

On a rational performance evaluation for the development of inorganic membrane technology in gas separation and membrane reactors

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Abstract

Inorganic membranes can be made of different materials. However, there have been only few reports on membrane evaluation to convert lab-scale membranes into a prototype for industrial applications. In order to fill this significant gap, new approaches for the development and optimization of membrane products are required. This work focuses on the different aspects related to the performance assessment of membranes used for gas separation and membrane reactors. This approach can be visualized as an algorithm consisting of three specific loops involving different aspects of the overall membrane evaluation. Several factors that have an impact on membrane performance are discussed. These factors are divided into two categories: directly affecting the measurements (setup leakage, concentration polarization, repeatability, pressure gradient) and related to the intrinsic characteristics of permeation flux across the membrane (single and mixture permeation, transport modeling, defect flux, microstructure flexibility). This evaluation protocol includes a literature review with the most recent breakthroughs in this research area.

1. Introduction

Membrane technology is becoming increasingly important in a variety of separation processes. Membrane operations are interesting from the point of view of industrial production. The membrane process is a simple concept and easy to operate. It is modular and relatively easy to scale up. Membrane technology also has promising perspectives to be highly integrated within sustainable energy processes.¹ As the process intensification concept becomes more important, new cost-effective inorganic materials capable of being integrated into highly compact membrane modules² are attracting both academic and industrial attention.

As new permselective materials are being generated, there is a huge potential for the development of new membranes in the nearest future. A number of these new materials when integrated into inorganic membranes are used as proof-of-concept for gas separations. Some examples include zeolitic materials (SAPO-34³ and DD3R (Deca-Dodecasil 3R)⁴), metal-organic frameworks (MOFs)⁵ and natural zeolites⁶. In order to make the transition from a proof of concept to a working prototype for industrial separation processes, a continuous, persisting, strict and systematic membrane testing to optimize the performance is necessary. A thorough understanding of the transport phenomena involved and troubleshooting of laboratory testing are also required.

The development of a synthesis method and tailoring of the material's properties are important goals in inorganic membrane research. Some interesting advances in this area were made during the last decade.^{7,8} However, the evaluation of membrane performance for industrial applications has been incomplete and under limited operating conditions. Molecular sieve properties of novel membranes^{9,10,11}, for example, are generally tested at ambient or low feed pressures.

The comparison of performance data from the literature, for different membranes in a particular application is often difficult due to the use of different operating conditions, selectivity definitions or membrane thicknesses. Even though the need for such information is industrially relevant there continues to be a significant lack of comparative data for membranes in the current literature.

In order to bridge the gap between bench-scale membrane research and applied membrane technologies high quality comparative data are necessary in addition to uniform definitions and a sound interpretation of results. The optimization of the product technology requires the synergy and interaction among material, chemistry and engineering researchers. Lab research advancements usually find a path to industrial implementation within an evaluation approach that emphasizes a feedback loop communication mechanism.

This work aims to develop a strategy for evaluation of inorganic membrane performance. It focuses on an evaluation framework to fill the gap between membrane preparation and performance evaluation for gas separations. This approach divides the problem into a) issues related to membrane testing and b) issues related to permeation behavior. Concentration polarization, repeatability, defect flux and post-synthesis treatments are discussed and their influence on inorganic membrane evaluation is thoroughly investigated.

2. Discussion

2.1. *The evaluation and optimization of membranes*

Figure 1 represents the schematics of development and performance optimization of inorganic membranes. This can be represented as an algorithm of three loops:

1. Testing loop - an inner loop related to the membrane permeation testing, identification of factors affecting measurements, and the necessary iterations to obtain reliable results.
2. Permeation loop - the intermediate loop associated with the research effort in understanding the permeation behavior and the iteration cycles that involve post-synthesis modifications to reach necessary selectivity and permeance.
3. Synthesis loop - the outer loop required when target is not reached on step 1 or 2. This loop includes the modification of the membrane synthesis.

