Turning Commercial Ceramic Membranes into a First Stage of Membranes for Post-Combustion CO₂ Separation

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Abstract
This report describes how commercial tubular ceramic membranes, initially designed for liquid filtration, can be modified to provide the core separation components of a first stage of flue gas treatment and enrichment in post-combustion CO₂ separation. Commercially available tubular NanoFiltration (NF) ceramic membranes were turned into a membrane for CO₂ separation by a two-step process including additional ceramic coating and chemical grafting. The combination of ceramic coating and chemical grafting drastically modify the membrane properties and turn the membrane initially designed for liquid filtration into a membrane that displays CO₂ vs N₂ selectivity at the opposite of Knudsen-based selectivity, with a CO₂:N₂ ideal selectivity of 2.3. A second step of this study addressed the reduction of membrane cost, by starting with a low ultrafiltration (UF) 200 nm ceramic support specifically manufactured for this application in place of a NF membrane. After successful coating of a 5 nm and a 1 nm ceramic membranes, this membrane, grafted with a commercial fluorosilane molecule was tested in pure gas permeation of CO₂ and N₂, with an ideal selectivity CO₂:N₂=3. Finally, the same membrane, grafted with glymo, was tested against separation of a CO₂ (20%):N₂ (80%) mixture, and as a function of the permeation stage-cut. A CO₂:N₂ selectivity of 4 was obtained for a stage-cut of 0.5, and even higher (CO₂:N₂ selectivity=14) for low stage-cuts usually used for testing dense polymer membranes. These results demonstrate that commercial ceramic porous membranes can be used as starting elements for a first stage of CO₂ post-combustion gas cleaning and CO₂ enrichment.

Introduction
Today, anthropogenic emission of greenhouse gases embraces CO₂ emissions peaking now at 2 billion tons per year [1]. Among them, capture of post-combustion CO₂ released by the combustion of fossil fuels in gas turbines or coal-fired power plants, is a major challenge because flue gas are emitted at atmospheric pressure, with rather low concentration in CO₂ (5-25%) compared with other sources, and contain a high proportion of water (~ 25%) as well as acid aerosols, flying ashes and corrosive elements like SO₂ and NO [2]. The problem is clearly defined by the scale of emissions to deal with: a 600 MW coal-fired power plant emits 500 STP m³/s flue gas, that is, 460 tons CO₂/h [3]. This means that among the elegant scientific responses like optimized chemical scrubbing [4], zeolites and Metal Oxide Frameworks (MOF) used as absorbent [5,6], or others [7,8], only technical pertinent solutions that can afford to treat such a huge amount of CO₂ will be worth being further explored. For example, among the best results reported until now for the adsorption of CO₂ by MOFs (MOF-177: 1.54g CO₂/g @ 4 bar [9], MOF-200: 2.4 g CO₂/g @ 50 bar [10], Ni-MOF-74: 0.19g CO₂/g @ 1 bar [11]), and without noticing the unacceptable energy cost required for pressurizing gas at 4 bars, the amount of MOF-177 required for continuously capturing CO₂ emission with a one hour adsorption/desorption cycle, would be close to 600 tons (300 for the adsorption stage, 300 for the desorption), which can be hardly considered. Combining the outstanding properties of MOFs for molecular selection with membranes is also on progress, but many problems have still to be solved [12]. So, as pointed recently, “… no current technologies for removing CO₂ from large sources like coal-based power plants exist which satisfy the needs of safety, efficiency, and economy; further enhancement and innovation are much needed” [13].

Separation processes such as cryogenic, absorption, adsorption and membranes are usually compared in technical-economic studies, but it has been reported that membranes used to be discarded in the early stage of these evaluations, as being considered as inappropriate [14]. However, with the development of both theoretical and experimental works, the solutions provided by membranes have been highlighted, and they happen now to be promising candidates for post-combustion CO₂ capture if some problems are correctly addressed and solved by involving both material science and system design engineering [2,3,14-16]. The challenges listed by these reports are the following: (i) membranes must display high selectivity toward CO₂ –at least 50-; (ii) it would be suitable to overcome the low CO₂ concentration in the feed flow (~ 12%), (iii) the large amount of gaseous or aerosol water (25%) present in flue gas would foul the membranes stages if not removed or drastically reduced beforehand, (iv) the low pressure of the feed gas (~ 1 bar) reduces the CO₂ recovery, which is a major drawback for low permeance membranes, and (v) the raw flue gas, even after the gas cleaning and desulfurization through the FGD stage, still contain corrosive components that will destroy polymer membranes if directly exposed.

