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Preparation and characterization of tubular ceramic membranes for treatment of oil emulsions

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Abstract

Multilayer membranes for the treatment of oily waters have been prepared from ceramic materials. Alumina and cordierite supports have been prepared as well as α-Al_2O_3 intermediate layers. γ-Al_2O_3 top layers with very high porosities were prepared by the sol–gel method and a detailed study has been performed because of the importance of this layer in the filtration process. A structural study by means of nitrogen adsorption–desorption, nitrogen permeability and scanning electron microscopy has been carried out on unsupported and supported top layers membranes. The effect of the sol concentration and calcination temperature on the structure of the membrane was studied to get an appropriate pore size and porosity. Also, the necessary amount of PVA as binder/plastizier to get defect-free membranes was investigated. Top-layer membranes in tubular configuration with an average pore diameter around 4 nm and porosities of 72% have been obtained.

Keywords: Membranes; Al_2O_3; Sol–gel process; Permeability

1. Introduction

There is much current interest in the application of membranes in separation procedures because of their application in the treatment of big amounts of wastewaters, and in places where the available space is small. In the last years, the volume of research and development of ceramic membranes has undergone a big advance,[1] because of their applications in filtration environments where polymeric membranes suffer changes in their structure. These are separations in chemically aggressive environments and at high temperatures, in applications requiring a long life-time (low fouling rate), a good mechanical strength and cost-effective production.

Ceramic membranes with high permeability can only be obtained in an asymmetric configuration, which consists in a multilayer system with a macroporous support (with the largest pore diameter), which provides the mechanical strength to the system, an intermediate layer, whose roles are to reduce any inherent defects of the support and to prevent the infiltration of the top layer material into the pores of the support, and the top layer, which is the true membrane of the system. In this layer is necessary a comprehensive control of the pore size.[2,3]

Alumina, silica, titania or zirconia are considered as the main ceramic materials for the formation of the asymmetric structures.[4,5]

The main synthesis route for the preparation of top layers is the modification of intermediate layers using a sol–gel method.[4,6] The advantages of sol–gel derived films include a lower densification temperature, a narrow pore size distribution with nanometer pore-scale, a high degree of chemical homogeneity and the possible production of multicomponent films.[7,8]

Different techniques of characterization are used currently in the structural study of ceramic membranes.[4,9] Methods such as mercury porosimetry and nitrogen adsorption

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porosimetry are very useful for the characterization of unsupported membranes, however, these methods are not suitable for the study of the supported layers because of the asymmetric structure. In this case, other types of methods can be used, such as the bubble-point, the bubble-point with gas permeation, permporometry and the permeability method.[4]

In the present study, the preparation and characterization of a tubular ceramic system for the treatment of oil/water is discussed. For this, it will be necessary to obtain a membrane with an average pore diameter below 10 nm. Oil emulsions in wastewaters can be separated by ceramic membranes because of the hydrophilic properties of oxide membranes.[10–16] The top layer has been obtained from a boehmite sol (γ-AlOOH). Leenaars and Burggraaf[17] published the preparation and characterization of unsupported and supported γ-Al_2O_3 top layers from boehmite sols. Later, Uhlhorn et al.[18] demonstrated that the addition of a polyvinylalcohol (PVA) (mol wt.: 72,000 g mol^{-1}) to the colloidal suspension in a proportion of 0.25 g PVA/g Al_2O_3 is necessary to make films more reproducible and to avoid the appearance of cracks during drying. Also, it was demonstrated in this work that with the addition of PVA, the structure remains almost constant in unsupported and supported γ-Al_2O_3 membranes, therefore, the structure of non-supported membranes can be used to predict that of supported membranes. These membranes have to be repaired to get a membrane without pinholes and cracks, as demonstrated in several works.[18–20] Also it has been demonstrated in the literature[21] that the transition of γ-AlOOH to γ-Al_2O_3 takes place at about 400 °C, so it is necessary to reach this temperature to obtain the γ-Al_2O_3 membrane.

However, these membranes suffer from a low liquid permeability because its small pore size, therefore, a high filtration pressure is needed across the membrane. To improve the permeability will be necessary an increase of the pore size or the porosity of the membrane. For the application of these membranes in separations of oil emulsions from wastewaters, is necessary to increase the porosity without the pore size suffers big changes. According to Uhlhorn et al.[18] and de Lange et al.[19] these membranes have a card-pack structure of around 55% porosity. Recently this result has also been obtained by Kikkinides et al.[22] In the present work, a higher amount of PVA has been added with respect to other authors with the object to increase the porosity of these membranes. This increase will cause the apparition of agglomerates between the boehmite particles and the PVA because the high molecular weight of this additive (mol. wt.: 72,000 g mol^{-1}).[8,18,23,24] These agglomerates will produce defects during drying in the membrane and will increase the average pore size, so a PVA with a lower molecular weight has been used to decrease the sol viscosity and the agglomeration level.

