

Novel concept for the preparation of gas selective nanocomposite membranes

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Abstract. In this work we report on a novel concept for the preparation of gas selective composite membranes by a simple and robust synthesis protocol involving a controlled *in-situ* polycondensation of functional alkoxy silanes within the pores of a mesoporous ceramic matrix. This innovative approach targets the manufacture of thin nanocomposite membranes, allowing good compromise between permeability, selectivity and thermomechanical strength. Compared to simple infiltration, the synthesis protocol allows a controlled formation of gas separation membranes from size-adjusted functional alkoxy silanes by a chemical reaction within the mesopores of a ceramic support, without any formation of a thick and continuous layer on the support top-surface. Membrane permeability can thus be effectively controlled by the thickness and pore size of the mesoporous layer, and by the oligomers chain length. The as-prepared composite membranes are expected to possess a good mechanical and thermomechanical resistance and exhibit a thermally activated transport of He and H₂ up to 150 °C, resulting in enhanced separation factors for specific gas mixtures e.g. $F_{\text{H}_2/\text{CO}} \sim 10$; $F_{\text{H}_2/\text{CO}_2} \sim 3$; $F_{\text{H}_2/\text{CH}_4} \sim 62$.

1 Introduction

In the past decades, a huge effort has been made in optimization of design, microstructure and formulation of gas selective membranes as energy-efficient tools for continuous extraction processes requiring high productivity and easy operation [1–5]. Extensive development has been made in the field of polymeric membranes which are versatile materials featuring high gas separation efficiency and low production cost, although suffering from limited mechanical, chemical and thermal stability [6,7]. For gas separation applications requiring higher membrane resistance, hybrid, composite or inorganic membranes (either dense or porous) should be considered [8–10].

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Molecular sieve ceramic membranes are attractive candidates for effective separation of gas mixtures from room temperature up to 500 °C, even in harsh conditions [1]. On the other hand tedious control of ceramic membrane preparation, often associated to costly synthesis protocols (support quality, clean room, multi-layer depositions. . .) remains a big concern in their big scale applications. Composite membranes combining the particular properties of both ceramics and polymer-based membranes are often considered as attractive selective barriers for gases or liquid separation with both well-balanced permeability/selectivity and improved membrane stability [11, 12]. Many possible approaches have been reported in the literature for both associating ceramic and polymer material [13–16]. When the mechanical resistance of a ceramic support is required, the polymer is generally deposited on the selected robust support, which provides the necessary mechanical integrity. Such composite membranes are generally prepared either by simple deposition of the polymer in/on the support (physical anchoring) or by covalent bonding of the polymer layer on the support surface (eventually functionalized for graft-polymerization) [16–19]. The above membranes can be prepared from a wide variety of monomers, allowing a perfect tailoring of the membrane design and performance for different separation purposes. Recently Wei et al. described a composite membrane synthesis by the infiltration of high molecular weight PDMS mechanically fixed in the pores of a ceramic alumina support [20]. Such strategy was useful to constrain the swelling of the separation layer. However, the mechanically anchored polymer might suffer from detachment or mechanical erosion in high flux operating conditions. Covalently bonded polymers onto the ceramic surface should grant higher stability to the composite membrane, providing the intrinsic polymer characteristics are adapted to the foreseen application [18]. Good quality ceramic supports are also essential for preparing performable membranes, without any surface defects (pinholes, cracks...) able to favor the formation of non-selective pathways and impact on the membrane integrity. This precondition is closely related to the final membrane cost, which is one of the key factors limiting the commercial development of ceramic membranes. In fact, successful deposition of a polymer thin layer on a ceramic support generally requires smooth surface, obtained by depositing one or several intermediate layers with decreasing pore sizes on a raw macroporous ceramic support [21, 22]. As far as the preparation of good quality intermediate layers is often a tedious task significantly increasing ceramic supports costs, the associated membranes are often restricted to lab-scale studies. Polymer/ceramic composite membranes could potentially overpass this limitation providing they could be prepared by robust and up-scalable synthesis methods adapted to existing low cost industrial supports (tubular, multichannel).