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It seems therefore that a double stage membrane system, designed according to the “enricher” double stage membrane concept [17], with a first one made of high permeance and resistant membranes, devoted to clean the raw flue gas and concentrate CO2 in the permeate side - the feed side of the second stage - , and a second one with high selectivity but fragile membranes, is a solution worth being studied, as far as all components can be produced and implemented for treating very large gaseous volumes. We report in the present study how commercial ceramic membranes can be modified by well-known procedures to achieve the requirements of this first treatment stage. As these membranes can be chemically modified to become hydrophobic, the solution offered in the present study can solve also the need for water removal, which will be demonstrated in another report.

Ceramic membranes, with pore size ranging from 2 to 50 nm, have proven to be promising in liquid separation technology but not really in gas separation. NanoFiltration (NF) membranes with pores sizes smaller or equal to 2 nm, having molecular weight cut-offs (MWCO) ranging from 200 to 1000 Dalton (Da) can be the good starting elements as their pore is small enough to allow surface interaction [18,19]. Indeed, separation mechanisms with NF membranes generally involve both size and Donnan exclusion effects in contrast to UF membranes, giving high salts rejection rates in liquid separation [20-22]. For example, Larbot et al. successfully prepared γ-alumina NF membranes using a sol-gel approach, with a MWCO of 375 Da (pore size of 1 nm), corresponding to 95% rejection of polyethylene glycol (375 Da) solutions. These NF membranes were successfully tested for mineral salts separation using Donnan exclusion [23,24].

Compared with polymer membranes that offer high selectivity but rather low permeability and poor chemical durability [25], developing PIMs (Porous Inorganic Membrane) for gas separation, especially CO2 recovery, was pursued by research groups and companies, for many years now, to use their surface property to enhance molecular sieving. Indeed, when considering flue gas treatment, porous ceramic membranes offer the suitable chemical and temperature resistance, but their porosity, which enhances permeance, is a drawback for selectivity, if it is too large, or if surface defects exist. Decreasing the membrane pore size appears as a key factor to enhance selectivity without altering the gas flux and permeance, and initial reports demonstrated that silica microporous membranes with pore size of 1 nm could provide successful gas separation [26]. Since then, the domain of PIMs has evolved and includes now different types of materials like silica, zeolites and MOFs [25]. Surprisingly, non-siliceous metal oxides are not broadly studied.

Since the actual recovery of CO2 will require very large membrane surface area, which can only be obtained by extrapolating from current industrial manufacturing, we attached our research to explore how current commercial non-siliceous PIMs could be adapted. More specifically, we studied how the suitable porosity could be achieved by starting from commercial PIMs, and how surface modification could improve gas selectivity to hit the requirements for a first membrane stage of post-combustion CO2 capture (high permeance, selectivity in the 5-10 range, chemical durability). This study was based on preliminary works that demonstrated that surface modification induced by fluorosilane grafting could improve CO2 separation [27].

The present work reports the combination of PIM improvement by adding first a low ultrafiltration (UF) or nanofiltration (NF) membrane layer onto the internal surface of commercially ceramic supports, with the suitable chemical grafting to provide a hydrophobic surface property in order to enhance CO2 permeance. The hydrophobic treatment was obtained using the fluorinated molecule since CO2 was reported to have a higher affinity than N2 [10-13] with fluorinated molecules, which is by far beyond the single Knudsen mechanism [28], frequently observed with PIMs.

A first part of this work was devoted to explore step-by-step the influence of each component on the membrane structure and property. Therefore, we developed a zirconia membrane (Membrane n°1) onto commercial 5 nm low UF alumina tubular membrane, by following the sol-gel route without plasticizer using Zr(OPr)4. This membrane was fully characterized, and the surface of this zirconia membrane was chemically modified in a second step with perfluorosilphonic acid CP2F6CH2POOH. Its performance was evaluated in pure gas separation with CO2 and N2, to determine ideal the gas selectivity. We used these results as a starting point to optimize both the performances and the manufacturing cost of membranes.