In this study, mercury porosimetry, nitrogen adsorption, permeability measurements and scanning electron microscopy (SEM) have been used for a total characterization of the system.

2. Experimental

2.1. Materials and methods

The forming process of the supports has been extrusion. Two different ceramic materials have been chosen for the preparation of the supports of these systems. One is alumina because of its chemical stability and the possibility to get a narrow pore size distribution.[1] The other one is a reactive mix, which sinters to form cordierite ($2MgO\cdot2Al_2O_3\cdot5SiO_2$). The reactive mix is chosen because of its excellent plastic behavior in extrusion step, since it is formed by talc, kaolinite and magnesite (Cordierita MG300-PO, Vicar S.A.). The intermediate layer and the top layer are alumina.

The particle size and the sintering temperature for each layer have been optimized to get a suitable pore size for the deposition of the next layer.

2.1.1. Membrane support

Alumina and cordierite pipes have been obtained starting from their corresponding pastes with an external diameter of 8 mm and an internal diameter of 4 mm.

Alumina pastes have been prepared using α-Al_2O_3 (Alumina DK-206, Martinswerk), 2 wt.% of colloidal SiO_2 (Prosider S.A.), 0.5 wt.% of polyethylene glycol with a medium molecular weight (mol. wt.: 1000 g mol^{-1}) (Carbowax PEG1000, Union Carbide) which acts as plastificant, 1.5 wt.% of carboxymethylcellulose of high viscosity (Optapix C1000G, Zschimmer & Schwarz) which acts as binder, 1 wt.% polyethylene glycol with a low molecular weight (mol. wt.: 200 g mol^{-1}) (Carbowax PEG200, Union Carbide) which acts as lubricant and 40 wt.% of distilled water. The extrudate was dried for 24 h at ambient temperature and sintered vertically in a furnace at 1600 °C for 2 h using a heating and cooling rates of 360 °C/h.

The paste starting from the one, which will be obtained the cordierite support, is formed by the reactive mix (Vicar S.A.) plus 30 wt.% of distilled water. The extrudate was dried for 24 h at ambient temperature, and sintered vertically at 1200 °C for 2 h using a heating and cooling rates of 300 °C/h.

2.1.2. Intermediate layer

Deposition of a α-Al_2O_3 intermediate layer was performed with a colloidal process. This involves the preparation of a stable suspension, which has been prepared using α-Al_2O_3 (Alumina Condea HPA05), 0.75 wt.% of deflocculant (Dolapix CE64, Zschimmer & Schwarz) and 1 wt.% of carboxymethylcellulose of low viscosity (Optapix C12G, Zschimmer & Schwarz). The obtained suspension has a 8 wt.% solids content.

Unsupported intermediate layers were obtained by slip-casting of the suspension on plaster molds. Intermediate layers were obtained by pouring the suspension on the internal side of the support and allowing to stand for 1 min. The system was dried vertically for 24 h at ambient temperature and was sintered vertically at 1100 °C (kept for 2 h) with heating and cooling rates of 200 °C/h.

2.1.3. Top layer

The preparation of the top layer was performed via a sol–gel process to obtain γ-Al_2O_3 membranes. For this, the process developed by Yoldas has been followed.[25,26] This starts from aluminium secbutoxide, which has been hydrolized totally with water above 90 °C in a proportion of 2 l H_2O per mole alcoxide. The resulting precipitate was peptized with 0.07 mol HNO_3 per mole alcoxide. The suspension was maintained at reflux conditions for 16 h and at 90 °C.

After previous studies in flat sheet configurations, it has been decided that the addition of an amount of 33 wt.% of polyvinylalcohol (PVA) (Optapix PAF 35, Zschimmer & Schwarz, mol. wt.: 10,000–20,000 g mol^{-1}) is necessary to obtain a defect-free supported membrane with a boehmite concentration 0.5 M. Now, in tubular configurations, sol concentrations of 0.5 and 0.72 M have been used, and the sol viscosity was adjusted by addition of three different amounts (33, 40, and 45 wt.%) of PVA (Optapix PAF 35, Zschimmer & Schwarz) used by Agrafiotis and Tsetsekou[27] to adjust the viscosity of boehmite sols. Non-supported membranes were prepared gelling the sol in a climate chamber at 40 °C and 60% relative humidity. The deposition of this membrane on the intermediate layer has been optimized in flat sheet configurations, and consists of three pouring steps: deposition by pouring the sol into the system for 45 s, first recycle by pouring the sol for 30 s and second recycle for 30 s. Between step and step the membrane has been dried and calcined. The drying was performed at 40 °C and 60% relative humidity in a climate chamber. The resulting gels were calcined at four different temperatures: 450, 550, 600, and 650 °C (kept for 3 h) at a heating and cooling rates of 60 °C/h in an electric furnace.

2.2. Characterization techniques

Mercury porosimetry with a PORO SIZER 9300 was used for the determination of the pore size and porosity of the supports and intermediate layers unsupported.