In this work, the preparation of nanocomposite polymer-ceramic membranes has been considered by developing an innovative *in-situ* controlled polymerization of functional oligomers inside the pores of a commercial ceramic membrane. Oligomers containing alkoxy silane functional groups with ethylene/propylene oxide (EO/PO) and methyl methacrylate (MMA) chains, featuring enhanced solubility of quadrupolar CO₂ molecules [23, 24], have been selected as promising candidates for the preparation of gas selective membranes adapted to the separation of biomass derived gas mixtures. A large number of experiments combining both different industrial ceramic supports and oligomers has been carried out in order to find optimal synthesis conditions for controlling the preparation of stable, fully infiltrated and reproducible gas selective composite membranes. A judicious choice of the oligomer size and functionality in relation with the ceramic pore sizes and surface groups could provide attractive control of both oligomers anchoring and their polymerization specifically within the pores of the support top-layer. Such approach should provide high versatility for producing different types of nanocomposite membranes materials which selectivity could be effectively tailored by both chemical and the physical nature of the oligomers.

According to our best knowledge, such an approach has never been reported in the literature and its implementation could pave an attractive way in developing stable, cheap and up-scalable nanocomposite membranes for gas separation/extraction processes.

2 Experimental

2.1 Membrane supports

The tubular ceramic supports were supplied by either Pall-Exekia or CTI SA (Céramiques Techniques Industrielles). The support dimensions were as follows: OD/ID = 10/7 mm (Pall-Exekia) and OD/ID = 10/6 mm (CTI) with a total length of 50 and 150 mm, respectively. Both supports have an asymmetric structure composed of a mesoporous inner top-layer (respectively 3–5 μm and 5–10 μm thick in Pall-Exekia and CTI supports) deposited on a macroporous support (1.5–2 mm thick) consisting of 3 layers with mean pore sizes of about 0.2 μm , 0.8 μm and 10 μm from the inner to the outer part of the tubes. The mesoporous layers on Pall-Exekia supports were mainly composed of γ -alumina (with pore sizes \sim 3–5 nm or 5–8 nm), while their CTI analogues were composed of ZrO_2 with pore sizes \sim 5–10 nm.

In order to avoid any gas leakage during permeation tests, both tube extremities were sealed with commercial enamel or epoxy resin (deposited on 1 cm length, in/out).

2.2 Polymer precursors

Four oligomers have been considered in this work, all of them were non-commercial functional alkoxysilanes provided by Specific Polymers (France). Their chemical composition was as follows: I) polyethylene oxide (PEO) triethoxysilane, II) polyethylene oxide (PEO) bis(triethoxysilane), III) polypropylene oxide (PPO) bis(triethoxysilane) and IV) polymethylmethacrylate (PMMA) triethoxysilane. All these oligomers were of analytical grade and were used as received without any further purification. Their characteristics are detailed in Table 1.

2.3 Composite membrane synthesis

2.3.1 Preparation of the sol

For each considered oligomer, the sol formulation was fixed in order to obtain a constant molar concentration (0.1 M) of trialkoxysilane groups. Depending on their chemical composition, oligomers were dissolved in water, isopropanol or acetone. To do so, the oligomers were inserted into a vial containing the corresponding solvent and the solution was stirred for 1 to 10 minutes at room temperature until their complete dissolution. When isopropanol or acetone were used as solvents, a minimum quantity of water equal to three times the molar amount of trialkoxysilane was added in the sol in order to ensure a hydrolysis all alkoxysilane groups. Nitric acid (0.01 M) was employed to activate the hydrolysis while limiting the premature condensation of the oligomeric alkoxysilane molecules before sol infiltration in the ceramic support. Finally, urea (0.01 M) was used as to promote the condensation of the pre-hydrolysed oligomers during the thermal treatment step. The above sol was further stirred at room temperature for 1.5 hours to complete both the hydrolysis of oligomers and urea dissolution.

Table 1. Characteristics of the oligomers used in the sols.

Sample ref.	Type of the oligomer*	Characteristics of oligomers			Physical state	Solvent
		Chemical formula	M _w (g mol ⁻¹)	MW _(triethoxysilane) mol/100g of product		
#1	I (PEO)	$\text{H}_3\text{C} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{Si}(\text{C}_2\text{H}_5\text{O})_3$	2 250	0.046	wax	H ₂ O
#2		$\text{H}_3\text{C} \text{---} \text{O} \text{---} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{---} \text{Si}(\text{OC}_2\text{H}_5)_3$	632	0.158	liquid	H ₂ O/ isopropanol
#3			1 161	0.086		
#4	II (PEO)	$\text{Si}(\text{OC}_2\text{H}_5)_3 \text{---} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{---} \text{Si}(\text{OC}_2\text{H}_5)_3$	1 550	0.128	wax	H ₂ O/ isopropanol
#5		$\text{Si}(\text{OC}_2\text{H}_5)_3 \text{---} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{---} \text{Si}(\text{OC}_2\text{H}_5)_3$	928	0.216	wax	acetone
#6	III (PPO)	$\text{Si}(\text{OC}_2\text{H}_5)_3 \text{---} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{---} \text{Si}(\text{OC}_2\text{H}_5)_3$	1 750	0.141	wax	isopropanol
#7	IV (PMMA)	$\text{Si}(\text{OC}_2\text{H}_5)_3 \text{---} \left[\text{---} \left(\text{---} \text{O} \right)_n \text{---} \right] \text{---} \text{C} \left(\text{CH}_3 \right) \left(\text{COOCH}_3 \right)$	1250	0.081	powder	acetone
#8			1690	0.059		

