



## Research Paper

## Characterization of Commercial Ceramic and Hybrid Membranes Using Gas Permeation and Permporometry Tests

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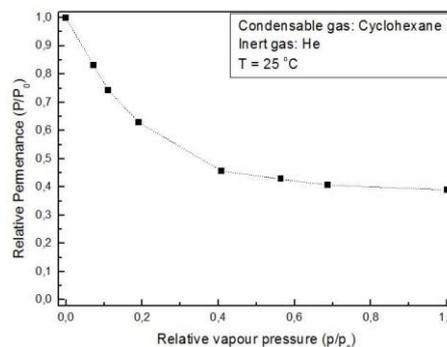
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### HIGHLIGHTS

- Highly selective hybrid Silica membranes for H<sub>2</sub> separation applications.
- Highly permeable Titania membranes with selectivities in Knudsen diffusion regime.
- A permporometry method for pore structure evaluation.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The gas separation performance of commercial ceramic Titania and hybrid silica (HybSi<sup>®</sup>) membranes was assessed using the gas permeation and permporometry methods. Results indicated that the HybSi<sup>®</sup> membranes have a hybrid surface containing regions covered by a polymeric matrix and others with inorganic pores. These membranes have high H<sub>2</sub> selectivity, which increases significantly with temperature and after exposure to H<sub>2</sub>O vapors. On the other hand, Titania membranes have a very narrow pore size distribution in the low mesoporous or in the upper microporous range. These membranes have very high permeance but moderate selectivity which is not affected by H<sub>2</sub>O exposure.

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### 1. Introduction

In the last few decades, membrane technologies have attracted the attention of the scientific community for many industrially important applications. Membrane processes have several advantages compared to the conventional separation techniques (e.g. distillation, extraction, absorption

and adsorption). Specifically, they are compact and easy to scale-up, fully automated and with no moving parts. They do not require energy intensive phase changes or potentially expensive adsorbents and/or difficult to handle solvents [1].

In the field of gas separation, considerably more effort has been put in the development of polymeric membranes. Consequently, polymeric membranes

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are commercially available at large-area membrane modules and can be bought at relatively low cost. Moreover, since mid '70s polymeric membranes are used effectively in the ammonia industry for hydrogen recovery from off-gases. However, the limited thermal and chemical stability of polymeric membrane materials renders them inadequate for many industrial applications, where there are needs for separation at temperatures  $>80$  °C (to avoid hydrocarbon condensation), or in the presence of corrosive and strong plasticizing gases. For this reason, there has been an important shift in research and development towards inorganic and hybrid (organic-inorganic) gas separation membranes the last two decades. These membranes are more chemically and thermally stable compared to polymeric membranes, while they offer high permeability and selectivity for small gas molecules like  $H_2$  and He over larger ones like  $N_2$ ,  $CO_2$  and  $C_3H_8$ . Furthermore, their application in membrane reactors seems to be very promising in order to enhance conversion in thermodynamically limited reactions (e.g. dehydrogenation reactions, the water gas shift reaction, etc.). This application fits perfectly in the industry's process integration and intensification strategies, and the main industrial trends in process development nowadays [2-4].

Metallic Pd-based membranes are the most studied material from this category since they are 100%  $H_2$  selective. Many modeling and lab-scale experimental studies demonstrated the high potential of the incorporation of Pd membranes to membrane reactors, in order to enhance conversion of thermodynamically limited reactions. In particular, palladium membranes were used in the electronics industry for the production of pure hydrogen in the second half of the 1990s. Since then, great progress has been conducted in membrane preparation methods in order to produce more permeable and stable membranes. This led to an expansion of the potential application field, covering from  $H_2$  separation processes for fuel cell applications to dehydrogenation or reforming reactions. Nowadays, self-supported or asymmetric Pd-based membranes and membrane reactors are commercially available worldwide for small scale applications [5]. Recently, a pioneering work has been established in Tokyo Gas Ltd., where an auto-thermal natural gas membrane reformer system was developed for simultaneous  $H_2$  production and  $CO_2$  capture. This work, except for a proof-of-concept demonstration, also proved that Pd-based membranes and membrane reactors are ready for scale-up towards an industrial scale application [6].

