases. Column breakthrough experiments have been very useful to have a better understanding on the relative difference in diffusivities between N₂ and CH₄.

To learn about these separation mechanisms, our group collected adsorption isotherms for N₂ and CH₄ measured for AIPO-18.⁴⁶ The adsorption isotherms at 140 kPa which corresponded to the transmembrane pressure used during the separation experiments showed CH₄ uptakes of 12 and 15 cm³/g at 298 K and 278 K, respectively, and N₂ uptakes of 4.5 and 10 cm³/g, respectively, (Fig. 6). These results indicated that, at the studied separation conditions of ~140 kPa and at room temperature,

TABLE II. Separation performance of AIPO-18 membranes for equimolar N₂/CH₄ mixtures.⁴⁷

Membrane	Separation selectivity α	N ₂ permeance (GPU)	Separation index π [mol/(m ² s)]
M1	4.6	1463	0.15
M2	3.8	3076	0.25
M3	4.4	1356	0.13
M4	3.0	1867	0.11

TABLE III. Comparison of molecular sieve membranes used for N₂/CH₄ separation.

Membrane composition	Separation selectivity α	N ₂ permeance (GPU)	Thickness (μ m)	Reference
CMS	7.7	~0.1	70 \pm 15	19
SSZ-13	13	66	7.8	24
SAPO-34	5–7	300	2.0–3.0	24
SAPO-34	8	500	6.2	12
SAPO-34	5.7–11.3	281–1200	2.3	40
SAPO-34	6.5–7.4	880–1300	3.0–4.2	41
SAPO-34	7.4–8.6	1728–2591	1.8–2.2	42
SAPO-34	6.2–9.2	1160–1801	2.8–3.5	42
AIPO-18	3.0–4.6	1356–3076	2.4	47

AIPO-18 adsorbed ~2.7 times more CH₄ than N₂. We attributed the preferential adsorption of CH₄ over N₂ in AIPO-18 to differences in polarizabilities of these two molecules. Specifically, CH₄ has higher polarizability ($25.9 \times 10^{25}/\text{cm}^3$) as compared to N₂ ($17.4 \times 10^{25}/\text{cm}^3$).⁵⁰ Therefore, stronger electrostatic interactions between the AIPO-18 surface carrying partial charges⁵¹ and the higher polarizability of CH₄ promoted its preferential adsorption over N₂. Ideal adsorbed solution theory (IAST) indicated that at the used separation conditions, AIPO-18 adsorbed more CH₄ than N₂, in well agreement with the single adsorption isotherms.⁴⁷

To learn about the relative diffusivity differences between N₂ and CH₄, we conducted column breakthrough experiments (Fig. 7) over AIPO-18.⁴⁷ We found

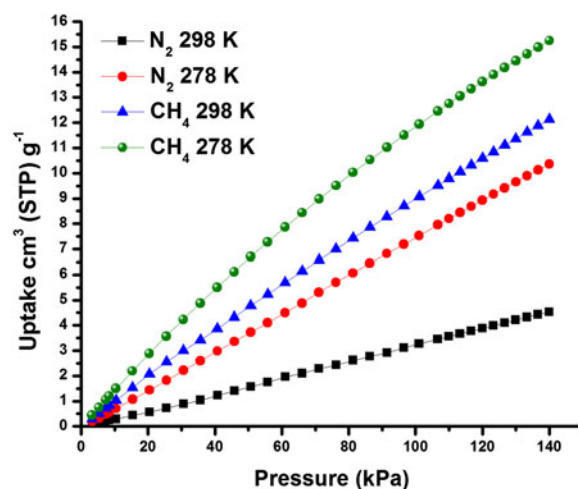


FIG. 6. Single component CH₄ and N₂ adsorption isotherms for AIPO-18 collected at 298 K and 278 K indicating CH₄ preferential adsorption. Reprinted from Ref. 47 with permission of American Chemical Society.