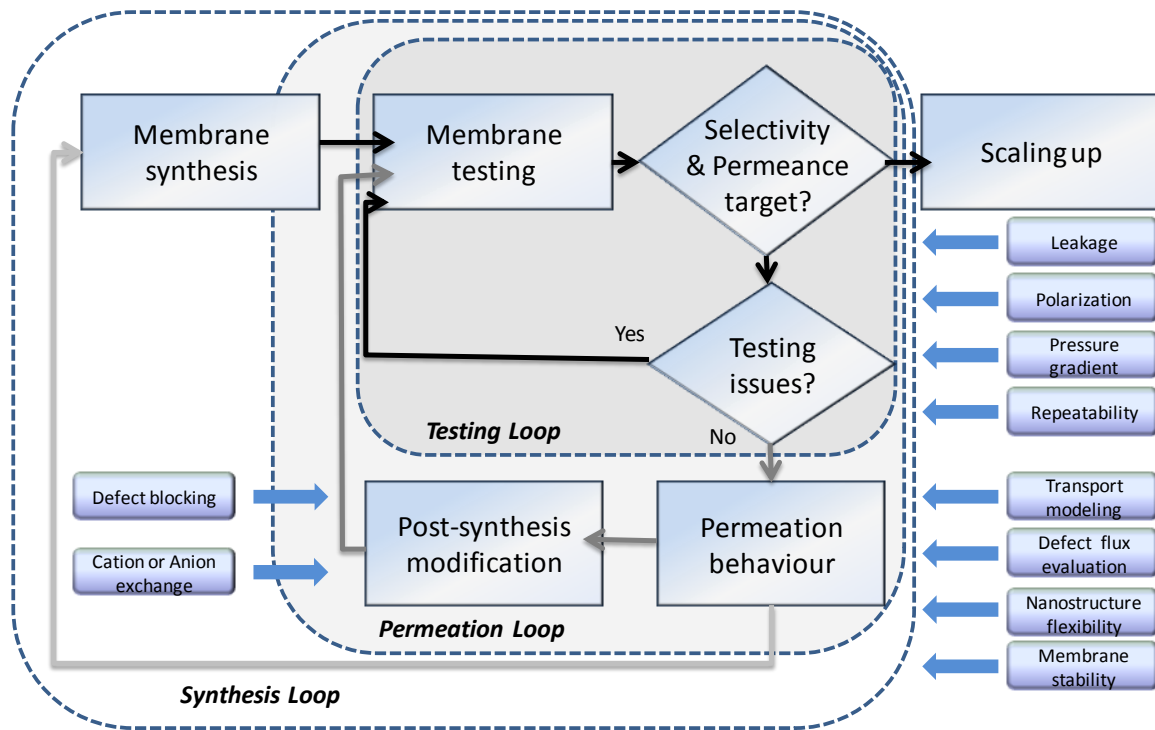



Figure 1. Scheme of an algorithm representing steps involved in the development and optimization of inorganic membranes.

The first step in development and optimization of membranes is the synthesis using the selected recipe. It proceeds with the required quality gas permeation experiments aiming at reaching targeted permeance and selectivity. Permeation experiments need to be carefully performed to secure that results are not being affected by testing issues (system leakage, concentration polarization, pressure gradient and repeatability). This iterative task represents the inner loop of the testing protocol. The iteration stops when a reliable set of permeation data is obtained.

The next step is understanding the permeation behavior of the membrane (the intermediate loop).

A required step is the study of the flux transport to quantify selective and nonselective fluxes.


This involves the identification of flux contribution mechanisms with the assistance of transport

modeling, identification of sizes, number and distribution of defects as well as the effects of nanostructure flexibility and stability. After understanding the reasons for obtaining underperforming membranes, different post-synthesis modification techniques can be proposed to optimize or remediate permeation behavior. These techniques include ion-exchange treatment, defect blocking methods or nanostructure flexibility stabilizer. 