However, it is often pointed out that Pd membranes have some serious drawbacks in terms of cost and stability, when a large scale industrial application is discussed [7]. Moreover, there is an intermediate temperature regime (e.g. 80-300 °C) between the application fields of polymeric and metallic membranes, where the application of Pd-based membranes is not recommended because of very low permeance values. Finally, it must be noted that Pd-based membranes can only focus on  $H_2$  separation applications. All these enhanced the interest for R&D in other types of gas separation inorganic membranes. Towards this direction, nanoporous ceramic and hybrid membranes have the advantages of unique chemical and thermal stability, high mechanical strength and long lifetime compared to polymeric membranes, and they are at the same time more permeable and stable, and less expensive than Pd-based membranes. These membranes have been commercialized mainly for micro-, ultra- and nano-filtration applications, but not for gas separation. Nevertheless, academic, lab-scale experiments showed that these membranes have a very high potential of use at various gas separation processes. The main problem that inhibited the industrial penetration of these membranes in the previous years was their poor reliability. It proved that they were very difficult to move from lab-scale to a larger scale mainly because of: (a) the uncertainty in producing defect-free large area supported membranes, (b) high temperature sealing difficulties and (c) the lack of demonstration experiments at real process conditions which could attract the industrial interest [7-11].

Silica membranes are the most well studied nanoporous ceramic membranes in the literature because of their ease of production and their proven high performance for many applications. An important drawback of these membranes is their poor stability in water vapor containing atmospheres, like in a water-gas shift (WGS) environment. Despite the early detection of this problem by many researchers, there is not much R&D in the literature regarding other nanoporous gas separation ceramic membranes. Therefore, there is a strong need at this point to develop nanoporous ceramic membrane materials of higher quality, which along with silica membranes could cover all the potential industrial needs for a hydrogen separation system [12]. In this study, the gas separation properties of commercial nanoporous  $TiO_2$  and hybrid silica membranes is evaluated. The nanoporous  $TiO_2$  membrane is a potential candidate material for highly stable porous membranes. It is known to be a superior inorganic material in chemical and physical stability and it is utilized for high performance filtration with a cutoff of less than 500 Da. Moreover, its photocatalytic activity opens new fields of application including, e.g. the photocatalytic wastewater treatment or even the photocatalytic water splitting for  $H_2$  production. Therefore, if  $TiO_2$

membranes could be effectively used as a material for gas separation membranes, those membranes could be applied to several chemical industrial processes [13,14]. On the other hand, nanoporous hybrid silica membranes could combine the high separation performance of silica membranes with the increased hydrothermal stability of polymeric membranes, reducing the maximum operating temperature of these membranes [15].

The membranes used in this study have been commercialized for pervaporation processes, but can be easily applied in gas separation or used as starting material for the development of more selective membranes with post-treatment methods. The main target of this study is to assess the gas separation performance of current state-of-the-art commercial ceramic and hybrid membranes and create a benchmark for further studies in the field. The results of the study could benefit the commercialization and engineering practice of the ceramic and hybrid membrane in gas separation applications and also attract the industrial interest for this technology.

Towards this direction, in the Materials and Methods section we report details for the commercial membranes used in this study and for the experimental methods employed for characterization and performance assessment. Next, in the Results and Discussion section we report the experimental results of the study and an overall evaluation of them, based on literature data. Finally, in the Conclusions section we report the main outcomes of the study along with some thoughts for further research in the field.