- * I) polyethylene oxide (PEO) triethoxysilane,
 II) polyethylene oxide (PEO) bis(triethoxysilane)
 III) polypropylene oxide (PPO) bis(triethoxysilane)
 IV) polymethylmethacrylate (PMMA) triethoxysilane.

2.3.2 Ceramic support impregnation

The ceramic support was entirely immersed in the pre-hydrolyzed sol (Sect. 2.3.1) placed in an open container and the whole system was subsequently transferred to a vacuum chamber for 10 minutes. Finally, the support was withdrawn and subjected to a thermal treatment (Sect. 2.3.3). If necessary, the impregnation step was repeated after the thermal treatment, in order to fill any non-selective pathways in the composite membrane layer.

2.3.3 Membrane thermal treatment

The ceramic supports, impregnated with the pre-hydrolyzed oligomers, were placed for 17 h in an oven at 80 °C with controlled relative humidity (RH) of 80%, then for 1.5 h at 90 °C and RH ~70%. Such treatment promoted the condensation of silanol groups and the polymerization/grafting of the oligomers in the pores of the mesoporous ceramic layers. Finally, membranes were stabilized by applying a conventional thermal treatment in air at 150 °C for 3 h.

2.4 Membrane characterization

The morphology, thickness and homogeneity of the membrane materials were studied at different locations on/in the supports using a high resolution scanning electron microscope (FESEM, Hitachi S-4800) at 1.5 keV. The uniformity and efficiency of oligomers infiltration in the mesopores of the ceramic support have been determined by EDX analysis of the support cross-section (Si mapping, Silicon Drift Detector (SDD), X-MaxN, Oxford Instrument). The permeance and selectivity of the

as-prepared membranes have been measured both for different single gas series and selected gas mixtures containing H₂, N₂, CO₂ or CH₄. Due to safety reasons He (kinetic diameter = 2.60 Å) has been used instead of H₂ (kinetic diameter = 2.89 Å) for single gas measurements. Membranes were equipped with silicon o-rings, placed in a dead-end stainless steel module and outgassed overnight under vacuum.

Single gas flow through the membrane was evaluated by a bubble flowmeter connected to the atmosphere enabling a rapid screening of the membrane permeance. Additional 30 minutes outgassing treatment in vacuum was operated when changing the gas. Permeance values were in the range 10⁻⁷–10⁻¹¹ mol·m⁻²·s⁻¹·Pa⁻¹. Ideal selectivities were calculated as the ratio of single gas permeances. Single gas permeation was measured in the temperature range 25 °C–150 °C and transmembrane pressure was $\Delta P = 4$ bar.

Gas separation experiments were performed with equimolar H₂/CO₂, H₂/CH₄, H₂/N₂ and CO₂/N₂ gas mixtures at $\Delta P = 3.7$ bar and temperatures of 100, 130 and 150 °C. The gas separation performance of the most promising membranes were also tested at 150 °C and $\Delta P = 3.7$ bar with a four gas mixture (10 mol% CH₄, 20 mol% CO₂, 30 mol% CO and 40 mol% H₂). Helium was used as a sweep gas and the gas concentration in the permeate was measured using a TCD-GC (PerkinElmer-Clarus 400) equipped with two columns (5A molecular sieve and Porapak Q). Gas mixture compositions were analysed by continuous dosing of the permeate diluted with He (sweep gas) and transported to the sampling loop of the gas chromatograph. The transmembrane flux was measured with an electronic flow-meter (PE 1000 Perkin Elmer). Membranes were outgassed overnight in vacuum before any new gas mixture separation experiment.

