Effect of MgO on the microstructure and properties of mullite membranes made by phase-inversion tape casting

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\textbf{ABSTRACT}

Flat microfiltration mullite (3Al\textsubscript{2}O\textsubscript{3}2SiO\textsubscript{2}) membranes were prepared via phase-inversion tape casting method. The sintering temperature has been reduced from 1700°C to 1450°C by adding 3 wt.% of magnesium oxide (MgO) as a sintering aid. The effect of this compound on the membrane properties was systematically investigated. The presence of MgO promoted at the same time a change in membrane morphology resulting in a symmetric structure, which is opposite to the asymmetrical structure obtained for mullite membranes prepared without this sintering aid. Porosity of 38.9% and average pore size of 2.33 \textmu m was achieved. Water and n-heptane vapor adsorption analysis showed an increment in hydrophilic behavior due to MgO. The reduction of sintering temperature from 1700°C (MgO free) to 1450°C (MgO added) produced mechanical stable samples with flexural strength about 15.3 MPa. The membrane was resistant enough to withstand the water flux permeation test up to 3 bar. Compared to the pure mullite membranes, the MgO containing sample displayed higher water permeation fluxes, which might be related to both the larger superficial pore size and its hydrophilicity.

1. Introduction

The use of ceramic membranes has attracted much attention in separation technologies because of their superior chemical, thermal and mechanical stability compared to organic membranes [1]. Thus, ceramic membranes present extended lifespan even under extreme fouling and cleaning conditions, which would easily damage their organic counterparts [2]. There are numerous methods to prepare ceramic membranes such as slip casting, tape casting, extrusion, sol-gel, freeze casting, phase-inversion, etc. [3,4]. For instance, tape casting is a standard technique to prepare thin flat ceramic tapes [5,6]. This technique starts from homogeneous ceramic slurries, which are cast onto a substrate resulting in thin “green tapes” after drying; and a consolidated ceramic tape after heat treatment [7]. In addition, phase inversion is one of the most popular techniques for the preparation of porous membranes, in which a polymer is dissolved in a suitable solvent and then formed into the desired shape in this process (thin film, tube, hollow fiber). The addition of a precipitant or nonsolvent (such as water) to this polymer solution causes the homogeneous phase to separate into a solid polymer (polymeric matrix) and a liquid solvent layer (porous network) [8,9].

Coupling the tape casting and the phase-inversion techniques has been proven to be a suitable method to produce flat organic and inorganic membranes with different morphologies [10,11]. The phase-inversion process contains both the thermodynamics of the ternary system and kinetics from mass transfer properties [12]. During the phase-inversion process, a thermodynamically stable polymer solution is converted into a solid state normally via non-solvent induced process also called immersion precipitation. The solidification is regulated by a liquid-liquid demixing process, which results into a polymer-rich (matrix structure) and a polymer-lean phase (pores) [13].

Therefore, the membrane morphology is highly dependent on composition of the slurry and the non-solvent precipitation bath. It is noteworthy that when ceramic particles are present in the polymeric solution a slurry is formed, which will result in a ceramic membrane after thermal treatment (debinding step).

Mullite is a promising material because of its excellent chemical stability, low coefficient of thermal expansion, good thermal and mechanical properties [14]. Mullite is a material in the binary SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} system following the stoichiometric composition 3Al\textsubscript{2}O\textsubscript{3}:2SiO\textsubscript{2}. Since mullite occurs very rarely in nature, it has to be synthesized, which conventionally demands very high temperatures (above 1600°C) [15,16]. Mullite...
powder compacts have poor solid state sinterability because of the low interdiffusion rates of $\text{Si}^{4+}$ and $\text{Al}^3^+$ cations within the mullite lattice [17]. In order to decrease sintering temperatures (and thus production costs) of mullite, several sintering aids have been studied. Magnesium oxide (MgO) is a well-established inexpensive sintering additive applied in the industry [18,19]. Small amounts of MgO (0.1–3 wt.%) can effectively reduce sintering temperature up to 1300–1550°C while maintaining considerable mechanical stability [20,21]. MgO enhances the densification of mullite phase due to the presence of a liquid phase, which is expected to start at temperatures as low as 1410°C. Thus, the formation of this MgO-containing liquid phase at the sintering temperature induces mullite dissolution in the ternary MgO-SiO$_2$-Al$_2$O$_3$ system [19].