As the membrane used in this first part, is rather expensive, with the need for coating several ceramic layers up to the 5 nm alumina film, a second part of this work explored if similar performances could be obtained by starting from a 200 nm ceramic support directly prepared by a single step extrusion process (Membrane n°2). These supports were directly coated with a 5 nm layer, then a 1 nm one, followed by chemical grafting with either a commercial fluorosilane, or glymo. Ideal selectivity of the membrane grafted with the hydrophobic fluorosilane was in the same range as for membrane n°1. As for the membrane grafted with glymo, it was tested against gas mixture (CO2:20%; N2:80%), as a function of the membrane stage-cut. An exceptional CO2:N2 selectivity of 14 for a porous ceramic membrane prepared from industrial components, was obtained at low stage-cut -where dense polymer membranes are usually tested-, and a selectivity of 4 was obtained for stage-cut of 0.5, which is demonstrated to be sufficient for using these membranes in a first membrane stage of cleaning and CO2 enrichment of post-combustion CO2 separation.

**Experimental Section**

**Materials**

For the membrane n°1, ultrafiltration γ-alumina membranes with pore size of 5 nm (T1-70) were purchased from Pall-Exeelia, France. Zr(IV) tetraisoopropoxide at 70 weight percent (wt.%) in propanol was purchased from Fluka and HNO3 (70wt.%) from SDS. For the membrane n°2, the 5 nm alumina layer was made by peptisation of a Plural SB sol (Sasol, Germany). The second coating of the 1 nm alumina layer was made with boehmite (Sasol, Germany). Ethanol, polyethylene glycols (PEGs) with molecular weights of 400, 600, 1000, 1500, 2000 and 3000 Da (Da) were purchased from Sigma.

**Synthesis**

**Membrane n°1:** Prior to its use, the commercial 5 nm γ-alumina membrane was thoroughly rinsed with 18 MΩ water and ethanol successively, and stored in an oven at 120°C for 1 hour. The ZrO2 polymeric sol was prepared at room temperature by adding 0.7 mL of Zr(IV) tetraisoopropoxide (in propanol) (2.25 x 10-3 mol) to 10 mL of a 0.45 M HNO3 solution. The sol was stirred for 24 hours and kept for another 48 hours at room temperature to allow the reduction by 15wt.

**Membrane n°2:** The PIMs sample was immersed in a solution of acetic acid C 6F13C2H4PO(OH)2. Its performance was evaluated in pure gas separation with CO2 and N2, to determine ideal the gas selectivity. We used these results as a starting point to optimize both the performances and the manufacturing cost of membranes.

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% of the sol concentration. The transparent resulting sol was then slip-
casted for 5 minutes on a γ-alumina membrane. The casted support was
finally air-dried at room temperature for 24 hours then flash-fired at
450°C for 1h to give the zirconia membrane. To evidence the influence of
the layer thickness, a second coating was realized following the same
procedure. Unless specified in the text, all the membranes described in
the here below manuscript were prepared with two coatings. Graffing a
10⁻⁵ M solution of CFP in ethanol turned this hydrophilic zirconia
membrane into a hydrophobic one. The membrane was maintained for
4 hours at reflux at 65°C in the grafting solution. After completion of
the reaction, the membrane was removed from the grafting solution,
rinsed with ethanol and acetone successively using an ultrasonication
bath to remove the unreacted molecules and placed in an oven at
60°C for 2 hours then at 150°C for 12 hours. Durability of this grafted
membrane was tested in real environment by exposing it directly for
four months to flue gas from a coal-fired power plant, thanks to the kind
contribution of a partner of the FP6 European Program NanoGLOWA
(www.nanoglowa.com).

Membrane n°2: For the membrane n°2, a 10 mm single channel
0.250 µm titania porous tubular support was prepared by direct
extrusion according to usual industrial processes by CTI (France).
The preparation of the 5 nm alumina layer was derived from a method
previously developed in our group [23]. The ceramic sol was made by
peptisation of a Plural SB solution by nitric acid and then the addition
of polyvinyl alcohol (PVA) to enhance viscosity. The prepared solution
was then tape-casted into the support. After the solution removal, the
supports were left to dry for a day a room temperature and fired at
540°C for 2 hours. The second coating of the 1 nm layer alumina was
performed on the top of the previous alumina layer. The alumina layer
was made from boehmite obtained by the precipitation of an aluminum
alkoxide in a water solution at 85°C. The slurry was then tape-casted into
the tube and left drying for 24 hours at room temperature. The support
was then flash fired at 450°C for 1 hour. Membrane surface modification
was made by grafting these membranes with either an octylfluorosilane
(C8FSi) or (3-glycidoxypropyl)trimethoxysilane (glymo).