## 2. Materials and Methods

The membranes used in this study were in the form tubes, with 10mm OD, 7 mm ID and 25 cm length and procured from Pervatech BV. Two different types of membranes were tested, a nanoporous  $TiO_2$  membrane and a hybrid silica membrane (HybSi<sup>®</sup>), with pore size ~1 nm and 0.3-0.5 nm respectively, according to the manufacturer. The membranes had a multilayered structure consisting of a macroporous tubular support, an inside mesoporous layer and an additional inside coating of a top-layer, which is responsible for the separation efficiency of the membranes. These membranes have been commercialized by Pervatech for  $H_2O$  removal through a pervaporation process, but their small pore size renders them potential candidates for gas separation processes as well.

The separation performance of the membranes was assessed with single gas permeation experiments. Specifically, single gas permeance of various gases ( $H_2$ , He,  $N_2$ ,  $CO_2$ ,  $C_3H_8$ ) was measured at pressures of 2-10 psig and temperatures of 25-150 °C, while the respective permselectivity values were calculated as the ratio of two single gas permeance values. The permeance measurement was conducted by applying a fixed pressure on the membrane's feed side and measuring the permeation rate of the gas in the permeate side at atmospheric pressure. A conceptual process flow diagram of the experimental unit is shown in Figure 1.

The porous structure of the membranes was evaluated with the permoporometry method. This method is considered as the most suitable for studying the porous structure of nanoporous membranes and especially for the evaluation of the "active" pores and for defects detecting [16,17]. The theoretical background of permoporometry is based on the combination of capillary condensation with gas permeation. Specifically, a non-condensable gas which contains a condensable vapor (at various concentrations up to saturation) is fed to the membrane. The condensable vapor fills the smaller pores of the membrane and blocks the permeation of the non-condensable gas through the membrane. By increasing the concentration of the condensable vapor, larger pores are blocked and the permeation is further reduced. A curve that shows the permeance of the non-condensable gas with the concentration of the condensable vapor gives important information about the porous structure of the membranes. In our experiments He was used as an inert gas. Condensable gas can be used as any vapor, provided that it has a reasonable vapor pressure and is inert with respect to the membranes that will be characterized. In our experiments, cyclohexane was used as condensable vapor because it is an agent commonly used in the literature for this type of membrane [18,19]. The permoporometry tests were conducted at room temperature and 5 psig feed pressure. A conceptual process flow diagram of the experimental unit is shown in Figure 2. More details regarding the experimental methods used have been presented elsewhere [20,21].

## 3. Results and Discussions

Figure 3 shows the permeance of various gases with temperature in the HybSi<sup>®</sup> membrane and Table 1 shows the respective permselectivity values compared to the theoretical Knudsen ones, at 5 psig feed pressure. Gas permeation is in the order of  $H_2 > He > CO_2 > N_2 > C_3H_8$  which is neither

according to their kinetic diameter (encountered in micropore diffusion), nor according to their molecular weight (encountered in Knudsen diffusion). Moreover, gas permeance increases with temperature, indicating an activated transport mechanism for all gases tested, while in many literature references about microporous silica membranes the permeance of the larger molecules (e.g.  $C_3H_8$ ) decreases with temperature [22]. This is probably due to the hybrid nature of the membrane, which allows parallel gas transport through

two different regions, the inorganic pores and the polymeric matrix. This is also probably the reason for the unusual behavior of some permselectivities with temperature, which increase up to 100 °C and then decrease at 150 °C. Specifically, the temperature dependence of permselectivity is determined by the effect of temperature on the permeation of the two gases through the two different regions.

