



Review Paper

Membrane Application to Gas Separation of Rare Mixtures: A Review

Joaquín Coronas^{1,2,*}¹ Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50018, Spain² Chemical and Environmental Engineering Department, Universidad de Zaragoza, Zaragoza 50018, Spain

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Highlights

- Membrane gas separation research mainly focuses on CO₂ and H₂ containing mixtures.
- There are mixtures such as H₂/He, H₂/D₂, ³He/⁴He, He/Ne, Kr/Xe, CO₂/He, etc. not very studied with membranes.
- In many cases, the membrane performance has only been studied from a theoretical point of view.
- The review done suggests that intensive work is needed to eventually think of an industrial operation.

Abstract

Typically, gas separation with membranes concentrates on mixtures profusely studied, such as CO₂/N₂, CO₂/CH₄, H₂/CO₂, O₂/N₂, H₂/N₂, He/CH₄, H₂/CH₄, and certain hydrocarbon mixtures, not addressing some non-common, rare but technologically interesting mixtures. However, membrane technology has the potential to address the efficient separation of such rare mixtures, not reported in the current upper bounds basically due to the lack of experimental studies. This review devotes to the membrane application to mixtures including the following: H₂/He, H₂/D₂, ³He/⁴He, He/Ne, Kr/Xe, CO₂/He, and traces from the air. In most cases, the membrane performance has only been studied from a theoretical point of view suggesting that a lot of work is still needed to eventually think of an industrial operation. In any event, there is no doubt about the fact that the advantages that the membrane technology presents for the most studied and better-established gas separations will contribute to solving the future gas separation of these rare mixtures.

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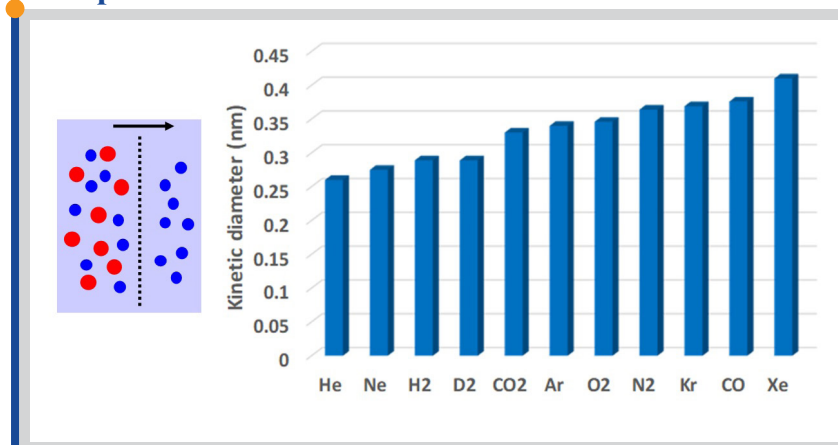
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1. Introduction

Membrane separation constitutes one of the most studied fields in the area of chemical engineering with important working lines devoted to both

liquid and gas phase processes. The effort on gas separation with membranes focus on a few mixtures such as those of permanent gases, including CO₂/N₂,

Graphical abstract



* Corresponding author: coronas@unizar.es (J. Coronas)

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CO₂/CH₄, H₂/CO₂, O₂/N₂, H₂/N₂, He/CH₄, and H₂/CH₄, and of hydrocarbons, including mixtures of linear and branched paraffins and olefins and paraffins. In fact, Robeson reputed work [1] on gas separation concentrates on upper bounds with membranes applied to most of the above-mentioned mixtures, not addressing some non-common, rare but technologically interesting mixtures, not that profusely studied. This category of mixtures is as those rare diseases that the medical science does not investigate with the interest that the patients concerned would desire. These mixtures would comprehend, for instance, mixtures with noble gases or hydrogen isotopes. These mixtures could be included in part in what Yampolskii denominated “unsolved problems of gas separation” [2], corresponding to membrane mixture separations with no satisfactory technical solutions. Yampolskii covered in this denomination the separations of He from natural gas and of CO₂ from gas mixtures [2]. These mixtures may not have found yet a permeability-selectivity membrane material with the required performance but it is clear that they, particularly the latest, have received a lot of attention [3, 4]. In fact, only a few gas separation membrane applications have nowadays a relevant market size: H₂ recovery, N₂ generation, natural gas treatment, and vapor recovery [5].