In our previous investigation, we have successfully demonstrated the synthesis of asymmetric mullite membranes [22]. However, the high temperatures required to achieve a mechanically stable membrane puts in question the viability of the synthesized material. Thus, this study aims for exploring the use of magnesium oxide as a sintering aid for mullite flat membranes prepared via phase-inversion tape casting. The effect of MgO addition on the sintering temperature is studied in order to enhance microstructure and mechanical properties of mullite membranes. Several properties are systematically evaluated such as slurry rheology, membrane macrostructure, morphology, surface characteristics, and water permeation flux.

2. Experimental

2.1. Materials

For the membrane preparation via phase-inversion process, a polyethersulfone (PES, 58,000 g mol$^{-1}$, GoodFellow Cambridge Limited) was employed as the polymer source and polyvinylpyrrolidone (PVP – K40, Sigma-Aldrich) as an additive. The solvent for the polymer and also the liquid medium for the ceramic particles was N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich). The ceramic mullite powder ($d_{32} = 3.045 \mu$m; $\rho = 3.045$ g cm$^{-3}$) has been described in our previous work, where it is referred to as “Diac-1200” [22]. Magnesium oxide (MgO, Sigma-Aldrich) powder was used as a sintering aid.

2.2. Membrane preparation

According to process scheme depicted in Figure 1, the first step of the membrane preparation involves the

![Figure 1. Schematic representation of the membrane preparation process.](image-url)
dissolution of 2.7 g of PES using 21.3 mL of NMP as solvent followed by the addition of 0.425 g of PVP. Afterward, 24.225 g of the synthesized mullite powder and 0.75 g of the sintering aid (MgO powder) were slowly added to the solution which was continuously mixed throughout this step. The amount of inorganic particles was calculated to result in a ratio of 3 wt.% of MgO and 97 wt.% of mullite in the end. The amount of MgO taken as “optimum” was described in the literature [17,23]. After 24 h of homogenization, the slurry was degassed (20 mbar, 30 min) to remove air bubbles that were introduced during the stirring process. Then, the slurry was cast over a polyethylene terephthalate carrier film (Mylar, G10JRM, Richard E. Mistler, Inc.) with a doctor blade using a gap of 1.2 mm. The cast slurry was solidified by immersion precipitation in deionized water (nonsolvent) for 24 h at room temperature. Afterward, the green tape was dried at room temperature for 3 days. The dried green tape was cut into the desired shape and size, heated with a rate of 3°C/min to 850°C in air, and kept at that temperature for 3 h to remove the organic matter. Then, the sample was heated with a rate of 2°C/min up to the final temperature (1450, 1550 or 1650°C) and kept at it for 2 h. Finally, the sample was cooled down at a rate of 2°C/min to room temperature.

2.2.1. Specimen denotation
The final sintering temperature was varied from 1450°C to 1650°C. The prepared specimens were denoted with “Mg” to indicate the presence of sintering aid (MgO) followed by “Mul” (Mullite) and the final sintering temperature. As an example MgMul-1450 contains 3 wt.% of MgO and 97 wt.% of Mullite powder, whereas the membrane was sintered at a final temperature of 1450°C. The comparison samples (without MgO) are denoted, for instance, as Mul-1650, which means the sample was prepared only with mullite powder sintered at 1650°C. To make the comparison easier, the Mul-X samples of this work are described in our previous work as “Diac-1200-X” [22], in which “X” corresponds to the final sintering temperature as well.