The structural study for non-supported top layers was performed with Nitrogen adsorption–desorption using a Micromeritics Tristar. The pore size distribution has been calculated from the desorption isotherm[28] and the Kelvin equation. Slit-shaped pores were assumed because of the special stacking, which is produced by the plate-shaped[21] or rod-shaped[20] boehmite crystallites. Also cylinder-shaped pores were assumed for comparison with the conducted permeability measurements. The desorption isotherm has been used because during adsorption, the meniscus produced by condensed N_2 cannot be formed in slit-shaped pores, however, during desorption a cylindrical meniscus is present.[28] The porosities of the samples were calculated using the Gurvitsch' rule with a value of true density for γ-Al_2O_3 of 3.7 g cm^{-3}.[21]

The structural study of the supported top layer was performed using the permeability method developed by Uhlhorn et al.[29] and later by Conesa et al.,[30] which can be summarized as follows.

The gas flow equation through a membrane is given by

$$\frac{NRT}{\nu \Delta P} = \frac{k_o}{L} + \frac{B_o P_m}{L\eta\nu} \tag{1}$$

where N is the gas flow per unit area; R, gas constant; T, temperature; ΔP, pressure difference, $\nu = \sqrt{8RT/\pi M}$ the mean molecular velocity, M the gas molecular weight, $k_o = (2\varepsilon/3\tau)r_p$ the term corresponding to Knudsen diffusion, ε the porosity; τ, tortuosity; r_p, pore radius; L, membrane thickness; $B_o = (\varepsilon/8\tau)r_p^2$ the term corresponding to viscous flow, P_m is the mean pressure and η, gas viscosity.

The permeability (F) of a gas through a membrane is defined as the gas flow per unit area and per unit of the pressure difference

$$F = \frac{N}{\Delta P} \tag{2}$$

Substituting the Eq. (2) in the Eq. (1) is obtained a first degree equation

$$F = a + bP_m \tag{3}$$

where F is the permeability; a, constant corresponding to Knudsen diffusion; b, constant representing viscous flow and P_m, mean pressure.

Knudsen diffusion is the transport mechanism when the pore diameters are smaller than the mean free paths of the molecules and it becomes important in membranes with small pore diameters[31] ($\phi < 10$ nm).[32] In this case the permeability will not be function of the mean pressure.

The transport by viscous flow (Poiseuille flow) arises when the pore diameter is bigger than the mean free paths of the molecules[31] yielding a pressure dependence on the permeability.

If the membrane displays only Knudsen diffusion, it will have only pore diameters below 10 nm and no major defects (this is the case of these membranes).[33] If the transport is produced both by Knudsen diffusion and by viscous flow, this indicates pore diameters bigger than 10 nm or defects in the membrane.

From Eq. (3), a pore radius can be calculated by

$$r_p = \frac{16b\eta}{3a}\sqrt{\frac{8RT}{\pi M}} \tag{4}$$

In asymmetric structures is necessary a previous characterization of the material on which is going to deposit the membrane, since the pore sizes are different. These measurements are subtracted of the total characterization of the asymmetric system, obtaining the characterization of the membrane.

Finally, the thickness of layers was examined with a scanning electron microscopy Carl Zeiss (DSM-950).

3. Results and discussion

3.1. Support

The obtained alumina supports have an average pore diameter of 1.2 μm and 35% porosity and the obtained cordierite supports have an average pore diameter of 10 μm and 45% porosity.

3.2. Intermediate layer

The unsuppported intermediate layer has an average pore diameter of 90 nm and a porosity of about 40%. The deposition of the intermediate layer on alumina and cordierite supports has been studied. Data obtained in permeability tests show that in both situations a pore diameter of 90 nm is obtained, which agrees with the pore size obtained by mercury porosimetry. From this affirmation, it can be concluded that there is not influence of the support on the structure of the intermediate layer and both supports can be used for the deposition of the intermediate layer. The layer on cordierite and alumina supports has a thickness of 20 μm (Fig. 1).

3.3. Top layer

3.3.1. Unsupported membranes

In Table 1, the average pore diameter and porosity is shown for two unsupported membranes deposited from a sol concentration 0.5 M and 0.72 M, both with 33 wt.% PVA and at different calcination temperatures. The porosities reach values around of 70% in all cases. It can be seen that at the same boehmite concentration, the average pore size increases when the calcination temperature is higher. This gradual increment indicates a process of coarsening of pores. This also it can be observed in the pore size distributions (Figs. 2 and 3). The distribution is displaced slightly at higher pores size when the calcination temperature increases. No big changes in total porosity are observed.