The focus of this work is on both unsolved and non-very studied gas mixtures but of great technological interest. Figure 1a collects the kinetic diameters of the typical gas components appearing in these rare gas mixtures where membranes have some clear potentiality because of their molecular separation ability. In fact, the simplest way to illustrate a membrane process depicts a vertical line, several different color and size balls on the left and then only one color and size ball on the right (Figure 1b). This is too simple but there is no doubt that future membrane separations will be like this: thin ultrasensitive and ultra permeable membranes fabricated from high performance porous sheet-like materials (e.g. graphene and its derivatives) and able to adjust their separation properties upon regulation with external input (e.g. an electric field [6]) or a certain operating parameter (temperature or pressure). In addition, besides the current commercial and non-commercial membrane applications dealing with water treatment, food processing, petrochemistry, and CO₂ and H₂ emerging technologies, an important future is augured for membranes in the fields of space engineering and exploitation [7].

Last but not least, when dealing with gas separation (e.g. air separation, probably the mixture closer in terms of practical requirements to the mixtures studied in this article), the most important competing technologies are cryogenic distillation, adsorption, and membrane separation. Table 1 compares those technologies for air separation.

2. H₂/He separation

The fusion energy is generated by combining deuterium (D₂) and tritium (T₂) to produce He. During the operation of the fusion system, a large amount of He (doped with 0.1% of H₂) is used to dilute T₂ and prevent its loss through the breeder blanket walls [10]. In principle, this would imply the study of the separation of binary mixtures of T₂ and He; however, in practice, this can be replaced by experimentation with H₂/He mixtures [11]. Simplicio et al. [10] have applied MFI-type zeolite hollow fiber membranes to carry out this separation with H₂ permeance of 1.8·10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ for the maximum H₂/He separation selectivity achieved of 4.2 at 293 K. H₂ is favored over He

due to its smaller molecular weight (Knudsen separation factor of 1.41). Similarly, a H₂ permeance of 1·10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ has been reported for silicalite-1 and ZSM-5 zeolite (both with the same MFI-type structure) flat membranes with respective H₂/He ideal selectivities (i.e. obtained from single gas permeance measurements) of 2.60 and 2.69 at 298 K [12]. These H₂/He experiments together with those corresponding to the separation of the H₂O/He mixture (emulating the T₂O species also involved in the future fusion) have been the base for the numerical analysis of the membrane separation of such mixtures [11]. Finally, even if separation selectivities are more desirable for a practical purpose for the mixture studied here, there are H₂/He permselectivity (i.e. ideal selectivity) values available for other microporous membranes such as those made of metal-organic framework ZIF-8 (2.47 together with H₂ permeance of 4.72·10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 308 K) [13].