Techniques

X-ray Diffraction patterns were recorded with a X’pert Pro
diffractometer (PanAnalytical, Netherlands) between 10-70 degrees
in the 20 range, using the Cu Kα radiation (λ= 1.54Å). Attenuated
Total Reflectance Infrared (ATR-IR) spectra were recorded on a FTIR
Nicolet 510 instrument (Thermo Scientific). To facilitate the spectra
acquisition, the measurements were realized on powder grafted or
coated with platinum for a minimum of 2 hours to reach rapidly a stable flux at the beginning of
the filtration experiment.

Gas permeation measurements were conducted using a typical
gas permeation pilot. A 20 cm long tubular stainless steel housing was
used to give a membrane permeation area of 3.4.10⁻³ m². The module
was linked to pressure gauges and gas flow systems that delivered
directly pure CO₂ or N₂, or a 20:80 CO₂:N₂ mixture. The feed pressure
was maintained in the range of 1.5 to 4.5 bar, while the downstream
permeate was vented to the atmosphere. The permeate flow rate of
each gas was measured by volumetric displacement method using a
soap bubble flow meter and the permeance j (m⁻³ (STP)m⁻¹h⁻¹bar⁻¹) was
calculated using Equation 1:

\[ J = \frac{273.15 \text{ v} \frac{1}{T} \frac{1}{A} (P^f - P^p)}{1} \]

Where T (K) is the room temperature, v (m³) the volume of
permeate collected over a period of time t (h) through the membrane
characterized by an effective area A (m²). P^f and P^p (bar) correspond
to the upstream and downstream pressures, respectively, and the term
P^f-P^p to the corresponding pressure differential. The feed and permeate
gases were analyzed using gas chromatography analysis (Varian,
MicroGC 4800) directly connected to the pilot. The permeation data
were recorded thirty minutes after that the feed composition was
similar to the canister one.

The stage cut is defined as the permeate gas flow over retentate gas
flow [29]. For the tests with pure CO₂ and N₂, the retentate line was
closed and permeate was kept opened, which corresponds to a stage-
cut of 1. The gas permeance was measured every 0.5 bar between 1.5
and 4.5 bar. All data presented are the average of five measurements
in the same conditions. The CO₂/N₂ permeance ratio was calculated
to evaluate the permselectivity of the zirconia membrane and thus the
ideal separation factor. For tests with a gas mixture, the stage-cut was
set at values lower than 1 by adjusting the outlet valve of the retentate
side.

Results and Discussion

Validation of membrane n°1

Characterization of the additional zirconia coating: The nature of
the zirconia crystalline phase present in the zirconia layer, was checked
by following the same procedure for the sol preparation, as the one
used for the support coating, with the powder being collected and fired
at 450°C. The analyses of the material after flash sintering, confirm
that a well-crystallized tetragonal zirconia is obtained even after a very
short calcination time. The resulting fine powder was ground and
analyzed by X-Ray Diffraction (XRD) (Figure 1). The XRD pattern of
the as-synthesized powder (dashed line) displays only broad peaks.
After calcination, diffraction peaks appeared at 30.11, 34.59, 35.14,
50.29, 59.46, 60.08 and 62.84 degrees for the lattice family plans (101),
(002), (110), (112), (103), (211), (202), respectively. This is in good
agreement with the reported peak positions for tetragonal zirconia
[30,31]. Sherrer analysis of the (101) diffraction peak broadening gives
an average crystal size of 15 nm. It is worth noting that even the (202)
family plan, with a reported relative intensity of 5% is clearly visible in
Figure 1, demonstrating therefore the high crystallinity of the obtained
zirconia sintered for only 1h at rather low temperature.

We characterized also the porous structure of this ZrO₂ powder after thermal treatment by N₂ adsorption-desorption (Figure 2). Both the porous volume (Vₚ=0.09 cm³.g⁻¹) and the BET specific surface (ss=47 m².g⁻¹) are small, compared to alumina or zirconia coatings previously prepared following a similar procedure [23,32]. We demonstrate in the following how this limited porous volume enhances performances in gas permeation. The N₂ isotherm (Figure 2A) is assigned to a Type IV curve, with a well-defined textural porosity between particles as a result of their small size (no adsorption at high partial pressure is observed). Figure 2B displays the pore size distribution (PSD) calculated by the BJH method. The PSD is defined within the 3 – 10 nm range, with a sharp peak at 3.5 nm, probably better explained as a result of a curve artifact resulting from the selection of data points. This zirconia powder appears rather dense compared to similar alumina or zirconia coatings prepared following a similar procedure, which explains well by the lack of organic porogens used in the current method.