3 Results and discussion

The strategy developed for preparing nanocomposite membranes in which functional alkoxy silanes are confined in the mesopores of a ceramic support, involves three key steps: i) hydrolysis of the functional alkoxy silanes; ii) infiltration of pre-hydrolysed alkoxy silanes in the support mesopores, iii) controlled *in-situ* polycondensation of the pre-hydrolyzed alkoxy silanes within the mesopores. The *in-situ* control of oligomer deposition/polycondensation process has been found to be a key point for producing attractive membranes with reproducible characteristics and performance. Moreover, the quantity of oligomers as well as their chain length/steric hindrance were also found to strongly influence the final membrane permeability and selectivity. Membranes characteristics are described and discussed hereafter in relation with their morphology, single gas permeation properties and gas mixture separation performance.

3.1 Control of the oligomer deposition/condensation process

The nanocomposite polymer/ceramic membranes have been prepared by a selective confinement of the oligomers in the mesoporous top-layer of the ceramic support. A schematic representation of the optimal membrane design as proposed in this work is shown in Fig. 1. A crucial parameter which can advantageously predict the efficiency of membrane formation in the mesopores (oligomer infiltration and condensation in the mesoporous top-layer) relies on the definition of an optimal ratio between the size of mesopores and the length of oligomer chains. The chain length of each oligomer has been determined by calculation of the total length of chemical bonds and hybridisation of the atoms forming the molecule. The chain lengths, corresponding to

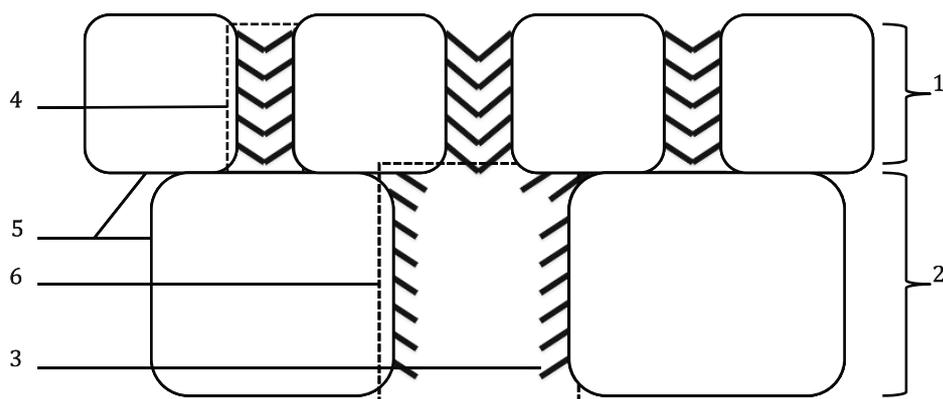


Fig. 1. Optimal design for the proposed composite membrane material. 1) Mesoporous support layer; 2) macroporous support layer; 3) oligomer molecule; 4) mesopores with reticulated oligomers; 5) support grains; 6) macropores.

unfolded molecular chains, are given in Table 2, together with the corresponding ratios support pore size/chain length. Respecting the optimal ratio should ensure both the full infiltrations of the oligomers in the support mesopores and at the same time limit the plugging of support macropores and the formation of a polymer top-layer detrimental to both membrane permeance and abrasion stability. When compared with thin polymer films anchored on a support top-surface, controlled infiltration of the oligomers in the support pores should increase the composite membrane stability by limiting the problems of differential thermal expansion between the ceramic support and the polymer. This stability is further enhanced by the covalent bonding between the oligomers and the ceramic support material. Indeed the particularity of the proposed synthesis protocol bears on the controlled *in-situ* oligomer anchoring and polycondensation (oxolation) in the mesoporous top-layer. The $-OH$ groups present on the ceramic grains surface are able to react with the silanol groups of the hydrolyzed alkoxy silane functional groups of the oligomers. Moreover, urea effectively induces polycondensation reaction during the thermal treatment in humidification chamber. In fact at temperatures above $\sim 80^\circ C$ urea decomposes to NH_3 and CO_2 , thus leading to an increase of pH [25,26] which activates the polymerization/grafting of the confined oligomers, after their infiltration in the bulk of the ceramic support. Although it was difficult to investigate this phenomena occurring in confined media, the protocol efficiency was confirmed indirectly by the fact that non-selective (not gas-tight) membranes were obtained before the condensation step.