In Fig. 4 the pore size distributions for two unsupported membranes are presented. In the pore size distributions corresponding to the unsupported membrane obtained from a boehmite sol 0.5 M with and without PVA and sintered at 600 °C. A narrow distribution with an average pore size of 2.9 nm can be seen for the deposited layer without PVA. When a 33 wt.% PVA is added, changes in the distribution pore size

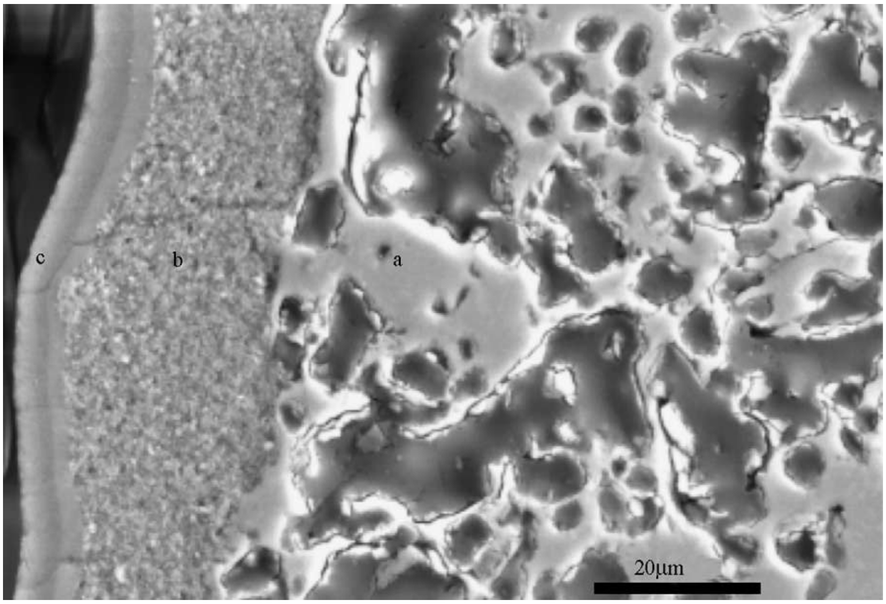


Fig. 1. Micrograph showing a multilayer system formed by a macroporous support of cordierite (a), an intermediate layer of α-Al_2O_3 (b) and a top layer of γ-Al_2O_3 deposited from a boehmite sol 0.72 M with 45 wt.% PVA (c).

Table 1
Structural characteristics of two unsupported membranes at different calcination temperatures

Concentration	Calcination temperature (°C)	D_{50} (nm) cylinder-shaped	D_{50} (nm) slit-shaped	Porosity (%)
0.5 M + 33 wt.% PVA	450	4.7	3	67
	550	5.2	3.3	69
	650	5.9	3.7	67
0.72 M + 33 wt.% PVA	450	5.8	3.6	72
	550	6.3	3.9	72
	650	7.5	4.6	71

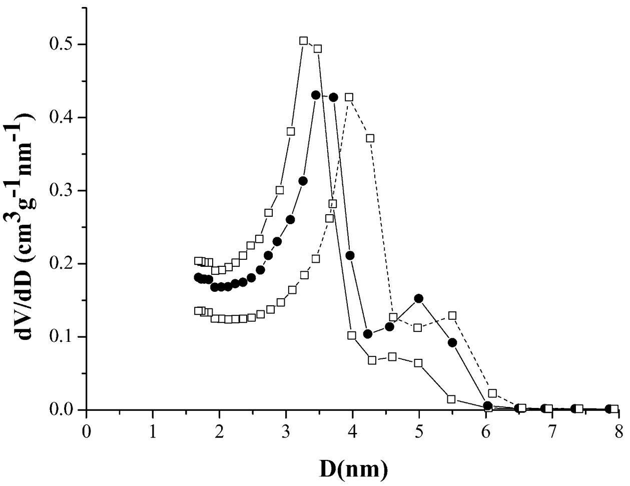


Fig. 2. Pore size distributions of three unsupported membranes prepared from a boehmite sol 0.5 M with 33 wt.% PVA at different calcination temperatures: (—□—) 450 °C, (- - -●- - -) 550 °C, (- - -□- - -) 650 °C.

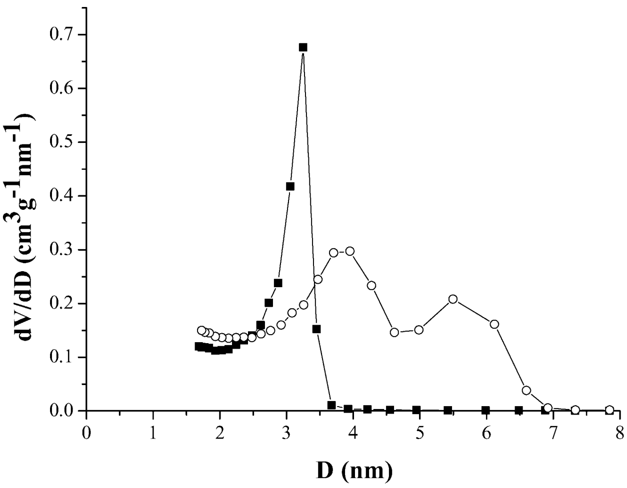


Fig. 4. Pore size distributions of two unsupported membranes sintered at 600 °C and prepared from: (■) boehmite sol 0.5 M, (○) boehmite sol 0.5 M with 33 wt.% PVA.

can be observed and a bimodal behavior is found. The primary pore size corresponds to pores between boehmite particles and the secondary one to pores between agglomerates of particles. These agglomerates are formed by the presence of PVA.