Changes in the synthesis method are required if post-synthesis treatments have not improved membrane performance. As this work focuses on evaluation strategies, the outer loop associated with membrane synthesis is only discussed briefly.

2.2. Testing loop - membrane testing issues

2.2.1. Leakage in the system

System leakage has to be tested at high pressures (defined separately by each application) to confirm that the seals are working properly. Results providing measurements of the sealing quality should be reported. For instance, flux through seals for each component should be $< 0.1\%$ of its respective permeating flux under the same pressure and temperature olar balance closure of species is required to assure that both leakage and gas composition detection are correct.

2.2.2. Permeation evaluation with/without total pressure gradient.

Newly developed membranes are usually tested with the single gas permeation experiments performed at ambient pressure on both feed and permeate sides. Since there is no total pressure

gradient under these conditions, the driving force for permeation is indeed associated with the partial pressure difference between feed and permeate. Thus, a high sweep gas flow rate is required to enhance permeation flux by minimizing partial pressure in the permeate zone. Comparative results obtained under these conditions can be often useful. However, there is no viscous flux if there is no total pressure difference. Viscous or Poiseuille-type transport is associated with the presence of relatively big defects in the membranes. Measurement conditions without total pressure gradient may eventually lead to misleading conclusions about membrane quality. Membrane testing that includes partial increase in feed pressure provides valuable information on membrane quality and defect characteristics.

2.2.3. Selectivity and separation factor

Permeance selectivity (PS) and separation factor (SF) are defined differently. However, they are often used interchangeably making it difficult to compare membrane performances.

Permeance selectivity of component i over j is defined as:

$$PS_{i/j} = \frac{N_i}{\Delta P_i} / \frac{N_j}{\Delta P_j} \quad (1)$$

where N is the molar flux and ΔP is the partial pressure difference.

The separation factor is defined as:

$$SF_{i/j} = \frac{x_i/y_i}{x_j/y_j} \quad (2)$$

with x and y are the permeate and retentate molar fractions, respectively.

Permeance selectivity is defined as the permeance ratio between species. It represents the flux ratio normalized by the driving forces in units of pressure. This means that changes in fluxes are corrected by the changes in partial pressure differences. Separation factor is proportional to the flux ratio. Occasionally, at low feed pressure the permeation flux of the targeted component is low due to the small partial pressure difference. This results in a very low value of separation factor since the flux ratio is low. However, permeance selectivity is high even under these conditions. Permeance selectivity data would provide a good estimate for membrane performance which may not be realistic at these pressure conditions.

$PS_{i/j}$ in Eq. (1) can be also expressed in terms of molar fractions as:

$$PS_{i/j} = \frac{x_i / P_R y_i - P_P x_i}{x_j / P_R y_j - P_P x_j} \quad (3)$$

From this equation, $PS_{i/j}$ and $SF_{i/j}$ only yield the same values when: i) a large sweep gas flow rate is used in the permeate side, i.e., $x_i, x_j \rightarrow 0$ and ii) membranes are tested either using vacuum in the permeate side or at sufficiently high pressures in the retentate side, i.e., $P_R \gg P_P$.

Membrane development and optimization requires a correct interpretation of results based on the proper selectivity definitions.

2.2.4. Sweep or no-sweep, effect of counter-diffusion.

The use of sweeping gas is required when the permeate flux is low. In general, a high sweep gas flow rate yields a low concentration of permeating gases at the permeate side and driving forces

across the membrane are enhanced. Depending on the module geometry, a lower sweep gas flow rate can lead to imperfect mixing at the permeate side affecting driving forces locally and decreasing the efficiency of the separation. Counter-diffusion of the sweeping gas can also be a reason for reduction of the permeating gas flux. However, to the best of our knowledge there are no comparative studies available quantifying the effect of sweeping gas counter-diffusion on permeation flux.