3. H₂/D₂ separation

Deuterium (D₂) is a stable isotope of hydrogen involved in chemical reaction mechanism labeling, pharmaceutical technology, nuclear fission, nonradioactive isotopic tracing, nuclear magnetic resonance, neutron scattering techniques, and lighting, among others [14]. In terms of Knudsen diffusion, both the H₂/D₂ and H₂/He pairs have the same value of theoretical separation factor (1.41). In consequence, the study of the separation of the H₂/He mixture can be used to test and validate potential membrane materials to obtain molecular deuterium. Antunes et al. [15] studied the single gas permeances of H₂, D₂, and He through an MFI-type zeolite (ZSM-5) membrane as a function of temperature (in the 298-398 K range). Interestingly, H₂/D₂ permselectivities were smaller than H₂/He ones with an average value of 1.46 (very close to the Knudsen value). The same authors measured smaller H₂/D₂ permselectivities (ca. 0.9) in the case of FAU and SOD-type zeolite membranes. MFI, FAU, and SOD-type zeolites are different in terms of Si/Al ratio and hence exhibit different polarity. However, adsorption plays no important role in the small permselectivities observed by the authors. In addition, Antunes et al. [15] claimed that the H₂/D₂ separation measurements could be extrapolated to other mixtures involving different hydrogen isotopologues for the calculation of Q₂/He (i.e. Q₂ being HD, HT, DT, and T₂) ideal selectivities as a function of the molecular weight. Such selectivities were higher than 1.0 even if DT and T₂ have larger molecular weights than He. In any event, the more hydrophilic zeolite membranes may favor some D₂ adsorption justifying the lower H₂/D₂ permselectivity presented. In this line of separation, despite its defects, a graphene membrane obtained by chemical vapor deposition on a Nafion/carbon support allowed an H₂/D₂ separation factor of ca. 8 at room temperature. [16] In this case, graphene, as part of an electrochemical pump, acts as both cathode and semipermeable membrane to protons and deuterons recombined in the permeate side to form H₂, D₂, and protium deuteride (HD). The authors claimed that the energy consumption based on the application of graphene membranes for heavy water production would be orders of magnitude lower than that involved in current technologies (i.e. electrolysis, combined electrolysis and chemical exchange, adsorption on Pd, crystallization, and distillation, among others) and that a readily accessible 30 m² graphene membrane could be integrated to provide the heavy water production of a modern plant [16].

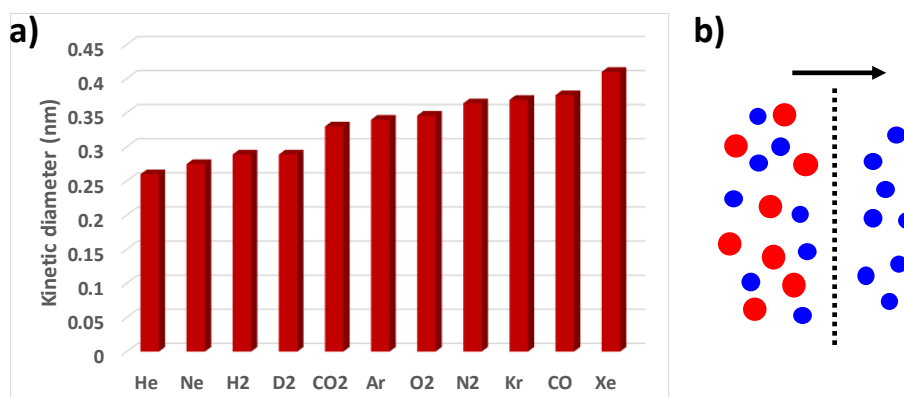


Fig. 1. (a) kinetic diameters of selected gases, (b) ideal membrane separation.

Table 1
Comparison of technologies for air separation.

Technology	Separation principle	O ₂ purity achievable (%) [8, 9]	Status [8]	Energy consumption (kWh/ton O ₂)
Cryogenic distillation	Differences in boiling points	99+	Mature	225 (95% O ₂) ^a
Adsorption	Differences in adsorption capacity and heat	95	Semi-mature	525 (93% O ₂ by pressure swing adsorption) ^a
Membrane	Differences in solubility and diffusivity	40-70	Semi-mature	ca. 250 (ca. 60% O ₂ with O ₂ /N ₂ membrane separation selectivity of 20) [9]

^a <https://www.cosia.ca/sites/default/files/attachments/22164-%20Oxygen%20Generation%20Technologies%20Review%20-%20Rev0.pdf> accessed on November 26th 2021.