3.2 Morphology of the deposits

Both FESEM observations (Fig. 2) and EDX analysis (results not shown) evidenced the formation of a fully confined hybrid material within the pores of mesoporous ceramic support when respecting the optimal ratio “support pore size/oligomer chain length”. EDX analysis (Si-mapping) confirmed a complete and uniform infiltration of the oligomers in the ceramic support (no remaining top-layer) and their preferential location in the mesoporous layer of the supports. When considering a $6\ \mu m$ thick mesoporous layer with 3 cm length and 40% porosity, the maximum amount of oligomer (density ~ 1) required to fill all the pores of the mesoporous layer was found to correspond typically to $\sim 15\%$ of the measured support weight increase. The quantity of oligomer in the macroporous support (85%) does

Table 2. Characteristics of both the mesoporous ceramic supports (pore size) and tested oligomers (molecular weight, chain length) and the corresponding ratios “pore size/chain length” for each couple of oligomer and ceramic support.

Membrane ref.	Support provider	Mesoporous layer pore size (nm)	Oligomers		Ratio pore size/chain length	
			Sample ref.	Molecular weight (g mol ⁻¹)		
A1	Pall-Exekia	[~3 to ~5]	#1	2 250	[0.18-0.30]	
B1		[~5 to ~8]			[0.30-0.48]	
A2		[~3 to ~5]	#2	632		[0.52-0.87]
B2		[~5 to ~8]				[0.87-1.40]
A3		[~3 to ~5]	#3	1 161		[0.32-0.54]
B3		[~5 to ~8]				[0.54-0.86]
A4		[~3 to ~5]	#4	1 550		[0.23-0.38]
B4		[~5 to ~8]				[0.38-0.61]
A5	CTI	[~3 to ~5]	#5	928		[0.34-0.57]
B5		[~5 to ~8]				[0.57-0.91]
A6		[~3 to ~5]	#6	1 750		[0.21-0.35]
B6		[~5 to ~8]				[0.35-0.56]
A7		[~3 to ~5]	#7	1 250		[1.12-1.86]
B7		[~5 to ~8]				[1.86-2.98]
A8		[~5 to ~10]	#8	1690		[1.49-2.98]

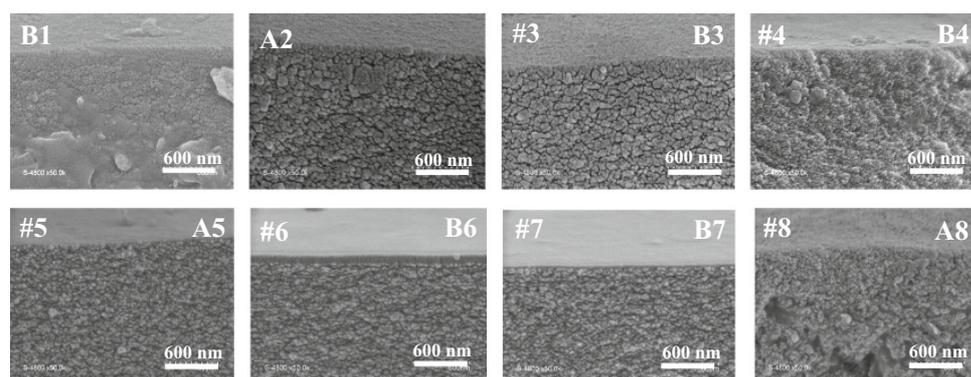


Fig. 2. Composite membranes obtained by respecting the optimal ratio (mesopore size)/(oligomer chain length). Sample Ref. are described in Table 2.

not contribute to selectivity; it could potentially be limited by choosing another material for the macroporous support (e.g. SiC instead of an oxide) featuring low surface interaction with the oligomers. For supports with pore sizes in the range $\sim 3\text{--}5\text{ nm}$, full infiltration (no top-layer formation observed by FESEM; membrane Ref. A2, A5; Fig. 2) was obtained with the PEO-based oligomers (type I & II, sample #2 & #5; Table 1) featuring a short molecular chain and low molecular weight. It must be noted that chain lengths were calculated for unfolded molecules, while in reality molecules are randomly twisted, thus explaining the ratio “pore size/chain length” < 1 . In fact the linear dimension of the unfolded molecules was considered as their maximum size before any condensation. This calculated maximum length was used to select the most adapted oligomers enabling effective and controlled occlusion of the pores in the mesoporous support layer. The optimal ration has been experimentally determined to be ~ 0.5 for pores sizes $\sim 3\text{--}5\text{ nm}$ (Table 2). If this ratio is below ~ 0.3 , the long chain of the oligomers prevent their complete infiltration and they remain (at least partially) on the support top-surface.