2.3. Characterizations
The slurry viscosity was measured using a cone-and-plate rheometer (Malvern Bohlin ADS) 40 mm and a shear stress up to 500 Pa during 1000 s at 25°C. The macrostructure of the membranes was analyzed by Scanning Electron Microscopy (SEM, 20 kV; Series 2, Obducat CamScan; Supra 40-Carl Zeiss). For this purpose, the samples were sputtered with gold (K550, Emitech, Judges Scientific). In order to evaluate the pore sizes presented on the bottom and top surface of the sintered membranes, the SEM images were processed and analyzed with an image processing software (ImageJ) [24]. The number of pores detected on the SEM images and processed with ImageJ varied from about 400 to 1200. Porosity and pore size distributions of the membranes were determined using mercury intrusion porosimetry (Pascal 140/440, Porotec).

X-ray diffraction analysis (powder XRD, Seifert 3003) was conducted to identify the obtained crystal phases of the sintered membranes (which were crushed until becoming a fine powder). In order to analyze and quantify the composition in terms of crystal phases, Rietveld refinement was performed using Profex (Open Source XRD and Rietveld Refinement version 4.3.1) [25]. The reference diffractograms were obtained from the existing database from Profex and also from the Crystallography Open Database (COD), which is an open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals (excluding biopolymers) [26,27].

Hydropilicity and hydrophobicity of the sintered membranes were studied by water and n-heptane vapor adsorption measurements, which were carried out by placing a vessel with ~0.4 g of sample powder (particle sizes ≤ 300 μm) inside a closed Erlenmeyer flask filled with the solvent at equilibrium with its vapor phase at room temperature (~22°C). Samples were weighted at the start and at the end of a 24 h measurement period in order to determine the vapor uptake of the material. Later, the uptake was recalculated to g m⁻² using the specific surface area of the respective sample.

The mechanical behavior of the sintered membranes was studied using the three-point bending test (Roell Z005, Zwick [28]). These measurements were performed using a 5 kN load cell (piezoelectric force sensor). The samples were cut into a rectangular shape (16 mm length, ~2 mm width, and 0.7–1.0 mm thickness) and placed in the center of a sample holder with 10 mm distance between the support rollers (diameter of 1.5 mm). The crosshead speed and pre-load were fixed at 0.1 mm/min and 0.25 N, respectively. Twenty samples for each composition and temperature were tested and statistically evaluated by Weibull analysis. Water permeation tests were performed using a homemade setup in a dead-end configuration. The membranes were cut into a circular shape (10 mm diameter) and tested in triplicate at various pressures. The permeation flux was calculated according to the following equation:

\[ J = \frac{1}{A} \frac{dV}{dt} \]  

where \( J \) is the membrane permeation flux (m³ m⁻² h⁻¹); \( A \) is the effective transverse area of the ceramic membrane (m²); \( dV \) and \( dt \) represent the variation in permeated volume (m³) and time (h), respectively.

To better understand the effect of MgO addition on the properties of mullite membranes, the MgMul-1450
sample will be compared to control samples (without MgO) from the previous work [22]. The comparison will focus on the morphological characteristics, mechanical behavior, surface properties, and water permeation flux.

3. Results

3.1. Slurry viscosity

The viscosity curves (Figure 2) display a pseudoplastic behavior for both slurries (without and with MgO), in which initially the viscosity reduces as a function of the applied shear rate; then, for high shear rates the viscosity assumes almost a constant value (at a constant temperature) [29]. This behavior is desired in the ceramic processing for tape casting since the slurry has to maintain its shape after being spread over a support [30,31]. In addition, the literature suggests that the viscosities of castable slurries are in the range of 1–20 Pa s (yellowish transparent rectangle indicated in Figure 2) [32]. Notably, the addition of MgO dislocated the curve to a lower viscosity range in contrast to the sample without the sintering aid.

![Figure 2](image2.png)

**Figure 2.** Viscosity (Pa · s) as a function of the applied shear rate (s⁻¹) for the slurries prepared with sintering aid (MgMul slurry) and without it (Mul slurry). (The data corresponding to Mullite slurry is taken from our previous work [22], in which this sample is named as “Diac–1200”).