Considering the influence of the sol concentration (Fig. 5), it can be seen that the amount of pores corresponding to agglomerates is higher for higher sol concentration, while the quantity of pores between the particles decreases.

The smaller pore size corresponds to the unsupported membranes deposited from a sol concentration 0.5 M, so firstly this concentration has been chosen to prepare supported membranes. Regarding the calcinations, it is necessary to use a high temperature in order to improve their thermal stability. A temperature of 600 °C has been used to improve the thermal stability.

According to this procedure a defect-free membrane deposited from concentration 0.5 and 0.72 M with amounts of PVA between 33 and 45 wt.% develops a porosity of around 70% (Table 1), that is to say values almost a 40% higher than the membranes obtained with additives of a higher molecular weight.[18,19]

3.3.2. Supported membranes

The N_2 permeability as a function of mean pressure for a membrane deposited from a boehmite sol 0.5 M plus 33 wt.% PVA and calcined at 600 °C is shown in Fig. 6a. In this figure, the permeabilities as functions of pressure for the support and for the intermediate layer are shown too, because

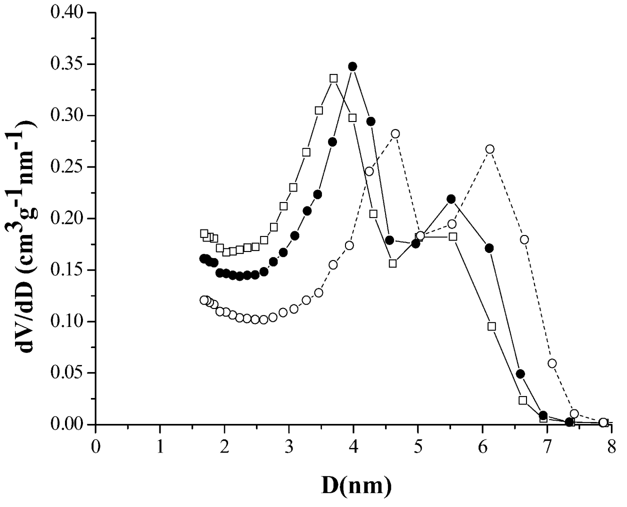


Fig. 3. Pore size distributions of three unsupported membranes prepared from a boehmite sol 0.72 M with 33 wt.% PVA at different calcination temperature: (—□—) 450 °C, (—●—) 550 °C, (- - -□- - -) 650 °C.

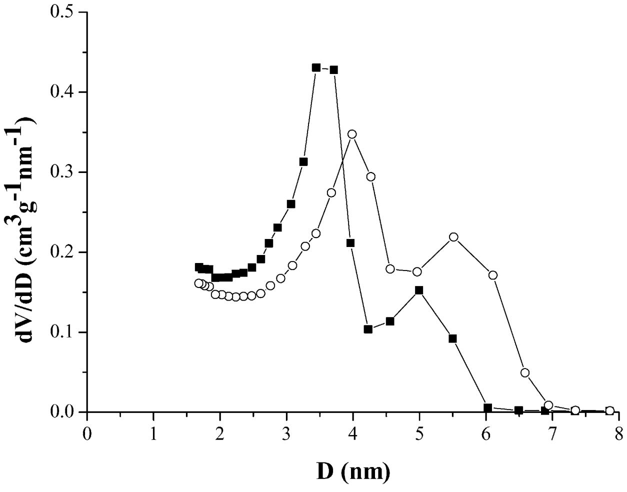
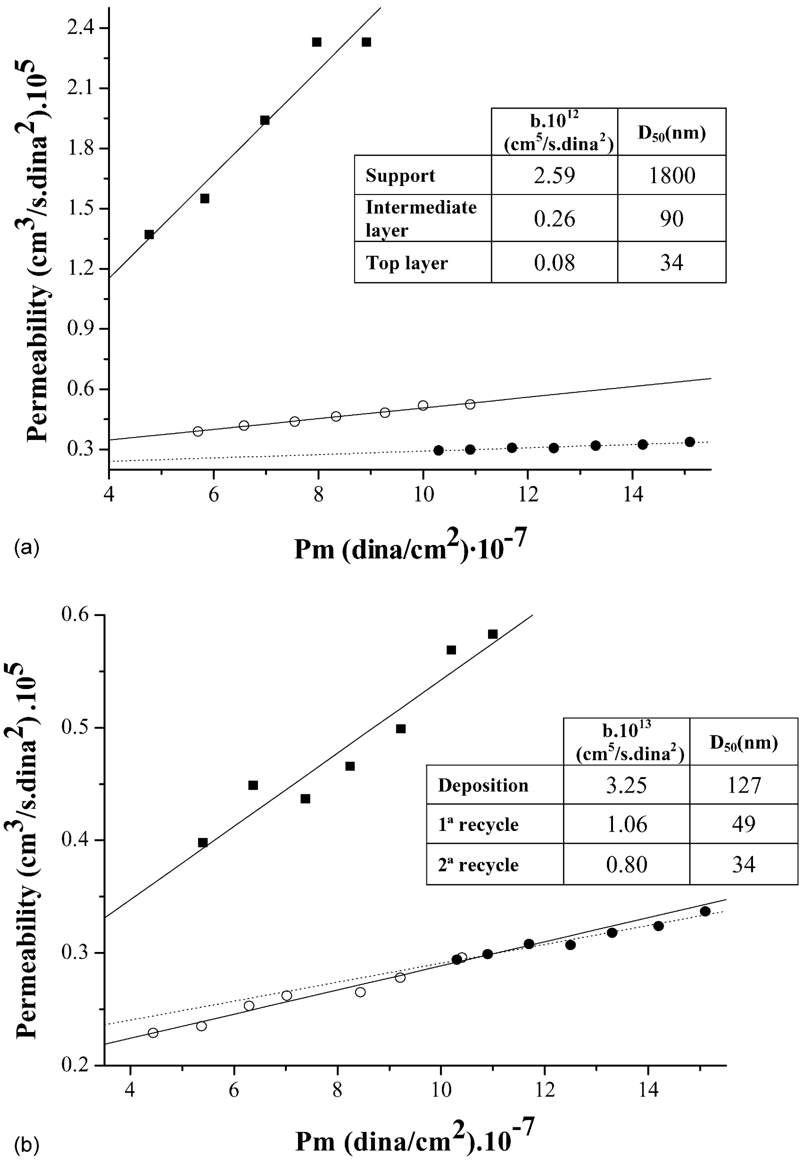