In the case of supports with larger pore sizes ($\sim 5\text{--}8\text{ nm}$) oligomers with longer linear chains and higher molecular weight were required to plug the pores. This behaviour has been confirmed for all PEO-based long linear chain oligomers tested in this work (types I & II, samples #1, 3, 4, Table 1) and again the optimal pore size/chain length ratio was found to be ~ 0.5 (membrane Ref. B1, B3, B4; Fig. 2). Obviously also short oligomers (#2, #5) can also infiltrate the support matrix (pore size/chain length ratio up to ~ 1.4) but do not accomplish full pore plugging, as discussed in Sect. 3.3 (non-selective membranes).

Compared to PEO-based oligomers, infiltration of their PPO analogues was a more tedious task, probably due to their branched and thus sterically more congesting molecular chains and only partial infiltration was obtained (membrane Ref. B6; Fig. 2). This assertion was also confirmed for the polymethylmethacrylate (PMMA) functionalized oligomers analogues (type IV, Table 1). This result could be related to the higher steric hindrance of the PMMA-based chains compared to the linear PEO-based chains. Consequently PMMA-based oligomers were found more attractive for the preparation of composite gas selective membranes by infiltration in ceramic supports with large pore size distribution (membrane Ref. B7; Fig. 2). The optimal pore size/chain length ratio for such oligomers was found to be in the range $[1.9\text{--}3.0]$. Reproducible results were also obtained with CTI supports having larger pores and larger pore size distribution ($\sim 5\text{--}10\text{ nm}$). In order to respect the same optimal “pore size/chain length” ratio for this PMMA-based oligomer, its counterpart with longer

molecular chain (sample #8, Table 1) has been used to ensure more efficient composite membrane formation. Complete infiltration of the mesoporous layer (CTI, pore sizes $\sim 5\text{--}10\text{ nm}$) was evidenced (membrane Ref. A8, Fig. 2) and FESEM observations of several sections of both 5 cm and 15 cm long supports revealed good uniformity of the composite membrane along the entire support length. These promising results thus demonstrated the robustness of the synthesis strategy, enabling a possible transfer to more complex systems, such as multichannel tubes or assembled multi-capillary bundles with high surface/volume ratio.

3.3 Evaluation of membrane performance for single gas permeation

Single gas permeation measurements were used to evaluate both the membrane performance and the reproducibility of the proposed synthesis protocol. In the case of ceramic supports with small mesopores ($\sim 3\text{--}5\text{ nm}$), gas selective membranes have been obtained when applying oligomers with short molecular chains and a high amount of trialkoxysilane functional groups (type I & II, membrane Ref. A2 & A5; respectively). This result is associated with an optimal membrane design characterized by fully infiltrated oligomer as already discussed in Sect. 3.2. The principal criterion for the preparation of gas selective membranes was first its gas tightness at room temperature. In fact, only such membranes exhibited a thermally activated transport for small gases up to $150\text{ }^\circ\text{C}$ (membrane stability limit) and yielded permselectivities (α^*) higher than 10 for He/N_2 and CO_2/N_2 single gas pairs, with He and CO_2 permeances of $\sim 10^{-9}\text{ mol m}^{-2}\text{ Pa}^{-1}\text{ s}^{-1}$ (Table 3). For the ceramic supports with large pore sizes ($\sim 5\text{--}8\text{ nm}$), reproducible values of single gas permeances and ideal selectivities were obtained with oligomers possessing a long molecular chain and high molecular weight (membranes #B3, B4). An exception was observed for oligomer #1 (membrane Ref. A2) having sufficiently long molecular chain, but too low amount of alkoxy-silane groups resulting in insufficient reticulation yielded formation of non-selective voids. Low selectivities were also obtained for composite membranes containing PPG-based oligomers because of their insufficient infiltration in the mesoporous support layer (membrane Ref. B7). PMMA-based oligomers (type IV, Table 1) were found efficient for infiltration of mesoporous supports with larger pores sizes even on relatively cheap industrial ceramic supports (CTI) (membranes Ref. A8). Considering the possible attractiveness of such membrane systems with limited fabrication cost, the PMMA-derived composite membranes on CTI supports have been further evaluated for the separation of model gas mixtures issued from the gasification of biomass.