3.2. Macroporosity and morphology of the membranes

Figure 3 shows the influence of the sintering temperature on the open porosity and pore size of the prepared mullite-based membranes with MgO as sintering aid. As one may expect, the lower the temperature, the higher the porosity. At the lowest temperature 1450°C, MgMul-1450 exhibits open porosity around 39% and average pore size of 2.33 μm. However, as the temperature increases the open porosity drops to 15.75% and 3.31%, for MgMul-1550 and MgMul-1650, respectively. Considering that the samples sintered above 1450°C presented open porosity inferior to 30%, they were not further characterized since they are not suitable to be applied in membrane technology. Additionally, a sample sintered at 1400°C (see Fig. S 1) was not considered as well due to its poor structural stability, albeit its porosity value and pore size distribution were within the desired range. The increment in sintering temperature also reflected as an increase in linear shrinkage (see Fig.

![Figure 3](image3.png)

**Figure 3.** Pore size distribution versus relative pore volume (bars) and open porosity curves (lines) measured by Hg-porosimetry as a function of the sintering temperature of the membranes prepared with MgO addition.
S 2), ranging from around 30% (MgMul-1450) to 37% (MgMul-1650).

The morphological analysis of the top surface, cross-section, and bottom surface of the MgMul-1450 membrane is displayed in Figure 4. The internal structure consists essentially of a sponge-like pore morphology where no skin-layer can be identified. Top and bottom surfaces present spheroidal and irregular shaped pores like the cross-section (see Fig. 3), in which the diameter distribution analyzed by image processing are quite similar. Hence, the MgMul-1450 membrane can be classified as a symmetrical ceramic membrane due to the analyzed pore structure. The Mul-1650 and Mul-1700 membranes, on the other hand, are asymmetric, so the bottom and top surfaces have different pore sizes, as well as the cross-section, where pore morphology varies within membrane thickness, as previously demonstrated [22] (see also Fig. S 4).

As mentioned at the end of the characterization section, the subsequent results are related to MgMul-1450 sample and its comparison to Mul-X samples (without MgO) from a previous study [22]. Therefore, Table 1 spots the differences between the MgMul-1450 and its counterparts without MgO (Mul-1650 and Mul-1700). Here the role of MgO can be emphasized particularly by analyzing the open porosity values. Although Mul-1650 and Mul-1700 were sintered at higher temperatures compared to MgMul-1450, they still present superior porosity. Consequently, the sintering aid performed as desired, reducing the temperature in which the ceramic particles start to densify. The mean pore size of the surface also reveals that an unexpected change in morphology took place due to the presence of MgO. Mul-X samples are asymmetric: the pore size on the top is in a smaller range compared to both the bottom surface and to the mean pore size obtained from Hg-intrusion analysis. Thus, the mean pore size obtained via Hg-intrusion should be considered with caution, especially, for asymmetric structures such as the Mul-X samples since they present a wide range of pore sizes along their cross-section. On the other hand, MgMul-1450 exhibits similar values for both top and bottom surface, even when considering their upper limits in contrast to the overall mean pore size value.

### 3.3. Membrane composition

The membrane composition was accessed by X-ray diffraction analysis in conjunction to Rietveld refinement method (Figure 5), which shows very sharp peaks indicating that the sample is highly crystalline. It is noteworthy that the analysis only takes into account the crystalline portion of the sample and the displayed phase quantities should be taken with caution. Moreover, a very small amorphous contribution might also be present. The analysis indicates minor presence of a crystalline phase of corundum (0.3 wt. % ± 0.1 wt.%) and quartz (0.2 wt. % ± 0.1 wt.%). Even though, in the ternary phase diagram of mullite and magnesia is not expected to have corundum and/or quartz, they were investigated in this work because our mullite precursor powder consists of an in-house prepared material by reacting silica and alumina precursors at low temperature (1200°C) and holding time (2 h); hence, small portions of unreacted alumina and silica might be present. The MgMul-1450 membrane is basically composed by mullite phase (96.5 wt.% ± 0.4 wt.%) with small contribution of spinel (2.9 wt.% ± 0.4 wt.%). This phase might be originated upon the