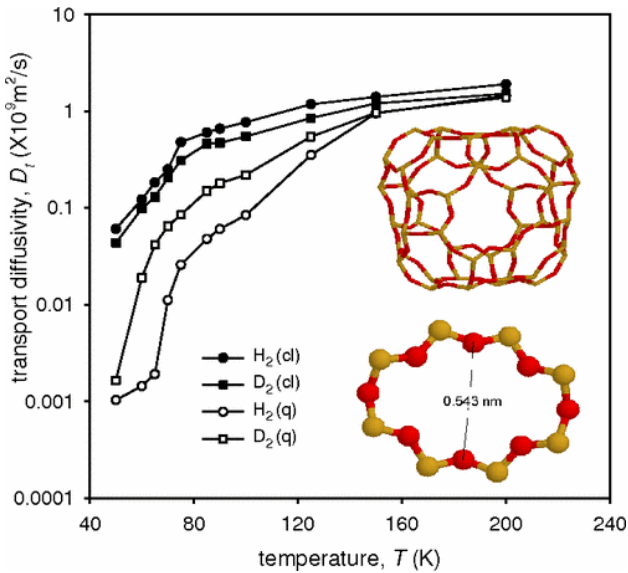


Fig. 2. Transport diffusivity of H₂ (circle) and D₂ (square) using classical (cl) Lennard-Jones potential (solid symbols) and the quantum (q) Feynman-Hibbs potential (open symbols). Inset: one α -cage of RHO-type zeolite and an 8-ring connecting two α -cages [17]. Reprinted figure with permission from A.V. Anil Kumar and Suresh K. Bhatia, Phys. Rev. Lett., 95, 245901, 2005, Copyright (2005) by the American Physical Society.

Finally, Kumar and Bhatia have observed that, when the working temperature is 65 K, atomistic molecular dynamics simulations incorporating quantum effects by using Feynman-Hibbs potential predict a reverse kinetic sieving effect through RHO-type zeolite favoring the heavier D₂ isotope when the classical Lennard-Jones potential would predict the reverse trend (see Figure 2) [17]. In such conditions, a D₂/H₂ selectivity of 46 was calculated.

4. ³He/⁴He separation

Helium-3 (³He) is a rare noble gas with application in several advanced technologies such as cryogenics, medical instrumentation for imaging, isotope labeling, power generation, and nuclear weapons. Even if ³He can be found in samples of natural helium, the industry applies ³He exclusively produced from the radioactive decay of tritium [18]. Qu et al. [19] have theoretically shown that an efficient separation could be achieved through nanoporous graphenylene membranes where quantum effects would promote a kinetic effect favoring the permeance of ³He over that of ⁴He with a ³He/⁴He selectivity of 12.5 at a ³He permeance of ca. 2000 GPU (see Figure 3). 1 GPU = 10⁻⁶ cm³ (STP)·cm⁻²·s⁻¹·cmHg⁻¹; when membrane thickness is 1 μ m, 1 Barrer is equal to 1 GPU. Graphenylene is a carbon allotrope possessing a unique 2D structure with a unit cell composed of two six-membered carbon rings connected by a four-membered ring [20]; it has homogeneous and evenly distributed pores of 0.55 nm in diameter. Graphitic carbon nitride and graphdiyne membranes have also been studied for this separation showing theoretical ³He/⁴He selectivity values below those achieved by either graphenylene (12.5) or N-passivated porous graphene (19 at 3·10⁻¹¹ GPU ³He permeance) [21].