3.4 Evaluation of membrane performance for gas mixture separation

The real separation efficiency of the nanocomposite membrane composed of “type IV” oligomer and ZrO_2 support provided by CTI (membrane #A8, Table 3) has been evaluated with different gas mixtures. Equimolar gas mixtures revealed lower gas permeances than those measured for single gases (Table 3). This classical trend is usually attributed to steric hindrance and competitive sorption/diffusion effects of the permeating gas molecules in mixtures. In addition, the kinetic diameter is smaller for He than for H_2 , thus facilitating its diffusion. Measurements performed in the temperature range $100\text{--}150\text{ }^\circ\text{C}$ evidenced thermally activated transport of H_2 resulting in increased separation factors observed for both H_2/N_2 and H_2/CH_4 gas mixtures. The separation factors reaches the values $F_{\text{H}_2/\text{N}_2} = 7.3$, $F_{\text{CO}_2/\text{N}_2} = 8.6$ and $F_{\text{H}_2/\text{CH}_4} = 8.8$ at $150\text{ }^\circ\text{C}$ (Fig. 3), i.e. largely overpassing the Knudsen selectivities. This phenomenon is particularly pronounced for the mixtures containing a

Table 3. Comparison of single gas permeances (Π) and permselectivities (α^*) for the studied composite membranes at 150 °C. Permeances were measured at feed pressure of 4 bar. (Knudsen selectivity values: $\text{He}/\text{N}_2 = 2.7$, $\text{CO}_2/\text{N}_2 = 0.8$.)

Membrane ref.	Support pore size	Oligomer ref.	Gas permeation characteristics			
			Permeance (Π) of He ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) at 25 °C	Permeance (Π) of He ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) at 150 °C	$\alpha^*_{\text{He}/\text{N}_2}$ at 150 °C	$\alpha^*_{\text{CO}_2/\text{N}_2}$ at 150 °C
A1	[~3 to ~5]	#1	$\sim 10^{-9}$	$\sim 10^{-9}$	3	1.5
B1	[~5 to ~8]		$\sim 10^{-10}$		6	5
A2	[~3 to ~5]	#2	NP	$\sim 10^{-7}$	$> 10^*$	$> 10^*$
B2	[~5 to ~8]		$\sim 10^{-7}$		2	1
A3	[~3 to ~5]	#3	$\sim 10^{-10}$	$\sim 10^{-9}$	5	2.5
B3	[~5 to ~8]		NP		$> 10^*$	$> 10^*$
A4	[~3 to ~5]	#4	$\sim 10^{-9}$	$\sim 10^{-9}$	3	2
B4	[~5 to ~8]		NP		10	8
A5	[~3 to ~5]	#5	NP	$\sim 10^{-7}$	$> 10^*$	$> 10^*$
B5	[~5 to ~8]		$\sim 10^{-9}$		5	4
A6	[~3 to ~5]	#6	$\sim 10^{-7}$	$\sim 10^{-7}$	3.5	2
B6	[~5 to ~8]		$\sim 10^{-9}$		3	1.5
A7	[~3 to ~5]	#7	$\sim 10^{-9}$	$\sim 10^{-9}$	3	1.5
B7	[~5 to ~8]		NP		$> 10^*$	$> 10^*$
A8	[~5 to ~10]	#8	NP	$> 10^*$	$> 10^*$	

* Nitrogen permeance below the detection limit ($\Pi_{\text{N}_2} < 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{Pa}^{-1}$) NP – not permeable.

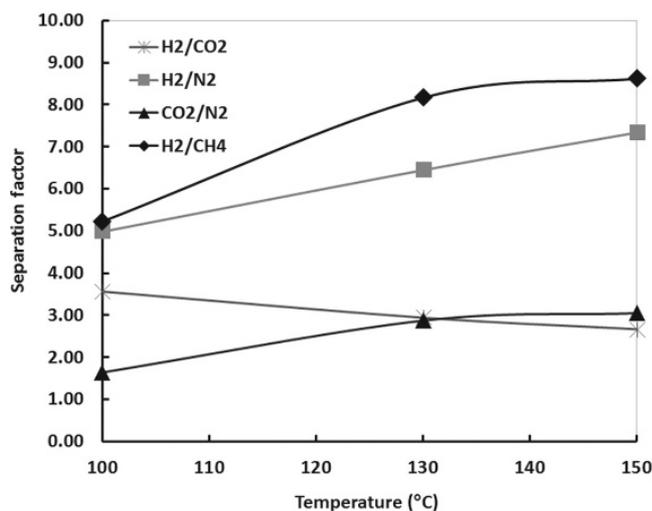


Fig. 3. Evolution of the separation factors of binary gas mixtures measured at 100 °C, 130 °C and 150 °C, with $\Delta P = 3.7$ bar. (Knudsen selectivity values: $H_2/CO_2 = 4.7$, $H_2/N_2 = 3.7$, $CO_2/N_2 = 0.8$, $H_2/CH_4 = 2.8$.)