2.2.5. Repeatability

The repeatability of results is key in membrane evaluation especially since industrial processes require that membranes maintain permeance and selectivities during prolonged periods of time. Water adsorption is known to affect permeate flux through hydrophilic selective layers. Different contents of water adsorbed in the zeolite film can be the reason for the lack of reproducibility of permeance and selectivity results for the same membrane. Water molecules adsorb strongly within hydrophilic zeolite crystals reducing the movement of other gas molecules. Consequently, the selective flux fraction and selectivity decrease. Moisture content in membrane layers depends on the temperature of the thermal treatment prior to the membrane permeation test. However, permeance and selectivity can also be affected during permeation tests if feed gases are not completely dry.

Thus, a comparative membrane evaluation has to identify whether the changes are reversible or permanent when the membranes are tested at high temperature, high pressure or prolonged periods of contact with the feed gas mixture.

2.2.6. Identification of concentration polarization effects

Polarization is a mass transfer phenomenon at a boundary affecting the separation efficiency of a mixture. Concentration polarization in processes involving membranes typically occurs when there is a mass transport limitation for the faster permeating species in the fluid phase compared to the transport in the selective layer. Consequently, there is a reduction of the more permeable component in the boundary layer adjacent to the membrane and there is an accumulation of the less permeable species (Figure 2). As a result, the efficiency of the membrane decreases.

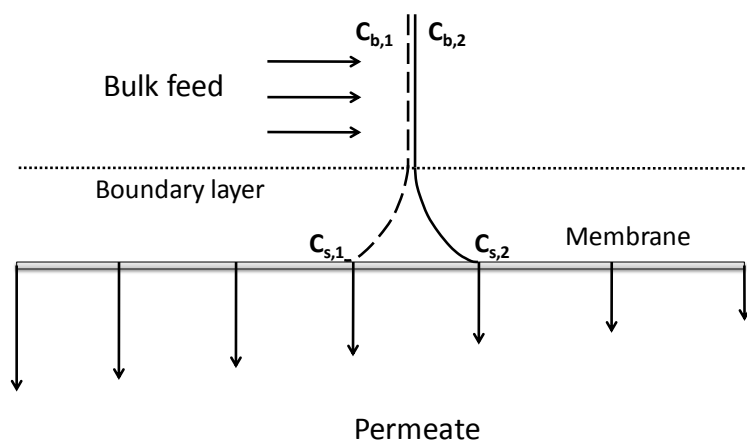


Figure 2. Schematics of the polarization phenomena in the boundary layer between the membrane surface and the fluid phase. C_b and C_s represent molar concentrations in the bulk phase and near the membrane surface respectively.

The evaluation of membrane performance should take into account the possibility that observed permeation data may be affected by concentration polarization. Under these conditions, results do not reflect the intrinsic flux functionality and selectivity of the selective layer. The presence of polarization phenomena occurring during membrane evaluation can be identified by the following observations: a) the increase of axial flux velocity favors the permeation transport of the fastest permeating component, b) as pressure increases the effect of concentration polarization on membrane performance is more pronounced. This is related to the fact that as pressure increases, diffusivity decreases, axial velocity decreases and permeate flux increases.

Concentration polarization conditions in gas permeation can be quantified by the polarization index ($I_p = C_s/C_B$). I_p is defined as the ratio between the concentration of the permeating gas near the membrane surface and the bulk phase concentration. Thus, as I_p deviates more from one the polarization effect becomes more pronounced. I_p can be expressed in terms of the Peclet number ($Pe = v \delta/D$) defined as the ratio of convective velocity across membrane to diffusive velocity in the boundary layer.¹²

$$I_p = e^{Pe} + \beta(1 - e^{Pe}) \quad (4)$$

To minimize concentration polarization ($I_p \rightarrow 1$), the value of Pe should approach zero. For this, the boundary layer thickness (δ) has to be minimized. The dependency of boundary layer thickness for laminar flow¹³ can be expressed as

$$\delta \sim \left(\frac{v_L d_h}{D}\right)^{-\frac{1}{3}} L^{\frac{1}{3}} d_h^{\frac{2}{3}} \quad (5)$$

where v_L is the velocity along the membrane, d_h is the equivalent diameter, L is the length of the membrane and D , the diffusivity.