We confirmed by SEM that the morphology of the zirconia coating is better compared with a thin ceramic skin instead of a membrane (Figure 3). The zirconia layer (Figure 3C and D) deposited on the alumina support (Figure 3A and B) shows indeed a very thin layer of ZrO₂ nanoparticles above the 5 nm alumina top layer. The 15 nm ZrO₂ nanoparticles could actually not enter the 5 nm porous alumina top layer, and remain on the surface (Figure 3C), with this ceramic porous skin being formed.

The influence of this additional ZrO₂ porous skin was tested with pure water permeation and compared to the γ-alumina 5 nm support alone. The flux is drastically reduced with this zirconia film compared to the bare support, decreasing from 20 L/m².h for the alumina support to 8 L/m².h at 5 bars for the zirconia membrane and from 40 to 16 L/m².h, respectively at 10 bars. The water permeability deduced from these values is 1.6 L/m².h.bar for the zirconia membrane against 4 L/m².h.bar for the bare alumina support.

The influence of this zirconia porous skin was confirmed by measuring the Molecular Weight Cut-Off (MWCO) of the modified membrane characterized with the rejection rate of 1mM PEG solutions with different molecular weights. The rejection rate was measured under different nitrogen pressure without any noticeable difference in the rejection rate of the different PEG solutions. The results obtained with a 5 bar pressure as a function of the Molecular weight is displayed in Figure 4. The MWCO defined as the 90% rejection rate is set at 2.2 kDa, which is far below the 20 kDa MWCO delivered by a 5 nm alumina membrane.

We conclude from this first series of test that the addition of a zirconia coating modifies drastically the performances of the commercial alumina membrane, by reducing its water permeability from 4.0 L/m².h.bar down to 1.6 L/m².h.bar, and the MWCO from 20 kDa to 2.2 kDa.

Characterization of the hydrophobic chemical grafting: Low UF membranes are promising candidates for large volume gas separation because of their higher permeability than dense polymer membranes, but their poor selectivity prevents them from being used as such. We confirm in this study that a true covalent grafting of perfluorophosphonic acid improves gas selectivity toward CO₂ without hampering their durability.
As it had been reported that the modification of the surface of a ceramic membrane by fluorinated molecule modifies the membrane gas selectivity [27], we modified the surface of the zirconia coating by grafting (3,3,4,4,5,5,6,6,7,7,8,8,8)-tridecafluoroctyl perfluorophosphonic acid (CFP) through its reaction between the acid function and the oxide surface.

The FT-IR spectra of bare and chemically modified zirconia as well as the CFP molecule are reported in Figure 5. Zirconia bare powder is characterized by a broad signal centered at around 3400 cm⁻¹ and a small vibration band at 1650 cm⁻¹, corresponding to hydroxyl groups or adsorbed water. The CFP FT-IR spectrum is characterized by several vibration modes in the 1,500-800 cm⁻¹ domain. Upon surface modification resulting from the chemical reaction between the acid functionality of CFP and the metal oxide surface, the OH groups react with the phosphonic acid groups (3,000-2,000 cm⁻¹ range) to give Zr-O-P bonds. This is evidenced by the reduction in the OH stretching domain (3,000-2,000 cm⁻¹) disappearance of the broad signal between 2700 and 2550 cm⁻¹ and the appearance of several vibration bands (1205,1130, 1070, 1020 cm⁻¹ for ν CF₈, ν P-C at 1145 cm⁻¹, ν P=O around 1350-1250) at low frequency, ranging from 1,400 to 800 cm⁻¹, characteristic of the perfluoroalkyl chains [33-35].