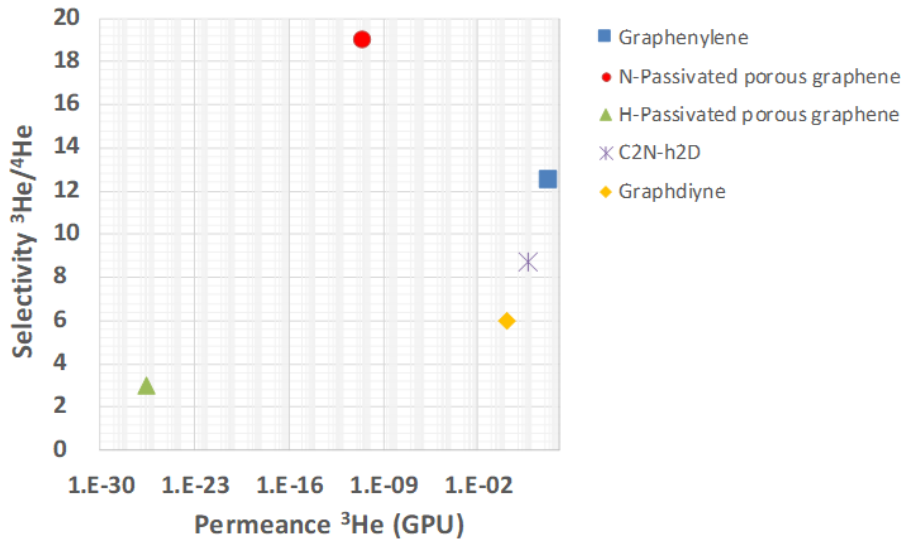


Fig. 3. Theoretical values of ³He/⁴He selectivity as a function of ³He permeance for several 2D porous membranes: graphenylene (at 10 K) [19], N-passivated porous graphene (at 20 K, a porous material obtained by removing two rings from a graphene sheet), C₂N-h₂D (at 10 K, porous graphene-like carbon nitride) [22] and graphdiyne (at 20 K, also called graphyne-2) [23].

5. He/Ne separation

Neon finds application in the electric lamp and radio-electronic industries, laser engineering, aerospace engineering, high-temperature superconductors, vacuum technology, and as a cryogenic agent when operating at 26–40 K [24]. Unlike He, natural gas contains almost no Ne. Thus this gas has to be separated from the He/Ne mixture, a by-product in the cryogenic distillation plants where oxygen is produced from air. The membrane application is, in this case, an alternative method to dephlegmation (i.e. partial condensation of a vapor stream with several components), liquefaction (i.e. cryogenic distillation), and freezing (i.e. distillation from partially freezing feed) [24]. Arkharov et al. [24] studied the He/Ne separation through silica glass membranes operating at 292 K and achieved a maximum Ne content in the retentate of 77.8 vol.% from a feed containing 71.8/28.2 vol.% Ne/He. In any event, the thermodynamic analysis demonstrated that the membrane separation method was more effective in achieving the lowest specific work. He/Ne and He/CO₂ selectivities of $3 \cdot 10^3$ and $1 \cdot 10^{24}$ together with He permeances of $1 \cdot 10^7$ GPU have been calculated at 300 K by density functional theory and molecular dynamics simulation through C₂N [25]. C₂N is a 2D carbon nitride material with the potential to constitute highly permeable monolayer membranes featuring periodically distributed uniform pores of 0.3 nm in diameter. Analogously, nanoporous boron nitride (BN) membranes have been simulated to obtain ultrahigh selectivities of He over Ne, Ar, N₂, CO₂, and CH₄, with a He/Ne selectivity as high as $1 \cdot 10^{13}$ at 300 K [26]. Figure 4 shows three possible porous BN membranes with different pore sizes simulated to separate the just mentioned molecules. In the case of the He/Ne mixture, as the pore size increases from 0.352 nm to 0.378 nm and 0.445 nm, the He/Ne selectivity decreases from $1 \cdot 10^{13}$ to $5 \cdot 10^7$ and 20 at 300 K [26]. In any event, even if these materials seem to be promising their practical implementation has not been demonstrated yet.

6. Kr/Xe separation

Xe finds application in flash and arc lamps, in lasers, and as an anesthetic and gas molecule for different characterizations due to its combined inertness and large size. As in the previous He/Ne separation, the current separation operation that produces these two gases is cryogenic distillation when applied to separate air. This process generates an 80/20 molar mixture of Kr and Xe that in turn is separated by cryogenic distillation to produce both pure Kr and Xe. As compared to membrane operation, cryogenic distillation is more expensive, consumes more energy, and is hazardous. Feng et al. reported the