To evaluate membranes under the condition of polarization minimization the high flux velocity is required. From Eq. (5), δ decreases as the gas velocity v_L increases. Also, the use of spacers helps to reduce the gap between the bulk phase and the membrane surface, i.e. by lowering d_h in Eq. (5), the thickness δ drops. As pressure increases, however, concentration polarization increases. Under these conditions the Peclet number increases because the convective velocity across membrane (v) increases, diffusivity D decreases and consequently boundary layer thickness (δ) increases. As Pe values increase, I_p deviates further from one. The effect of concentration polarization on zeolite membranes performance under high pressure conditions was shown by Avila et al.¹⁴. As inorganic membrane development moves toward industry-scale configurations, concentration polarization becomes more important during membrane evaluation. A recent report showed that concentration polarization had a dramatic effect during the performance evaluation of a monolith membrane for CO₂/CH₄ separation.¹⁵ Similarly, serious concentration polarization effects were found during the evaluation of ceramic hollow fiber supported membranes for H₂/C₃H₈ separation.¹⁶

2.3. Permeation loop - permeation behavior issues

After all the testing issues are addressed, the permeation results should reflect the permeance characteristics of the membrane. The observed permeation flux may depend on several factors:

- 1) The intrinsic functionality with pressure and temperature of the selective flux fraction.

Generally, the selective flux in inorganic membranes depends on the coupled effect of

adsorption and diffusion processes which, indeed, are dependent on pressure and temperature conditions.

- 2) Non-selective flux through membrane defects. Defect flux depends on the characteristic size and number distribution of the defect pores as well as on pressure and temperature conditions during the test.
- 3) For supported membranes, the macroporous support may provide a mass transport resistance as the thickness of the selective layer is reduced.
- 4) External and internal surface barriers associated with adsorption/desorption kinetics can be present, and, thus, cause additional resistance to transport through the membrane.
- 5) In the case of using a sweep gas, counter-diffusion may affect permeation flux.

2.3.1. Single gas permeation

The single gas permeation test supplies the basic information regarding the permeation characteristics of a membrane. The identification of patterns in the permeation behavior as temperature and pressure change provides insights on the membrane characteristics. For this purpose, measurements across a large range of temperatures and pressures are recommended. Table 1 summarizes the expected permeance responses of single gas flux across inorganic membranes to changes in the operating conditions (temperature and pressure).

Effect of temperature. The increase of temperature enhances the flux through the selective layer due to the activation process of diffusion.¹⁷ However, permeation flux may decrease for strong or moderate adsorbing species at low temperatures. The adsorption loading on the selective layer decreases as the temperature rises providing a negative impact on the permeation flux. The non-

selective flux decreases as temperature increases. Defect flux can be Knudsen-, Poiseuille- or transition-type (between Knudsen and Poiseuille). Knudsen and viscous transport mechanisms have a decreasing trend as temperature increases.¹⁷

Effect of pressure. Observed permeance data as pressure increases provide complementary information for better understanding of the permeation behavior. Permeance through the selective layer generally decreases as feed pressure increases. As feed pressure increases, the adsorbate loading within zeolite membrane crystals increases. Adsorption isotherm approaches saturation and as a result membrane permeance decreases. In contrast, permeance through nonselective channels does not decrease as feed pressure increases. Knudsen-type permeance through pore defects remains constant as feed pressure rises, while viscous or Poiseuille-type permeance increases.

Table 1. Typical permeance responses of single gas flux across inorganic selective layers to partial step-like changes of operating conditions (pressure and temperature).