### Table 1. Comparison of the open porosity, mean pore sizes, and image analyzed pore sizes of the MgMul-1450 sample and Mullite samples prepared in previous work.

| Sample       | Open porosity (%) | Mean pore size (μm) | Surface mean pore size (μm) | Ref.          |
|--------------|-------------------|---------------------|----------------------------|---------------|
| MgMul – 1450| 38.91             | 2.33                | 1.40 ± 0.9                  | This          |
| Mul – 1650   | 68.27             | 3.06                | 1.18 ± 0.8                  | [22]          |
| Mul – 1700   | 53.68             | 4.46                | 0.72 ± 0.5                  | [22]          |

*Measured by mercury intrusion porosimetry.

*Measured by image analysis of the SEM picture using ImageJ free software.
liquid phase sintering reaction of the MgO (3 wt.%) with the mullite-based matrix. Regarding the goodness of the fit from the refined profile (Fit), satisfactory values of weighted R profile ($R_{wp} = 14.9\% / R_{exp} = 13.5\%$) and $\chi^2$ (1.22) were obtained. The residuals show small local fluctuations due to fitting mismatches regarding peak intensities. However, the obtained quantification is not supposed to be significantly affected by this since all of the peaks have been assigned and well fitted by the Rietveld refinement method. Based on the amount of MgO initially mixed with mullite, the theoretical expected weight for Mg is about 1.87 wt.%. However, the experimental results displayed in Figure 5 indicate a lower value of 0.50 wt.% (Mg), which is understandable given the unlikelihood of detecting all Mg-containing components only by this method. It is noteworthy that these values are an approximation, which is highly affected by the quality of the XRD measurement plus the refinement analysis. Hence, the values observed should be considered as rough estimations rather than proper quantitative analyses.

3.4. Mechanical behavior

The Weibull analysis of the flexural strength measurements for MgMul-1450 sample is displayed in Figure 6. The characteristic strength ($\sigma_0$) obtained is 15.3 MPa and the Weibull modulus (m) is equal to 5.44. For comparison purposes, the Weibull modulus of Mul-1650 and Mul-1700 were 4.31 and 4.25, respectively [22]. Despite the lower $\sigma_0$, the Weibull modulus of MgMul-1450 clearly indicates that this membrane possesses a more homogeneous flaw distribution [33,34].

The Kruskal-Wallis test (Figure 6b) was performed to compare the median flexural strength values of the samples. All the samples differ statistically from each other (p < 0.001). Even though MgMul-1450 sample exhibits an inferior mechanical strength, the data are less scattered since the median value, the upper and lower limits are quite close when comparing to the other two samples, in spite of the presence of a bottom outlier.

3.5. Surface characteristics

The membrane surface characteristics in terms of hydrophobicity-hydrophilicity was determined by water and n-heptane vapor adsorption. As shown in Figure 7 all samples present a tendency toward hydrophilicity (ratio > 1, dash red line). Nevertheless, samples without MgO demonstrate higher n-heptane uptake than the MgMul-1450 sample, leading to a ratio of water to n-heptane around 2. The MgMul-1450 specimen shows a reduced interaction with the organic solvent vapor, resulting in a ratio of 14.2. Therefore, this improvement in hydrophilicity may be attributed to the presence of MgO, which has already been reported as a hydrophilic modifier agent [35,36].