gas whose transport can be thermally activated and gases exhibiting low adsorption affinity towards the membrane material. The gas permeances were in the range 10^{-11} – 10^{-10} mol.m⁻².s⁻¹.Pa⁻¹ and H₂ permeance was generally higher in gas mixtures containing CH₄, which could result from a slight polymer swelling in the presence of hydrocarbons. Interestingly, the membranes also exhibit enhanced selectivity for CO₂, whose permeance is increased by the factor of ~4 when increasing the temperature from 100 °C to 150 °C. Finally, the separation performance of the above nanocomposite membrane has been evaluated for a quaternary gas mixture composition corresponding to that typically obtained from biomass gasification: 10 mol% CH₄, 20 mol% CO₂, 30 mol% CO and 40 mol% H₂. The measured gas permeances and corresponding separation factors are given in Table 4. In spite of relatively low permeances in the range of $\sim 10^{-10}$ mol m⁻² s⁻¹ Pa⁻¹, the membranes exhibit very promising separation efficiency for selected gas pairs, with a particular interest for the extraction of H₂, and eventually CO₂ from methane containing mixtures.

Table 4. Separation of a quaternary gas mixture (10 mol% CH₄, 20 mol% CO₂, 30 mol% CO and 40 mol% H₂) at 150 °C and $\Delta P = 3.7$ bar for a PMMA-based composite membrane (A8 membrane, Table 3). Gas permeances and associated separation factors.

Membrane ref.	Single gas permeance mol/(Pa s m ²))				Separation factors			
	CH ₄	CO ₂	CO	H ₂	H ₂ /CO	H ₂ /CO ₂	H ₂ /CH ₄	CO ₂ /CH ₄
A8	0.01	9	0.5	0.2	9.8	3.0	61.5	20.6

It must be recognized that the reported membrane performance is below those typically reported in the literature for polymer-grafted ceramic membranes prepared in clean room conditions with high quality supports. Numerous parameters will thus have to be investigated in order to fully evaluate the potential of this new concept for the preparation of nanocomposite membranes as an alternative to other polymer grafted/ceramic gas selective barriers. For example, further improvement of performance in terms of higher permeance should derive from a judicious

adjustment of the membrane architecture, e.g. decreasing the mesoporous layer thickness. A larger selection of functionalised oligomers (with different functional groups) should also help to improve the extraction efficiency (e.g. amino- groups should increase the membrane CO₂ selectivity). In addition, given the pore size and size distribution of the selected mesoporous support, an appropriate choice of the oligomer regarding its chain conformation/steric hindrance and silanol groups, should be also taken into account to ensure an optimal pore plugging and membrane performance in terms of gas permeance/selectivity ratio.

4 Conclusions

A novel concept for the preparation of nanocomposite membranes with attractive gas separation performance has been developed considering a confinement of functional oligomers in the mesoporous top-layer (host matrix) of tubular ceramic supports. This approach involves the infiltration of pre-hydrolysed functional oligomers in the mesopores, followed by their controlled *in-situ* polycondensation, as patented by our group [13]. Under optimal reaction conditions this synthesis protocol leads to the formation of hybrid gas selective barriers fully confined in the bulk of mesoporous support, without occluding the support macropores or forming a thin polymer top-layer on the support. The ratio between the support pore size and the oligomer chain length has been found as an attractive tool to predict the feasibility of membrane formation using specific pairs ceramic supports/polymer precursors. In fact, such approach targeting a full infiltration of oligomers in the support pores should both overcome the problems of differential thermal expansion between the ceramic support and the polymer and at the same time lead to high separation efficiencies whatever the mesoporous layer surface quality. Particularly promising results have been obtained with PMMA-based alkoxy-silanes, enabling the formation of gas selective composite membranes on cheap industrial mesoporous ceramic support. Additional studies are currently in progress targeting improvement of membrane performance. Indeed, in the present state, the performance of the composite membranes is still below what is needed for industrial applications and hardly competes with those of classical thin top-layer membranes supported on ceramic supports. As permeability is a function of membrane thickness, an appropriate choice of support architecture might be beneficial for obtaining higher gas fluxes. Decreasing the mesoporous layer thickness and limiting the anchoring of the oligomer in the macroporous support by using a more inert material (i.e. with a limited number of –OH surface groups) should be considered primarily.

Moreover, other specifically functionalized oligomers with chain lengths enabling their effective infiltration in the specific membrane supports are also being considered for increasing the membrane separation efficiency. The development of such nanocomposite membranes deserves special attention because of their high attractiveness in terms of both up-scalability on commercial tubes and promising gas separation/extraction efficiency.

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