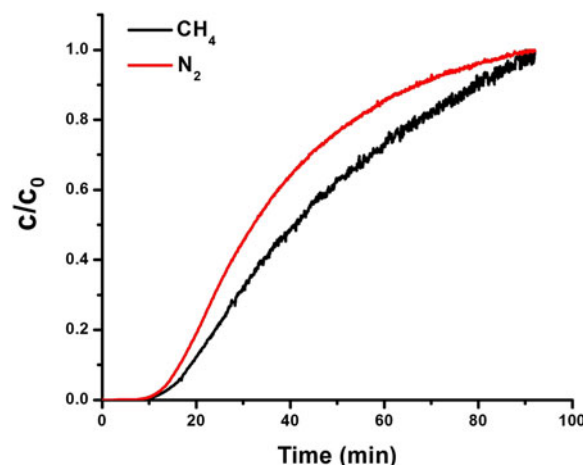


FIG. 7. Column breakthrough experiments for 50:50 CH₄/N₂ gas mixture over AIPO-18. Reprinted from Ref. 47 with permission of American Chemical Society.

that the retention time of CH₄ in the breakthrough was longer, and therefore N₂ diffused faster than CH₄. This was expected since nitrogen has lower affinity to AIPO-18 as demonstrated by the single adsorption isotherms and IAST, as well as to its smaller kinetic diameter. Therefore, breakthrough column experiments suggested that differences in diffusivity favor the separation of N₂ over CH₄ in the gas mixture.

Adsorption isotherms and IAST indicated that CH₄ adsorbs more strongly than N₂. Therefore, the preferential adsorption of CH₄ would favor separating CH₄ over N₂ in the mixture. On the other hand, breakthrough experiments confirmed higher diffusivity of N₂ over CH₄ favoring N₂ selectivity. Thus, the differences in diffusivities would favor separating N₂ over CH₄ in the mixture. These results suggested that for AIPO-18 membranes, differences in diffusivities between N₂ and CH₄ played a more dominant role than competitive adsorption.

For SAPO-34 membranes, adsorption isotherms and single-gas permeation were measured for N₂ and CH₄ to help explain the N₂/CH₄ separation mechanism for the N₂-selective membranes.⁴¹ As shown in Fig. 8, adsorption isotherms showed that CH₄ adsorbs more strongly than N₂ on SAPO-34 crystals (CH₄ adsorbs 1.8–4 times more for than N₂). Therefore the ideal N₂/CH₄ adsorption selectivities were in the 0.25–0.55 range. Thus, the preferential adsorption of CH₄ would favor separating CH₄ over N₂ in the mixture. The preferential adsorption of CH₄ over N₂ in SAPO-34 was explained by differences in dipole polarizabilities of these two molecules. Due to local electronegativity differences between framework Si, Al, and P, SAPO-34 has an anionic framework with a net negative charge depending upon the silicon substitution into the framework.⁴³ Therefore, stronger electrostatic interactions between the negatively charged SAPO-34 surface and the higher polarizability of CH₄ promoted its preferential adsorption over N₂. On the other hand, N₂ a smaller molecule, as compared to CH₄,

diffuses faster. In fact, it has been reported that diffusivity of N₂ is 24 times that of CH₄ through a SAPO-34 membrane.⁵² This indicates that differences in diffusivity would favor separating N₂ over CH₄ in the mixture. Since the reported SAPO-34 membranes were N₂ selective,⁴¹ these results (and similar to AIPO-18 membranes) suggest that differences in diffusivity played a more critical role than the competitive adsorption.⁴¹

VIII. CONCLUSIONS AND OUTLOOK

During the last few years promising research progress has been done in the development of molecular sieve membranes for N₂/CH₄ separation. Some of these membranes display separation performances which are appealing for its potential use at industrial level for nitrogen rejection from natural gas. Although these membranes display overall good separation performance for N₂/CH₄ gas mixtures, practical challenges that may prevent its potential industrial application need to be addressed. Some of the keys aspects that require attention from the scientific community to envision these molecular sieve membranes as a potential economic viable technology to effectively separate this highly challenging gas mixture are discussed in the next paragraphs.

A. Novel membrane compositions

In principle, a “sharper” molecular sieving effect leading to higher N₂/CH₄ separation selectivities can be achieved by developing membranes with rigid pore sizes lying exactly between the kinetic diameters on N₂ and CH₄. In this respect, two ideal candidates for N₂/CH₄ separation are: SAPO-17 and AIPO-17. These microporous crystalline phases display an effective pore size of 0.36 nm,⁵³ ideal to molecular sieve N₂ (0.36 nm) from CH₄ (0.38 nm). Recently, the molecular sieve properties of SAPO-17 and AIPO-17 have been demonstrated for CO₂/CH₄ and CO₂/N₂ mixtures.⁵⁴ Another potential candidate to effectively separate N₂/CH₄ via molecular sieving is the zeolite DNL-6. This zeolite is composed of α -cages linking through 8-rings pore size of 0.36 × 0.36 nm having a body-centered cubic symmetry structure of RHO.^{55,56} If prepared in membrane form, DNL-6 can potentially separate N₂/CH₄ mixtures at high separation selectivities.