Permeance response (Mol / m ² s Pa)				
Membrane pathway				
By increasing	Nonselective	Selective	Example	Ref.
Temperature	Decreases	Increases (weak adsorbing species)	H ₂ through small pore zeolite layers	(18)
		Decreases (strong adsorbing species)	CO ₂ through MFI films	(19)
Pressure	Remains constant or increases	Decreases	CO ₂ through SAPO-34 films	(20)

2.3.2. Mixture gas permeation

After basic characterization with single gas permeation, the evaluation using a gas mixture is required to enhance membrane performance according to industrial application standards. The permeation flux of species in the gas mixture through inorganic membranes may significantly differ from the single gas permeation flux. Mixture gas permeation flux can be indeed affected by competitive adsorption and the interaction among diffusing molecules. Competitive adsorption plays a key role at low and moderate temperatures. Under these conditions, the

comparison between single gas and mixture permeations in the same membrane can be used as a method to show the contribution of selective flux. Competitive adsorption plays a significant role in the permeation of CO₂ mixtures with CH₄, N₂ or H₂ through zeolitic materials at moderate temperatures. CO₂ molecules interact strongly with most zeolite frameworks. The loading of the weak-adsorbing gas for the CO₂ mixture at the zeolite cavities becomes relatively low in comparison to a single component at the same pressure. Figure 3 depicts permeate flux profiles of the weak adsorbing species for two membranes with different qualities. The permeation flux of the weak adsorbing gas decreases in the presence of CO₂. The decrease of flux in the mixture may be associated with the quality of the membrane. The larger decrease of CH₄, N₂ or H₂ permeation fluxes occurs in membranes with less defect flux, i.e. more selective membranes.

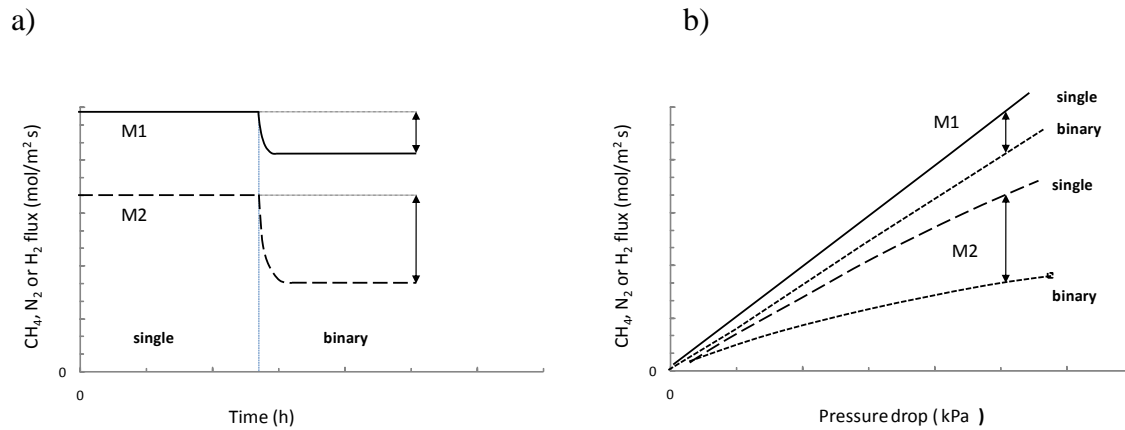


Figure 3. Changes of permeation flux of relatively weak adsorbing gases (CH₄, N₂ or H₂) at low or moderate temperatures when testing system switches from single to binary permeation mode with CO₂: a) with time and b) pressure drop. M1 and M2 correspond to less and more selective membranes, respectively.

2.3.3. Transport model assistance to study permeance behavior.

The modeling and simulation of gas transport through zeolite membranes is a useful tool to understand membrane behavior and predict its permeation and selectivity under different operating conditions. The simulation of membrane permeance assists in the analysis of experimental observations of different membranes and the effect of membranes modifications on their performance.