Fig. 5. Pore size distributions of two unsupported membranes sintered at 550 °C and prepared from: (■) boehmite sol 0.5 M with 33 wt.% PVA, (○) boehmite sol 0.72 M with 33 wt.% PVA.



	b.10^{12} (cm^5/s.dina^2)	D$_{50}$(nm)
Support	2.59	1800
Intermediate layer	0.26	90
Top layer	0.08	34

	b.10^{13} (cm^5/s.dina^2)	D$_{50}$(nm)
Deposition	3.25	127
1ª recycle	1.06	49
2ª recycle	0.80	34

Fig. 6. (a) N_2 permeability as a function of mean pressure for a support (■), intermediate layer deposited on this support (○), a top layer deposited on this intermediate layer from a boehmite sol 0.5 M with 33 wt.% PVA and calcined at 600 °C (●). (b) N_2 permeability as a function of mean pressure for the top layer of (a). Deposition (■), deposition plus the first recycle (○) and deposition plus the first recycle and plus the second recycle (●).

the permeability of the top layer must be calculated from the permeability of the system on which it deposited. According this, a previous characterization by permeability of the support and the intermediate layer is necessary to characterize the top layer.

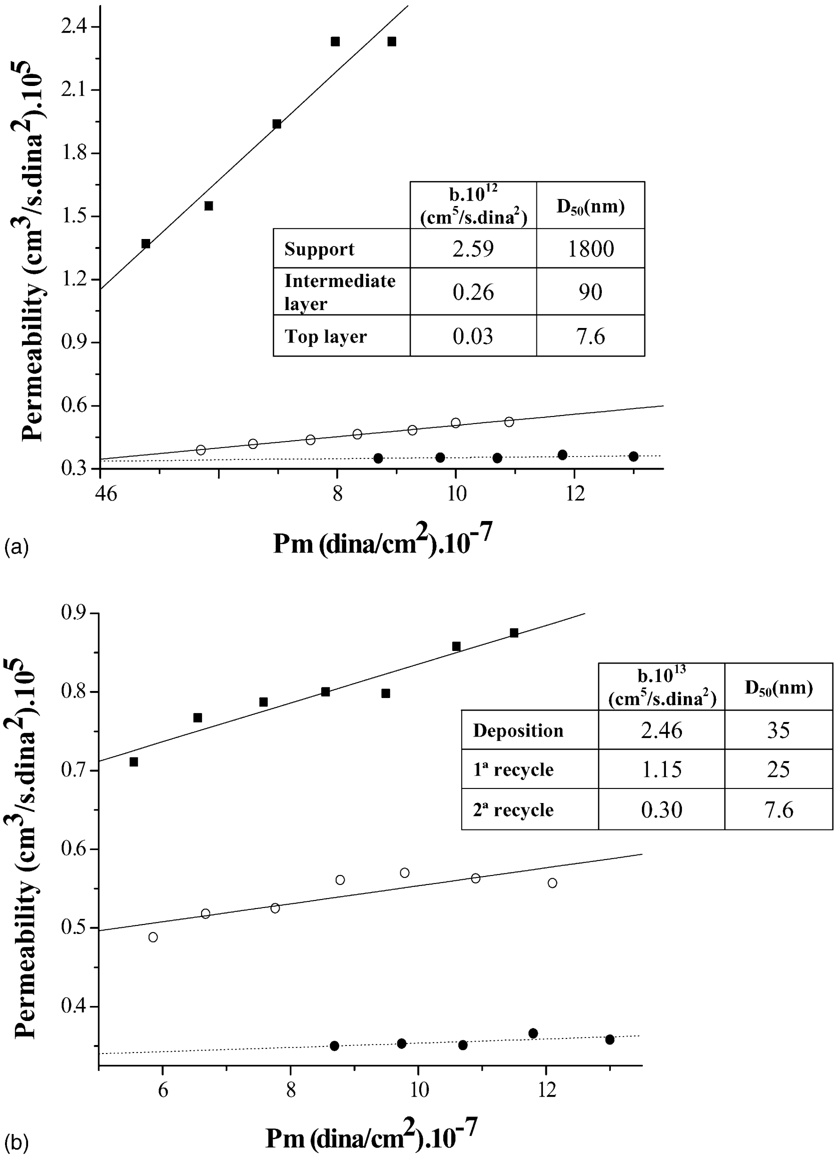
In the Fig. 6a, a support of cordierite has been used. The support permeability is linearly dependence on pressure, with a slope of 2.59×10^{-12} cm^5/s dina^2. This slope indicates the presence of viscous flow due to large pore sizes. The pore diameter calculated by permeability is 1800 nm, which is not in concordance with the mercury porosimetry data for supports of cordierite. The permeability measurement for the support is not valid to calculate high pore diameters (in this case around of 10 μm), since the transport by Knudsen diffusion is not produced across the support, however, it is necessary for the characterization of the intermediate layer.