3.6. Water permeation flux

The water permeation flux of the MgO modified membrane is compared to the non-modified membranes (Figure 8). Although MgMul-1450 presents a symmetric morphology and inferior open porosity, it outperforms the asymmetric counterparts. For instance, at 1 bar the performance of MgMul-1450 is almost equivalent to Mul-1650 at 2 bar and Mul-1700 at 5 bar, respectively.
Figure 6. (a) Characteristic strength ($\sigma_0$) and Weibull modulus (m) of the MgMul–1450 sample obtained from Weibull analysis of the failure probability (%) as a function of the flexural strength (MPa). (b) Boxplot comparing the flexural strength of the MgMul–1450 membrane with mullite samples without sintering aid from previous work [22]. (Kruskal-Wallis test was performed to determine statistical differences between the samples).

Figure 7. Insight on membrane hydrophilicity-hydrophobicity via water and n-heptane vapor adsorption (left y-axis) and ratio (right y-axis) analysis. (The data corresponding to Mul–1650 sample was extracted from [22]).
Nevertheless, the higher fluxes obtained for MgMul-1450 are mainly due to its larger top surface pore size compared to the Mul-X samples. Moreover, due to its lower mechanical properties it was not possible to perform flux measurements above 3 bar, which makes the MgMul-1450 membrane suitable for pressures below this limiting range.

Table 2 summarizes the transport properties of the prepared symmetric MgMul-1450 membrane and compares to the values obtained for asymmetric mullite-based membranes from previous work [22]. The equations and assumptions employed to determine the membrane properties are provided in the supplementary material. The asymmetric membranes (Mul-X) exhibited a similar thickness ($\delta_m$) in the range of 6–8 µm (related to the top surface region), while the symmetric membrane (MgMul-1450) is almost a hundred times thicker (591 µm) since encompass all the thickness extension of the membrane. Nonetheless, taking into account the larger effective pore size of the MgMul-1450 membrane, it is quite expected a higher permeance value ($k_w = 40.8 \pm 0.8 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), which can also be inferred in Figure 8 by the slope of the fitted lines through the data points. Consequently, the clean membrane resistance displayed by the MgO modified sample (Mull-1650, $R_m = 0.99 \times 10^{10} \text{ m}^{-1}$) is almost half of the second best performer ($R_m = 1.86 \times 10^{10} \text{ m}^{-1}$). Moreover, the intrinsic permeability ($k_{V, intr}$), which is given by the ratio of membrane thickness ($\delta_m$) over the membrane resistance ($R_m = 0.99 \times 10^{10} \text{ m}^{-1}$), resulted in a superior value for the MgMul-1450 membrane ($k_{V, intr} = 596 \times 10^{-16} \text{ m}^2$).

4. Discussions

In this work, we demonstrated the use of phase-inversion technique to prepare flat symmetric mullite membranes containing MgO as sintering aid. The compound employed not only acted as a sintering aid but also as a membrane modifier, changing its morphology and surface characteristics. Concerning the reduction in the sintering temperature, an expected side effect was observed, the weakening of the mechanical properties ($\sigma_0 = 15.3 \text{ MPa}$). Possibly, the existence of a free glassy phase owing to MgO may have resulted in a reduction in open porosity without a corresponding increase in mechanical strength. Pure mullite membranes sintered at higher temperatures, on the other hand, exhibited superior mechanical properties, which is likely related to the formation of an interlock network structure of mullite grains without the presence of a glassy phase [37]. Hence, when comparing MgMul-1450 to the Mul-X membranes a reduction in mechanical strength was observed; however, it is important to stress that Mul-1600 samples prepared in previous work were not able to be mechanically tested due to their poor structural stability [22]. Therefore, one can conclude that the mechanical properties of MgMul-1450 sample were enhanced due to magnesia.
presence, which is in agreement with several reports in the literature where the mechanical properties are a function of sintering temperature and MgO content [21,38]. Nonetheless, the homogeneity of the symmetric structure against the asymmetric ones was reflected by the box plot displayed in Figure 6b, and by the higher Weibull modulus of the MgMul-1450 membrane (m = 5.44) in contrast to Mul-X membranes (m \( \approx \) 4.3 [22]).