We tested the surface property of the grafted zirconia by measuring the water contact angle on a flat zirconia support made with the same conditions. The value obtained with a homemade apparatus, is equal to 149° (Figure 6A), which ranges the hydrophobic support close to superhydrophobic materials [36]. Before going further in the study of gas separation, we validated that this membrane can be exposed for a long time (4 months) to actual flue gas emitted by a coal-fired power plant (Figure 6B and C) without any macroscopic degradation of structure or property. Unlike polymeric materials tested in parallel, which were destroyed within several hours, our membranes did not display any obvious deterioration, and the water angle contact, measured after this 4 month exposure, remained the same and even higher (153°) as a result of soot deposited onto. This stability is the result, not only of the high thermal and chemical resistance of ceramic membranes, but also of the CFP polymer, which is very stable up to 250°C, as displayed in Figure 7.

Gas permeation tests and ideal selectivity: The influence of each addition to the initial 5 nm alumina membrane was studied against gas permeance with pure CO₂ and N₂. We compared the bare support, a membrane with a single zirconia layer (ZrO₂/1/), a membrane with two zirconia layers (ZrO₂/2/), and this double-coated membrane after grafting (ZrO₂/2/-CFP). We observed a significant reduction in gas permeance with the double-coated zirconia membrane, and grafting of this double-coated membrane (ZrO₂/2/-CFP), provided an increase in the CO₂/N₂ selectivity up to 2.5.

For the bare support and the ZrO₂/1/membrane (Figure 8A), the single coating of the ZrO₂ skin does not modify drastically the transmembrane gas flow, and the values of permeance, which varies linearly with the applied pressure, are in the same range (~ 45 m³/m².bar).
Applying a second coating (ZrO$_2$/2/) divides by 2 the permeance (Figure 8A), but the difference in gas flow does not demonstrate a high selectivity.

Figure 8B displays the results of permeance measurements made with a double-coated zirconia membrane modified by grafting (ZrO$_2$/2/-CFP). The permeance was measured for pure N$_2$ and CO$_2$ within a broader pressure difference range (0.4 to 3.5 bars) than in Figure 8A. The gas permeance varies linearly with the applied pressure, and it is markedly reduced from 25 m$^3$/m$^2$.bar for the initial non-grafted membrane (ZrO$_2$/2/), down to less than 0.15 m$^3$/m$^2$.bar after grafting (ZrO$_2$/2/-CFP). The ideal selectivity calculated from the CO$_2$ over N$_2$ permeance (Figure 8B) is equal to 2.3. This ideal selectivity of 2.3 obtained with a tubular commercial ceramic support modified by a well-known slip casting method and the chemical grafting of a suitable chemical, compares well with the most recent values obtained with hybrid materials like ZIF-9 metal oxide framework (MOFs) membranes prepared onto limited alumina supports, which offered an ideal selectivity of 6.9 but with a method that can hardly be extended to large membrane surface area [37], or ZIF-8 MOFs prepared on stainless steel porous tubes, which presented an opposite pure Knudsen-based CO$_2$/N$_2$ selectivity of 0.75 [38].

**Validation of membrane n°2**

**Membrane preparation:** Figure 9 displays SEM micrographies of the CTI 250 nm support (a,b). Hg porosimetry gives 47% porosity and a median pore diameter of 0.235 µm. Observation of the additional membranes (Figure 9C) show homogeneous defect-free layers. This membrane was grafted with either the C8FSi molecule, or a silane bearing an epoxy function (glymo), which is known for displaying specific interaction with CO$_2$.

**Membrane properties:** This membrane was tested against pure gas and the evolution of gas flow (STP conditions) for pure CO$_2$ and N$_2$ as a function of the pressure difference, is given in Figure 10. Permeance calculated from the slope of the linear fit for each gas, gives a value of 0.104 STP m$^3$/m$^2$.h and of 0.03 STP m$^3$/m$^2$.h for CO$_2$ and N$_2$, respectively, with an ideal selectivity evaluated at 3.4. This value confirms that the membrane obtained by a direct coating of a 5 nm and 1 nm grafting (ZrO$_2$/2/-CFP). The ideal selectivity calculated from the CO$_2$ over N$_2$ permeance (Figure 8B) is equal to 2.3. This ideal selectivity of 2.3 obtained with a tubular commercial ceramic support modified by a well-known slip casting method and the chemical grafting of a suitable chemical, compares well with the most recent values obtained with hybrid materials like ZIF-9 metal oxide framework (MOFs) membranes prepared onto limited alumina supports, which offered an ideal selectivity of 6.9 but with a method that can hardly be extended to large membrane surface area [37], or ZIF-8 MOFs prepared on stainless steel porous tubes, which presented an opposite pure Knudsen-based CO$_2$/N$_2$ selectivity of 0.75 [38].