The measured permeability of the intermediate layer deposited on the support shows also a dependence with the pressure, but now with a lower slope, which indicates less transport by viscous flow than that of the support. The pore size obtained by permeability is 90 nm. This shows that the intermediate layer has covered totally the defects and pores of the surface of the support, since the obtained pore size corresponds to the pore size obtained for the intermediate layer by mercury porosimetry. If the obtained pore size was bigger, it would mean that defects or pores of the support have not still been covered by the intermediate layer.

The plot corresponding to the top layer has a slope of 0.08 × 10^{-12} with a pore size of 34 nm. By N_2 adsorption, the pore size with cylinder-shape in these conditions should be about 6 nm and not 34 nm. It can be concluded that this 34 nm correspond to defects at the membrane. If the deposition of top layer is studied step by step (Fig. 6b), it is observed that after deposition the top layer has a slope of 3.25 × 10^{-13} and a pore size of 127 nm. This result is not representative, because here the pore size is not measured but defects of the membrane. After 1st recycle the slope has decreased to 1.06 × 10^{-13}, but after the second recycle defects still exist. This also can be observed if the slopes corresponding to the 1st recycle and the second recycle are compared. It can be seen that the slope is practically the same. So, it can be concluded that the quality of the membrane has not improved after the second recycle.

This performance has been observed also for membranes deposited from the sol concentration 0.5 M with amounts of additive of 40 and 45 wt.%.

In Fig. 7a is represented the permeability as a function of mean pressure for a membrane deposited from a boehmite sol 0.75 M plus 45 wt.% PVA and calcined at 600 °C. The representation corresponding to the top layer seems to show no dependence with the pressure of permeability, like the last situation at lower concentration of boehmite, but now the average pore size calculated by permeability is 7.6 nm, which agrees with that obtained by N_2 desorption. In Fig. 7b, a gradual decrease of the slope and the pore size can be observed.



	$b.10^{12}$ ($cm^5/s.dina^2$)	D_{50}(nm)
Support	2.59	1800
Intermediate layer	0.26	90
Top layer	0.03	7.6

	$b.10^{13}$ ($cm^5/s.dina^2$)	D_{50}(nm)
Deposition	2.46	35
1ª recycle	1.15	25
2ª recycle	0.30	7.6

Fig. 7. (a) N_2 permeability as a function of mean pressure for a support (■), intermediate layer deposited on this support (○), a top layer deposited on this intermediate layer from a boehmite sol 0.72 M with 45 wt.% PVA and calcined at 600 °C (●). (b) N_2 permeability as a function of mean pressure for the top layer of Fig. 6a. Deposition (■), deposition plus the first recycle (○) and deposition plus the first recycle and plus the second recycle (●).