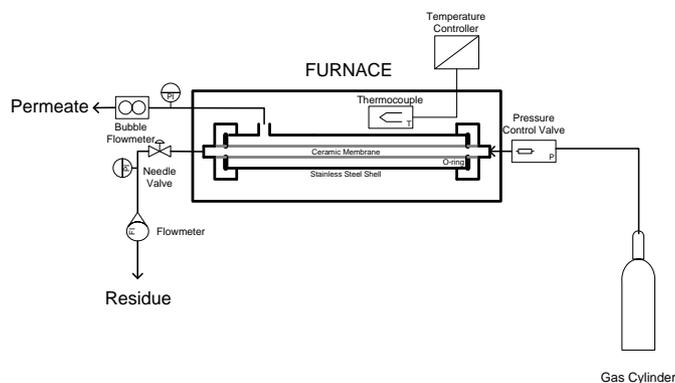


Fig. 1. Process flow diagram of the gas permeance experimental unit.

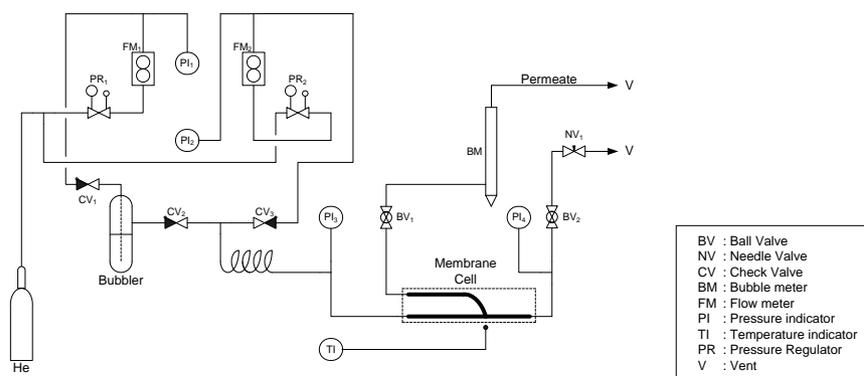


Fig. 2. Process flow diagram of the permperometry experimental unit.

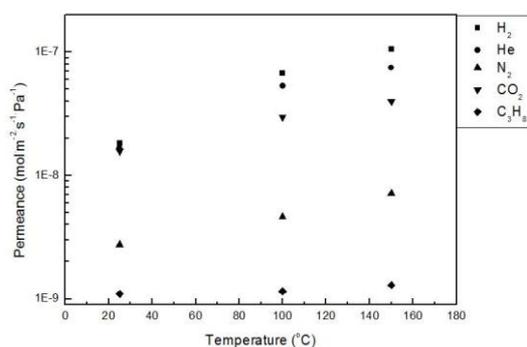


Fig. 3. Gas permeance of various gases with temperature in the HybSi® membrane at 5 psig feed pressure.

At this point it must also be noted that the membrane's permeance was constant with pressure for all gases tested, indicating the absence of defects (e.g. macropores) from the membrane's top-layer. This is also confirmed from the permselectivity values of the membrane, which are considerably higher than the theoretical Knudsen ones, as even a small number of defects can dramatically reduce the selectivity of the membrane [23]. Especially, the  $H_2/C_3H_8$  selectivity is high enough to render the membrane potential candidate for many industrially important gas separation applications (e.g.  $H_2$  recovery in refineries).

Figure 4 shows the relative He permeance with relative cyclohexane vapor pressure for the HybSi® membrane. The relative permeance decreases with relative vapor pressure in the range of 0-0.4 and remains almost constant thereafter. At a relative pressure of 1 (He saturated with cyclohexane vapors) the He permeance is at 40% of its initial value (pure He gas). This behavior

confirms the hybrid nature of the membrane's surface with a narrow distribution of inorganic pores (all pores blocked from cyclohexane vapors at relative vapor pressure up to 0.4) and a polymeric matrix (where He permeance remains unaffected from the cyclohexane vapors). In a parallel resistance model, these data indicate that ~60% of gas transport resistance comes from the inorganic pores and ~40% from the polymeric matrix.

Table 1

Permselectivity values of various gas pairs at different temperature and 5 psig feed pressure, compared with the theoretical Knudsen ones for the HybSi® membrane.