Gas transport through the selective layer has been described by many models. The Maxwell-Stefan formulation has been extensively applied to explain transport mechanisms in zeolite films.²¹ The use of nanoscopic models based on the molecular dynamics has been useful to predict diffusivities. These models have been useful in providing parameters for macroscopic models.²²

Defect flux characterization is required to improve membrane performance. Defect flux is generally dominated by Knudsen and viscous transport mechanisms. The Knudsen number K_n , the ratio of mean free path to pore radius, indicates the flux regime. Viscous flux occurs when $K_n < 0.01$. For $K_n > 10$, Knudsen diffusion transport prevails.²³ Defect characteristics and operating conditions for inorganic membranes generally result in Knudsen numbers between 0.01 and 10, reflecting a transitional flux regime with both Knudsen and viscous flux contributing to defect flux.²⁴

Within a framework of membrane development and optimization it is important to construct models capable of screening hundreds of membrane prototypes. Thus, the building of comparative parameters to rank membrane performances becomes increasingly important.

Membranes can be classified based on selective and nonselective flux fractions, average defect size or defect area fraction.¹⁷

2.3.4 Membrane defects

Current research is concentrating on the synthesis of inorganic membranes with a minimum of defects. Most of the inorganic membranes show a non-selective pore size distribution. Defect flux has a negative impact on the overall selectivity. The gas flux through the defects depends on their relative size and the operating conditions. Defect sizes, their number and distribution are usually estimated by perporometry experiments. However, these experiments often have to be confirmed by additional measurements. Gas permeation data with molecules passing only through defects provide useful information that complements perporometry data.²⁰ It has recently been shown that defect density in zeolite membranes can be non-uniformly distributed along the membrane surface.²⁵ The gas permeation was measured locally through a mapping of the membrane surface using a mass spectrometry probe along with a motion control system. This information was used to identify defect zones of the membrane.

2.3.5. Proper evaluation of post-synthesis modification

Blocking treatment of defects: defect sealing techniques can be associated with a new trend in the development of inorganic membrane technology. A significant increase of membrane selectivity proves the effectiveness of the blocking treatment. The sealing treatment of the membranes is

also associated with a decrease in permeation flux. This flux drop is related to the plugging effect on defects reducing nonselective flux. However, this flux drop can also be partially associated with the presence of the sealing material, blocking a fraction of the membrane area that was functional before the treatment. Therefore, the defect blocking treatment should be applied to defects rather than to functional areas reducing selective flux. An accurate evaluation is required to properly detect the effects of membrane modification on permeance and selectivity.

The effectiveness of the blocking treatment also depends on the intrinsic pore sizes and their number distribution within the membrane. Small molecules (0.4-0.8 nm) could block effectively small defect areas with Knudsen-type permeation. Large molecules are able to block large defects causing a decrease of the Poiseuille-type flux. Often, relatively large defects are the reason for the selectivity drop under high pressure conditions.

The evaluation of the effectiveness of the membrane treatment to block defects should include the comparison of membrane permeances as a function of pressure before and after modification. Also, single gas permeation data using a component with a molecular diameter large enough to flow only through defects are of primary importance to reach an accurate assessment of the treatment. Table 2 summarizes the performance results of a variety of inorganic membranes post-treated with different blocking agents. In all cases the treatments improved selectivity. The permeance values of faster species decreased dramatically. The cyclodextrin treatment of SAPO-34 membranes was successful and increased CO₂/CH₄ selectivity at high pressure while the CO₂ permeance decreased only slightly (about 10%).

Table 2. Blocking defect treatments on inorganic membranes and their performance results for gas permeation reported during the last four years.