use of SAPO-34 (a pseudozeolite with the CHA-type zeolite structure) membranes with Kr permeance of $1.2 \cdot 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹) and Kr/Xe separation selectivities of 35 (at 9/1 Kr/Xe feed molar composition) and 45 (at 9/91 Kr/Xe feed molar composition) at room temperature [27]. As the authors pointed out, the preferential adsorption of Xe would favor the separation of Xe from Kr in the gas mixture; however, the high Kr/Xe separation selectivity achieved agrees with the fact that diffusivity differences and molecular sieving due to differences in kinetic diameters (see Figure 1a) are the dominant mechanisms [27]. As an alternative to pseudozeolites SAPO-34 [27] and AIPO-18 [28] (in this case with the AEI-type zeolite structure), metal-organic framework (MOF) ZIF-8 [29] was constituted as a continuous membrane for the same Kr/Xe separation. However, as shown in Figure 5, ZIF-8 membranes displayed a modest Kr/Xe separation performance (Kr/Xe selectivity of 10.6 at 24 GPU Kr permeance) probably due to its flexible porosity, while SAPO-34 membranes exhibited the best Kr/Xe selectivity (25 at 254 GPU Kr permeance) and AIPO-18 membranes the highest Kr permeance (463 GPU together with a Kr/Xe selectivity of 6.4). The worst performance of AIPO-18 in terms of Kr/Xe selectivity as compared to SAPO-34 is explained by the larger AIPO-18 polarizability giving rise to a higher Xe/Kr adsorption selectivity [28]. Finally, a crosslinked polyarylate membrane was displayed at room temperature and 1/9/90 Kr/Xe/He feed molar composition with a Kr/Xe selectivity of 3.6 together with a Kr permeance of 0.22 GPU [30]. However, the membrane lost 25% of its selectivity and 40% of its Kr permeance upon γ irradiation at 20 kGy, what is a relevant information since radioactive ⁸⁵Kr and ¹²⁷Xe are involved in the processing of fission waste.

7. CO₂/He separation

Ilicovich et al. [31] have suggested that the CO₂/He gas pair is useful as a safer emulating mixture for the study of the CO₂/H₂ separation (widely studied), important in precombustion CO₂ capture applications [32]. For this purpose, the authors used a polymeric supported ionic liquid membrane which exhibited a CO₂/He selectivity of 8.7 (10 for the CO₂/H₂ separation) at a CO₂ permeability of 744 Barrer (1 Barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹ = $3.35 \cdot 10^{-16}$ mol m⁻² s⁻¹ Pa⁻¹) at 310 K. This selectivity, favoring the CO₂ transport, is due to the ionic liquid [hmim][Tf₂N] impregnating a commercial porous polymeric support and decreases to 3.1 at 398 K. As expected, as the temperature increases the interaction with CO₂ weakens and the selectivity approaches the typical behavior for H₂/CO₂ and He/CO₂ separations where the faster diffusion of the smaller kinetic in diameter molecules dominates [33].