	Permselectivity			Knudsen selectivity
	25 °C	100 °C	150 °C	
$H_2/N_2$	6.7	14.6	14.8	3.74
$He/N_2$	6.1	11.5	10.5	2.65
$H_2/CO_2$	1.2	2.3	2.7	4.69
$CO_2/N_2$	5.7	6.4	5.6	0.80
$H_2/C_3H_8$	16.7	58.6	82.2	4.69

The stability of HybSi® membranes to water vapors was studied by measuring gas permeance before and after exposure of the membrane in a He gas stream containing ~3% water vapors at 150 °C for 48h. Table 2 shows permeance and permselectivity values for the HybSi® membrane before and after the exposure. It is impressive that while  $H_2$  permeance decreases slightly, the permselectivity values of  $H_2$  over larger gas molecules increase significantly. This is probably caused by rearrangements in the inorganic pore

structure, because when a silica surface is exposed to water vapors, the “condensation” reaction between neighboring surface silanol groups can lead to structure densification [24,25]. All these rearrangements probably created a denser inorganic pore structure with lower permeance but considerably higher selectivity. The permselectivity values are considerably high and higher than others reported in the recent literature. For example, Qureshi et al. [26] employed a sol-gel process to prepare microporous organosilica membranes, using BTESE as precursor. The derived membranes had a  $H_2/N_2$  permselectivity ranging from 10 to 21 at 200 °C. In another study, Hove et al. [27] prepared zirconia doped organosilica membranes, using BTESE as precursor, which exhibited an  $H_2/N_2$  permselectivity up to 100 at 200 °C.

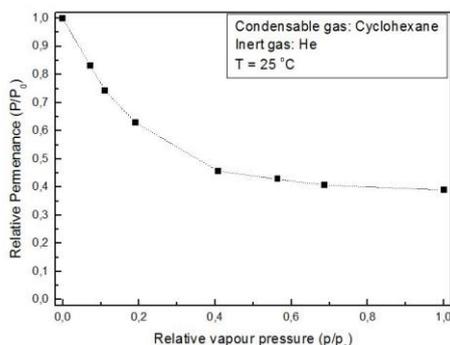


Fig. 4. Relative permeance with relative vapour pressure of cyclohexane in the HybSi® membrane.

Table 2

Permeance and permselectivity values for the HybSi® membrane before and after H<sub>2</sub>O exposure at 150 °C and 5 psig feed pressure.

	Permeance x 10 <sup>8</sup> (mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> )					Permselectivity				
	H <sub>2</sub>	He	N <sub>2</sub>	CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>	H <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	CO <sub>2</sub> /N <sub>2</sub>	He/N <sub>2</sub>
Before H <sub>2</sub> O exposure	10.61	7.49	0.72	3.99	0.13	14.8	2.7	82.2	5.6	10.5
After 48h exposure in H <sub>2</sub> O/He (3/97%)	8.12	6.18	0.04	3.12	0.01	203	2.6	812	78	155

The overall performance of HybSi® membranes render them ideal for applications in many industrial gas separation processes, where the gas mixtures often contain water vapors, and the conventional microporous silica membranes have proven to be unstable.

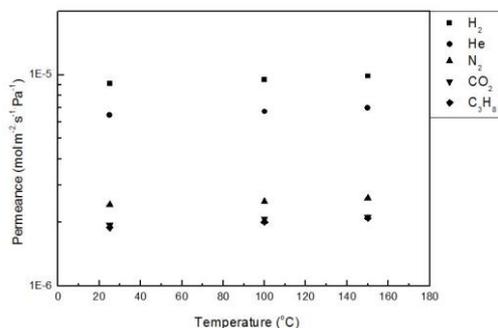


Fig. 5. Gas permeance of various gases with temperature in the Titania membrane at 5 psig feed pressure.