Membrane	Blocking Agent	Performance				Ref.
		Gas mixture	Pressure / Temp	Permeance	PS / SF	
			kPa / K	Mol / m ² s Pa x 10 ⁷		
				From - To	From - To	
Silica	PDMS ^(a)	H ₂ /CO ₂	506 / 403	~ (0.8 – 0.08) (H ₂)	~ (4 - 30)	(26)
Silicalite-1	SSQ ^(b)	CO ₂ /N ₂	530 / 300	~ (3.4 – 0.5) (CO ₂)	~ (1 – 15)	(27)
SAPO-34	CD ^(c)	CO ₂ /CH ₄	4600 / 295	0.47 – 0.42 (CO ₂)	48 - 63	(20)
SAPO-34	Al ₂ O ₃	H ₂ /CO ₂	1500 / 473	(5-10) - ~0.65 (H ₂)	~ (1 - 20)	(28)

^(a) Polydimethyl siloxane

^(b) Silsesquioxane/silicate hybrid

^(c) β -cyclodextrin

Microstructure flexibility. Inorganic membranes are prone to suffer from structure flexibility.

There have been numerous reports describing the distortion of zeolite membranes because of crystal expansion/contraction.^{29,30} The stability issue could be worse in the novel MOF-based membranes because many MOF structures are flexible as pressure increases.³¹

However, it is not yet clear whether the zeolite structure flexibility as pressure rises can affect membrane performance more than the nonzeolite flux contribution. Similar to MOF structures, there are no comparative reports explaining the effect of flexibility on membrane performance. Membrane evaluation has to investigate whether the performance drop as pressure increases is dominated by the defect flux originated from the synthesis or by non-selective flux coming from defects depending on flexibility structure issues. A complete evaluation of defect distribution in size and number of the original membrane is required. However, there is an increasing demand for new and practical methods to obtain number and size distribution of defects and their location on the surface. Kumakiri et al.³² and Funke et al.²⁵ measured gas permeation locally using a mass spectrometry probe along with a motion control system. This information was applied to identify the defective zones of the membrane. This technique provides a more complete picture than other integral methods mentioned above.

Cation and anion exchange. Many attempts to modify membrane permeation by cation exchange have been reported. However, the comparative evaluation is not easy. Cations inside zeolite pores can affect permeation according to their different sizes and polarities. Large cations may hinder the flux through zeolite pores. Multi-valent cations have stronger interactions with permeating species than mono-valent cations by modifying adsorption affinities and permeation flux. On the other hand, non-selective flux through defects often masks results related to cation exchange modification. The success of a membrane post-treatment through cation exchange depends on the original defect size distribution of the membrane and the nonselective flux fraction under the given operating conditions.

Anion exchange was also reported as a method to boost membrane performance. It proved to be successful, both in zeolite³³ and MOF-based³⁴ CO₂ selective membranes. By incorporating amino groups within the zeolite pores, CO₂ adsorbs stronger and the permeance increases. Initially, CO₂ permeance increases as more amino molecules get into the zeolite cavities. However, permeance drops as loading approaches saturation. Amino groups may block diffusing pores and affect membrane separation performance.

Conclusions

Guidelines for the development and optimization of the inorganic membranes are discussed. An effective evaluation strategy is outlined by considering the problem as an algorithm of three loops: testing, permeation and synthesis.

Membrane testing can be affected by leakage, polarization and, the pressure gradient. These factors often result in the appearance of permeation data artifacts. The correct identification of these factors is crucial in order to avoid misleading conclusions.

The understanding of the intrinsic permeation flux through inorganic membranes requires the contribution of different evaluation aspects: single permeance dependencies on pressure and temperature; interactions of diffusing species within mixture permeation; characterization of defect flux and valid models to treat data comparatively. Identifying the reason for poor performance of inorganic membranes is the key step in order to obtain effective membranes after post-synthesis modification.

A uniform evaluation of inorganic membranes is required to facilitate their development and optimization. The organization of the evaluation protocol using a systematic approach is a key

factor to make the leap from bench-scale membrane research into commercial products for real world gas separations.

Acknowledgements

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