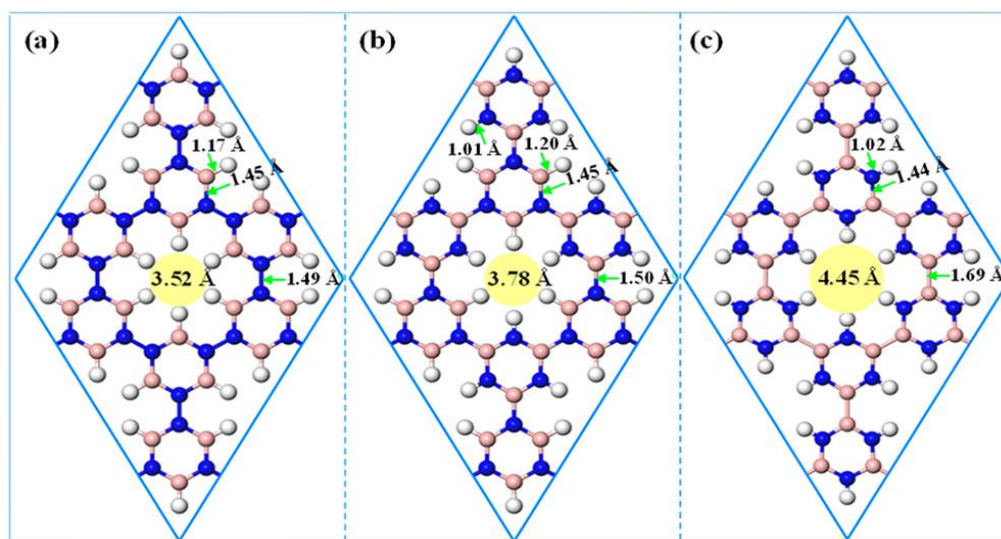


Fig. 4. Three possible porous BN membranes to separate He from other gases. These membranes were named “PBN-BH” (a) porous BN with B atom in the nanosized ring pore and H atom passivation), “PBN-BNH” (b) porous BN with B and N atoms in the nanosized ring pore and H atom passivation), and “PBN-NH” (c) porous BN with N atom in the nanosized ring pore and H atom passivation) [26]. Reprinted with permission from S. Zhou, Z. Wang, M. Wang, J. Wang, S. Wei, W. Guo, and X. Lu. Nanoporous Boron Nitride Membranes for Helium Separation. ACS Appl. Nano Mater. 2019, 2, 4471–4479. Copyright (2019) American Chemical Society.

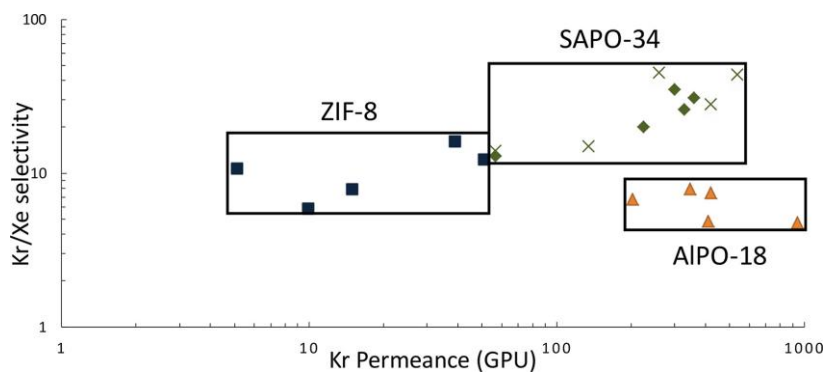


Fig. 5. Kr/Xe selectivity as a function of Kr permeance for ZIF-8, SAPO-34, and AIPO-18 membranes at room temperature and 92/8 Kr/Xe feed molar ratio [28]. Reprinted with permission from T. Wu, J. Lucero, Z. Zong, S.K. Elsaïdi, P.K. Thallapally, M.A. Carreon. Microporous Crystalline Membranes for Kr/Xe Separation: Comparison Between AIPO-18, SAPO-34, and ZIF-8. ACS Appl. Nano Mater. 2018, 1, 463-470. Copyright (2018) American Chemical Society.

8. Separation of traces from air

Minor components from the air such as volatile organic compounds (VOCs), CO₂, and even carbon monoxide have received some attention from membrane researchers. In particular, the separation of different types of VOCs present in the air at trace level has been carried out with several kinds of membranes [34], while CO₂ separation from the air, i.e. the so-called DAC (direct air capture) is a very recent application proposed for membranes [35]. Moreover, the purpose of the separation of the CO/air mixture is the concentration of carbon monoxide to facilitate its analysis from the air. In this regard, an MFI-type zeolite membrane was able to separate carbon monoxide from its mixture with air at 160 ppbv CO concentration obtaining separation factor values of up to 3.1 (at a CO permeance of $7.8 \cdot 10^{-14}$ mol m⁻² s⁻¹ Pa⁻¹) at 245 K [36]. However, carbon monoxide separation results in more interest from its mixture with hydrogen, since to avoid the poisoning of fuel cell electrodes carbon monoxide has to be below 0.01%. This implies high selective membranes to achieve a hydrogen purity of around 99.99%. Palladium membranes can perform the separation with limited operating temperature in the 773-823 K range, which cannot be enough if the H₂/CO mixture comes from a reforming operation at 1073-1170 K [37]. If the goal temperature can be reduced, Castro-Domínguez et al. [38] have demonstrated at a pilot scale (i.e. involving 1050 cm² of membrane area) the production of H₂ with 99.87% purity at 723 K with a Pd-Au membrane prepared on a porous stainless steel support.

Acknowledgments

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