**Figure 7:** TGA analysis of the CFP polymer alone (red) and the ZrO$_2$/CFP grafted ceramic.

**Figure 8:** (a) N$_2$ and CO$_2$ permeance for the bare support (circle), the zirconia membrane ZrO$_2$/1/ with one coating (square), and the zirconia membrane ZrO$_2$/2/ with 2 coatings (triangle) as a function of the applied gas pressure; (b) N$_2$ and CO$_2$ permeance and selectivity of the double coated zirconia CFP-modified membrane (ZrO$_2$/2/-CFP).

**Figure 9:** SEM micrographies of the surface (a) and cross section (b) of the 250 nm ceramic support, and (c) of the successive 5 nm (bottom) and 1 nm alumina layers coated on the previous support.
Testing the actual membrane properties requires a stage-cut lower than one, which will create a trade-off between the actual membrane selectivity, hence the gas purity, and the gas flow in the permeate, hence the global gas recovery. This is illustrated in Figure 11A with the membrane n°2 grafted with C8FSi where the actual CO₂ molar fractions in both permeate and retentate sides, of a (20% CO₂ : 80% N₂) feed mixture, are reported as a function of the stage-cut (SC). For a SC of 0.5 (50% feed flow across the membrane), the permeate gas is 30% enriched in CO₂ (0.2 to 0.26), and the retentate is impoverished in parallel (0.2 to 1.3).

The CO₂:N₂ selectivity is also reported. This selectivity decreases from 4.0 at SC=0.1, where only 10% of feed flow goes across the membrane, down to 1.7 at SC=0.6, with 60% of the feed flow going across the membrane (the line plotted in Figure 11A is the result of a second degree polynomial fit of the experimental values). These results illustrate well the difference between the ideal CO₂:N₂ selectivity of the material equal to 3.4, and the actual membrane selectivity, which can be evaluated for different stage-cuts (0.1; 0.3; 0.5; 0.6) and equal to 3.8, 2.7, 2.0, and 1.8, respectively.

Despite their promises for blocking the water aerosol present in the flue gas, which makes the membranes grafted with perfluoro chemical groups, good candidates for a first stage of postcombustion CO₂ separation, the CO₂:N₂ selectivity remains too small to achieve the performances in gas enrichment expected for such a first separation stage. We confirmed that our method of PIM surface functionalization could work with other chemical groups. (3-glycidoxypropyl)-trimethoxysilane is mostly used as a precursor for dense hybrid membranes for proton exchange in fuel cells [39], but the epoxy group was demonstrated to exhibit affinity toward CO₂ [40,41]. Tests with a membrane n°2 grafted with (3-glycidoxypropyl)-trimethoxysilane (glymo) demonstrate a significant improvement with a CO₂:N₂ selectivity doubled for a stage-cut of 0.5, and equal to 10 for a stage-cut of 0.1 (Figure 11B). These values do not reach selectivity of 50 observed with dense hybrid membranes [41], but a selectivity of 4 for a stage-cut of 0.5, would allow the feed gas in the second membrane stage to be 50% enriched in CO₂, compared with the initial flue gas (see Figure 11A), which could significantly increase the CO₂ purity and recovery in a second high selectivity membrane stage, as demonstrated by modeling studies [2,15].

Conclusion

We have successfully modified commercial gamma alumina 5 nm membranes by applying an additional coating of tetragonal zirconia, using a sol-gel process, in order to achieve a final pore size reduction down to 3.5 nm, compatible with gas permeation. This pore size reduction was confirmed by the drastic reduction in water flow. Surface modification of this modified membrane, with the chemical grafting of (3,3,4,4,5,5,6,6,7,7,8,8,8)-tridecafluorooctyl perfluorophosphonic acid, using a phosphonic acid function as grafting head, led the membrane surface to become superhydrophobic. This new surface property allowed us to achieve a significant CO₂ over N₂ selectivity in gas permeation, especially by tuning the membrane stage-cut, to allow a significant flow going to the permeate. These properties, along with the chemical and abrasion resistance of ceramic membranes, make them the perfect candidates for a first membrane stage dealing with gas cleaning and CO₂ enrichment in the treatment of power plant raw flue gas, before sending this cleaned flue gas to a second high selectivity stage of polymer membranes.

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References


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