Figure 5 shows the permeance of various gases with temperature in the Titania membrane and Table 3 shows the respective permselectivity values compared to the theoretical Knudsen ones at 5 psig feed pressure. Gas permeance is in the order of  $H_2 > He > N_2 > CO_2 \approx C_3H_8$  and remains almost constant with temperature. The permselectivity values of the membrane are almost identical with the theoretical Knudsen ones, indicating that Knudsen diffusion is the dominant mass transfer mechanism in the Titania membrane. At this point it must be noted that the membrane's permeance was constant with pressure for all gases tested, indicating the absence of defects (e.g. macropores) from the membrane's top-layer, which could decrease the membrane's permselectivity lower than the theoretical Knudsen values. This means that the Titania membrane has pores in the low mesoporous range or in the upper microporous range, but not small enough to add a molecular sieving

effect in the tested gases. However, it is important that the  $H_2/CO_2$  selectivity is 4.7 at 150 °C, compared to 2.7 for the HybSi® membrane. This, along with the much higher  $H_2$  permeance of the Titania membrane ( $9.88.10^{-6} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) compared to the HybSi® membrane ( $1.06.10^{-7} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$ ) renders it a better candidate for potential application in this separation process (e.g. for  $H_2$  separation after a WGS reactor).

Figure 6 shows the relative He permeance with relative cyclohexane vapor pressure for the Titania membrane. The relative permeance is almost constant for relative vapor pressure up to ~0.25 and then decreases rapidly to almost 0 for relative vapor pressure up to ~0.35. This behavior is typical for defect-free membranes with a narrow pore size distribution in the low mesopore range and upper micropore range [21].

The stability test of the Titania membrane to water vapors revealed no changes in the membrane's permeance and permselectivity values, indicating a membrane with substantial hydrothermal stability.

Table 3

Permselectivity values of various gas pairs at different temperatures and 5 psig feed pressure, compared to the theoretical Knudsen ones for the Titania membrane.

	Permselectivity			Knudsen selectivity
	25 °C	100 °C	150 °C	
H <sub>2</sub> /N <sub>2</sub>	3.8	3.8	3.8	3.74
He/N <sub>2</sub>	2.7	2.7	2.7	2.65
H <sub>2</sub> /CO <sub>2</sub>	4.7	4.6	4.7	4.69
CO <sub>2</sub> /N <sub>2</sub>	0.8	0.8	0.8	0.80
H <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	4.8	4.7	4.7	4.69

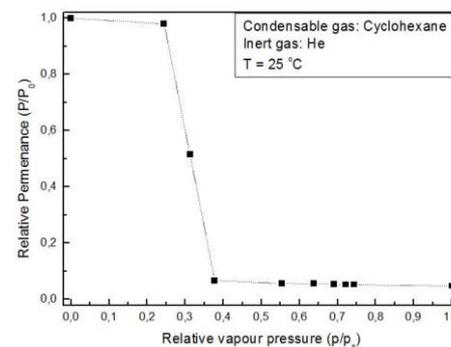


Fig. 6. Relative permeance with relative vapour pressure of cyclohexane in the Titania membrane.

#### 4. Conclusions

The gas separation performance of commercial ceramic Titania and hybrid silica (HybSi®) membranes was assessed in this study. The results revealed that HybSi® membranes have a hybrid surface structure, consisting of regions covered by a dense polymeric matrix and regions with inorganic pores. These membranes are highly selective for  $H_2/C_xH_y$  separation processes. It must be noted that the selectivity of these membranes increased significantly after 48 h of H<sub>2</sub>O exposure at 150 °C and very high permselectivity values were observed ( $H_2/N_2 = 203$ ,  $H_2/C_3H_8 = 812$ ).

On the other hand, Titania membranes have much higher  $H_2$  permeance (about two orders of magnitude) but the permselectivity values of all gases tested were in the Knudsen diffusion regime. However, the narrow pore size distribution, the defect-free surface and the high hydrothermal stability render Titania membranes an ideal substrate for the application of post-treatment methods for selectivity increase [28].

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