The change in membrane morphology in the phase-inversion process is primarily related to the composition of the system, which also affected the slurry viscosity [12]. The phenomenological description of the mechanism by which this change takes place is still quite unclear. Nevertheless, it is well known that the pore formation is dictated by the thermodynamic equilibrium of the system (governed by the composition, i.e. ternary diagrams); and by kinetic processes influenced by diffusion or exchange rates, in which viscosity might be an important parameter [13]. In this work, a small change in viscosity was observed (see Figure 2); however, the overall pseudoplastic behavior remained the same as for the slurry without MgO. Furthermore, the change in composition by adding the sintering aid can also be accounted as a factor that promoted the morphology change. For instance, the literature reported the use of nano-sized TiO\(_2\) fillers to improve filtration performance in polysulfone ultrafiltration membranes [39]. Another work presented the use of nano-sized Al\(_2\)O\(_3\) as a suitable filler for enhancing the hydrophilicity of PVDF (polyvinylidene fluoride) ultrafiltration membranes [40]. In both studies, the presence of those fillers promoted also a change in membrane morphology, resulting in a symmetric membrane with sponge-like structure due to variations in composition and rheology. Moreover, a gain in hydrophilicity and membrane performance was also stressed. Even though these observations can be extrapolated to this work, it should be stressed that they were made in these studies for polymeric membranes.

The MgO–Al\(_2\)O\(_3\)–SiO\(_2\) ternary phase diagram in the temperature region of 1460°C and with 3 wt.% of MgO indicates the possible presence of mullite, spinel, and corundum phases [19], which are present in the XRD analysis. The presence of the spinel phase (3%) implies that spinel is formed by the majority of the Mg\(^{2+}\) ions, with the residual Mg\(^{2+}\) ions absorbed into the mullite lattice to replace Al\(^{3+}\) [16, 41]. One outcome is a relatively open mullite network (1/2 O\(^{2-}\) is no longer compensated by additional Mg\(^{2+}\)), which might explain the increased hydrophilicity of the MgMul-1450 sample. Additionally, interstitial and/or segregation of Mg-related phases at grain boundaries are two further options to be considered according to several studies from the literature [42–44]. Regarding the surface characteristics of the MgMul-1450 membrane, the vapor adsorption clearly demonstrated an increment in hydrophilic behavior (\(\text{Ratio}_{\text{Water/Heptane}} = 14\)) owing to MgO incorporation, as aforementioned. The improvement in membrane performance might be related to the higher hydrophilicity of MgMul-1450; however, in this case, it is most likely that it is due to the presence of larger top surface mean pore size compared to Mul-1650 and Mul-1700 membranes (see Table 1). Furthermore, probably also due to the larger overall pore size of the MgMul-1450 membrane, its transport properties are superior than the asymmetric Mul-X membranes.

5. Conclusions

Symmetric microfiltration mullite membranes with 3 wt.% of MgO as sintering aid have been successfully prepared by the phase-inversion tape casting method. The addition of MgO has promoted the shift in morphology from asymmetric to symmetric structure. Despite the addition of MgO, the XRD analysis mostly indicated the presence of mullite (96.54 wt.%) with minor contributions of other characteristic phases. The resulting membrane exhibited a monomodal pore size distribution with an average pore size of 2.33 μm and open porosity around 39%. Sintering temperature was effectively reduced to 1450°C accompanied by an improvement in mechanical properties since Mul-X samples sintered below 1650°C could not be tested owing to poor mechanical stability. The water permeation flux analysis revealed a great potential of the material prepared to be applied in membrane process at pressures below 3 bar. Furthermore, the inclusion of MgO significantly increased the hydrophilic behavior of the mullite membranes which also may contribute in combination with the membrane morphology to the observed improvement in water flux. Therefore, when compared to traditional procedures such as slip casting, pressing, etc., the phase-inversion tape casting process described in this study provides a higher degree of flexibility in tailoring membrane characteristics, which may positively impact its performance.

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