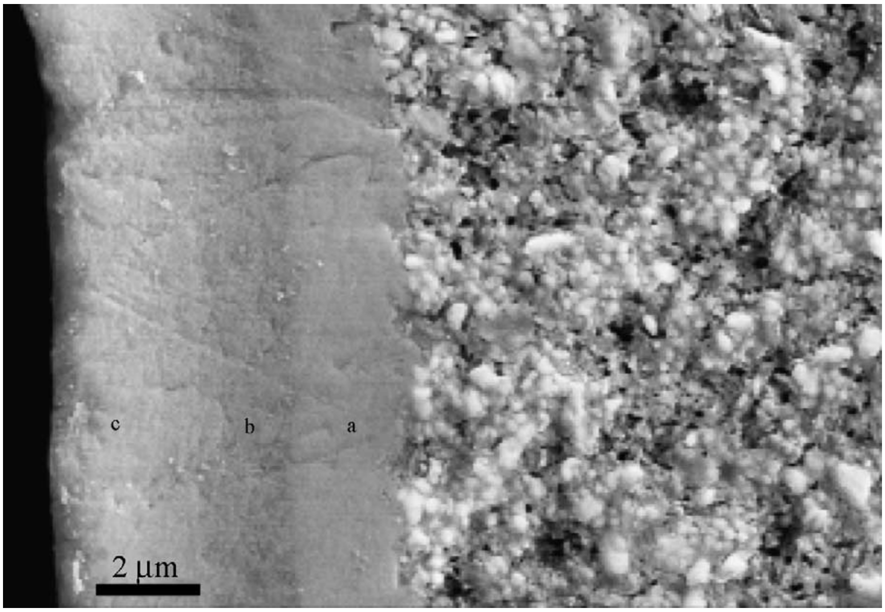


Fig. 8. Top layer deposited on intermediate layer in three steps: deposition (a), first recycle (b) and second recycle (c) (detail of Fig. 7).

In this situation it can be concluded that we have a defect-free membrane.

The average pore size for a supported membrane from sol 0.72 M has been obtained by permeability with different amounts of PVA (Table 2). When the addition of PVA increases, a higher pore size is obtained. After recycling the data of average pore size of the obtained supported membranes show that there is no transport by viscous flow and defect-free membranes are obtained.

The micrograph presented in Fig. 1 shows this multilayer system. It can be seen how the intermediate layer eliminates the defects of the support and provides a plane surface for deposition of the last layer. In Fig. 8 in can be observed a top layer deposited from a boehmite sol 0.72 M with 45 wt.% additive on intermediate layer. The total thickness of this top layer is approximately 7 μm. In this top layer it can be appreciated the deposition (with a thickness of 2.5 μm), the first (1.5 μm) and the second (3 μm) recycle of the top layer. The differences between the thicknesses are produced by the different infiltration of the layer into the previous one. The deposition must fill the pores of the intermediate layer. This implies that part of the boehmite particles are used to full this pores and not to form the layer. The capillary force produced by the pores of the intermediate layer will affect more the particles which are inside the pores than those which form the layer, so the packing will be different. Because of the different packing, cracks will appear during calcination. In the table corresponding to Fig. 7b the pore size measured by permeability is 35 nm, but this result corresponds to the defects size produced during the calcination. The first and the second recycles eliminate these defects. Part of the particles of the first recycle will eliminate the defects formed in the previous deposition, and other part will be deposited; for this reason the thickness of the layer produced by the first recycle has decrease until 1.5 μm. Here, the capillary force will not be as high as the produced one in the intermediate layer, because now it is produced by the pores of the top layer which are smaller. The difference between the packings will be smaller and the defects produced during the calcinations also will be smaller as seen in the table corresponding to the Fig. 7b. The second recycle is used to cover the little defects produced in the first recycle and to provide a defect-free membrane. Here the amount of boehmite particles used in the covering of the defects is smaller, and therefore, the thickness of this layer will be higher (3 μm).

Table 2
Pore diameters (nm) obtained by permeability of a supported top layer prepared from a sol boehmite 0.72 M with different amounts of PVA

Concentration	Top layer	
	Deposition	After recycle
0.72 M + 33 wt.%	12	5.9
0.72 M + 40 wt.%	25	7.1
0.72 M + 45 wt.%	35	7.6

4. Conclusions

The obtained membranes in a tubular configuration, consist of a support of cordierite or alumina, one intermediate layer of α-Al_2O_3 and a top layer of γ-Al_2O_3.

Cordierite and alumina supports have been obtained by extrusion and the intermediate layer has been deposited on their internal side. The deposition was performed by introduction a suspension of α-Al_2O_3 for 1 min and it was demonstrated that this intermediate layer eliminates the defects of the support by measurements of permeability. Also it has been checked that the intermediate layer has the same structural characteristics when is deposited on cordierite or alumina supports.

The unsupported and supported top layers show a different structural behavior, produced by the capillary forces of the intermediate layer. It has been seen that the quality of top layers prepared from boehmite sols 0.5 M is not good (in contrast to that in flat sheet configuration). At least, a boehmite sol 0.72 M and with amounts of PVA between 33 and 45 wt.% are necessary to get defect-free top layers. High amounts of PVA with a medium molecular weight allow to prepare defect-free membranes with high porosities. With this, membranes with an average pore size of 4 nm and porosities above 70% have been prepared in a tubular configuration, improving the porosity of these membranes by reaching 40% more, with respect to the published data.

Permeability measurements are a useful method to evaluate the quality of a supported membrane and to give an estimated result of the pore size.

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