B. Ion exchanged membranes

In principle, membrane surface modification should change the adsorption capacity of N₂ and CH₄. SAPO-34¹² and AIPO-18⁴⁷ membranes display preferential adsorption of CH₄ over N₂, leading to a strong competitive separation mechanism for N₂/CH₄ gas mixtures. Therefore, if the preferential CH₄/N₂ adsorption selectivity is reversed or at least attenuated, then much

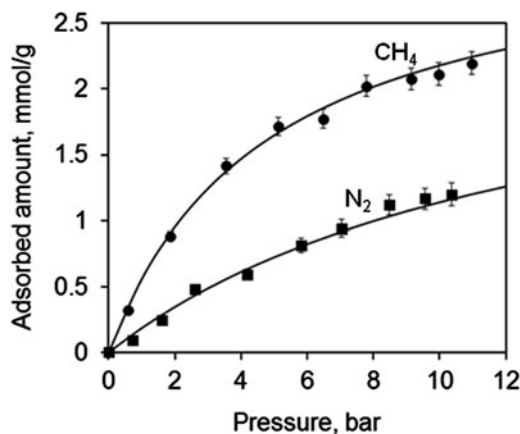


FIG. 8. Adsorption isotherms of N₂ and CH₄ on SAPO-34 at 23 °C. Reprinted from Ref. 41 with permission of Elsevier.

higher separation selectivities than those reported so far can be achievable. Several mono and divalent cations have been used successfully to modify the surface of zeolite membranes and have been demonstrated to be successful in improving gas pair separation selectivities.^{57,58} In particular, Li⁺, Na⁺, and K⁺ ions are suitable candidates to ion exchange zeolite or aluminophosphate membranes to enhance the N₂ adsorption capacity. It has been demonstrated that these cations considerably enhance the adsorption capacities to nitrogen as compared to non-exchanged zeolites.⁵⁹

C. Presence of impurities and realistic separation conditions

Realistic separation conditions for nitrogen rejection from natural gas may require the membrane to perform well at high pressures and or temperatures and in the presence of other natural gas impurities (see Table I). The overall separation performance of the membranes under high pressure and temperature as well as in the presence of other natural gas impurities, will likely decrease. To our best knowledge there are no reported studies in the open literature addressing the stability and performance of membranes under real natural gas conditions (presence of impurities, effect of temperature, and pressure).

D. Membrane reproducibility

Limited reported data on membrane reproducibility is a common problem found in microporous crystalline membranes. Studies on promising membrane compositions for N₂/CH₄ separation should address this issue. The separation index (π)³¹ has been used as a metric to “quantify” membrane reproducibility for zeolites and aluminophosphates. Other metrics would be useful to assess membrane reproducibility.

E. Membrane scale-up studies

Once promising membrane compositions displaying good separation performance for N₂/CH₄ mixtures have been identified at laboratory level, scale-up studies may be required to assess the potential use of these membranes at pilot plant scale. Scaling-up membrane synthesis is not a trivial issue and requires considerable effort from the scientific community. Li et al.⁶⁰ demonstrated the successful scale-up of SAPO-34 membranes for CO₂/CH₄ separations, a binary mixture which is of central relevance for natural gas purification. Studies like this are needed to assess the potential effectiveness of membranes for molecular gas separations not only at laboratory scale but also at pilot plant level.

F. Cost

The relatively high cost associated to the membrane support (in particular for zeolite and aluminophosphate

compositions) may limit its potential practical application for N₂/CH₄ separations. The support accounts for the higher total membrane cost. Therefore, research efforts should consider the use of cheaper membrane supports. In addition, the economics of any separation technology needs to be evaluated in the context of metrics such as cost per kilogram of product and energy use per kilogram.⁶¹

If these challenges and issues are properly tackled, one may see in the near future some of these molecular sieve membranes as a feasible economic technology for nitrogen rejection in natural gas processing.

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