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# Preparation of multilayer ceramic systems for deposition of mesoporous membranes

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Two ceramic systems in a flat sheet configuration have been prepared. These systems will be used for deposition of mesoporous membranes with a high porosity volume, therefore the quality of these supports must be also very high. These systems consist of a support and a different number of intermediate layers deposited on it. Two different system have been prepared and compared. The supports are obtained by pressing and the intermediate layers will be deposited by dipping. Rheological studies have been carried out to adjust the viscosity of the suspensions. Mercury porosimetry, permeability measurements and microscopic characterization are used to evaluate the quality of the intermediate layers and the final membrane system.

## 1. Introduction

Nowadays the filtration procedures by means of membranes have become a very important method in chemical industry, mainly due to its cost-effective performance and high selectivity.

During 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 [2, 3]. New advances in preparation and study of ceramic membranes, such as the use of sol-gel process [4–12], template process [13, 14], chemical vapour deposition [2, 9], hydrothermal synthesis [9, 15] or modification of membranes [16, 17], have allowed the preparation of ceramic membranes with narrow pore distributions and with nanometer pore-scale.

These porous materials have a very low permeabiltity because of its pore size. The solution is the preparation of very thin layers. Such layers must be deposited on macroporous supports to provide them with mechanical strength. Unfortunately it is difficult to obtain a defect-free membrane when it is deposited on a support with a very different pore size. Therefore an asymmetric configuration [18–20] is used, which consists in a multilayer system with a macroporous support (with the largest pore diameter) which provides the mechanical strength to the system; one or several intermediate layers, which roles are to reduce the inherent defects of the support and to prevent the infiltration of the top layer material into the pores of it, and the top layer, which is the true membrane of the system. In this layer it is necessary a comprehensive control of the pore size. The quality of a top-layer comes defined by the mass flow through the membrane and the selectivity. A high permeability can be obtained with a high porosity and a low thickness, and the selectivity with a suitable pore size and with a defect-free membrane.

Taking into account the above mentioned properties, the successively deposited layers must have a decreasing pore size. If the difference between pore size of one layer and the particle size of the next one is excessive, the particles of the new layer could penetrate into the support; this fact can produce the appearance of pinholes and an increase of the resistance to the flow. As an empiric rule, it can be stated that the particles of the deposited layer must not be higher than a fourth of the pore size of the support, or the layer which serves like support.

The main methods of synthesis for the preparation of supports are the traditional ceramic techniques such as pressing, extrusion and tape and slip-casting [21].

Usually, the used supports for depositon of the intermediate layers have a pore diameter around 10 $\mu$m, since with this pore size the resistance to the flow is very low. At pore sizes above 10 $\mu$m, a significant improvement in the permeability is not achieved and it is difficult to get a narrow pore size distribution. Alumina is the most used ceramic material as support because of its chemical stability [21].

Usually, the intermediate layers are formed by dipping the porous support in a suspension. The slip is forced into the pores of the support by capillary suction. This forming mechanism is called slip-casting [22] and

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TABLE I Pore sizes of the different layers of the ceramic systems

| | Scheme 1 | Scheme 2 |
|---|---|---|
| Support | 10 $\mu$m | 1 $\mu$m |
| 1st layer | 0.8 $\mu$m | 0.1 $\mu$m |
| 2nd layer | 0.1 $\mu$m | – |

the critical parameters are the pore size of support, the dipping time and the suspension concentration. There are complex expressions which relate the thickness of the layer with the rest of the involved variables [23] and it can be summarized that the layer thickness increases linearly with the square root of dipping time and decreases with viscosity.

The quality of the support (or layers which serve as support) will determine the final quality of the supported layer. Any defect in the support could cause defects in the deposited layer. So, the study and development of good supports are very important when mesoporous or microporous membranes are going to be deposited.

In this paper, two different schemes have been followed for the obtaining of ceramic systems in flat sheet configuration for deposition of mesoporous membranes. The purpose of both procedures is the preparation of systems with pore diameters of 0.1 $\mu$m and with a thickness of 10 $\mu$m in the last layer. In the first scheme two intermediates layers have been used, in the second procedure only one (Table I). High permeabilities and mechanical strengths are necessary in these ceramic systems. A mesoporous membrane of $\gamma$-$Al_2O_3$ with a very high porosity (around 70%) was deposited on these multilayer ceramic systems to check its validity, since it is necessary to have supports with high quality to deposit a defect-free membrane with such a high porosity.

In this study, mercury porosimetry, permeability measurements, light reflected optical microscopy and field emission scanning electron microscopy have been used for a total characterization of the system.

## 2. Experimental

### 2.1. Materials and methods

Supports with a thickness of 3 mm have been obtained in flat sheet configurations by uniaxial pressing. The pressing has been performed at 125 MPa and with a cylindrical die of 30 mm.

For the first configuration, the supports were prepared using $\alpha$-alumina with an average particle size of 75 $\mu$m (Alumina and Elektrocorundum Ltd., Hungary), hereafter named as $Al_2O_3$-75 $\mu$m. A 5 wt% of a solution at 1 wt% of a binder (Zusoplast PS1, Zschimmer & Schwarz, Germany) has been added to the alumina. To improve the mechanical strength of the obtained supports from $Al_2O_3$-75 $\mu$m, different additives have been added: $Al_2O_3$-6 $\mu$m (DK-206, Martinswerk, Germany), $Al_2O_3$-2 $\mu$m (PN202, Martinswerk, Germany), $Al_2O_3$-0.5 $\mu$m (HPA05, Condea, USA) and colloidal $SiO_2$ (Prosider S.A., Spain). A study at different sintering temperatures and with different additives has been performed to get suitable structural properties.

In the second configuration, supports of $\alpha$-alumina of an average particle size of 6 $\mu$m ($Al_2O_3$-6 $\mu$m) (DK-206, Martinswerk, Germany) was used. A 5 wt% of a solution at 1 wt% of a binder (Zusoplast PS1, Zschimmer & Schwarz, Germany) has been added. The samples have been sintered at different temperatures in an electric furnace to get the most suitable pore size and porosity.

The deposition of the intermediate layers on the supports was performed by dipping. This involves the preparation of stable suspensions. The solids content in the suspension was calculated taking into account the thickness ($l$) of the layer which is going to be deposited. This theoretical calculation can be summarized as follows:

$$\%sc = m/V_{H_2O} \tag{1}$$

where $\%sc$ is the solids content, $m$ is the amount of solids and $V_{H_2O}$ is the volume of water absorbed by the support. $m$ and $V_{H_2O}$ can be defined as:

$$m = \pi R^2 l \rho \tag{2}$$

$$V_{H_2O} = \pi R^2 L P \tag{3}$$

where $R$ is the radius of the disk-shaped support, $\rho$ the density of the layer, $L$ the thickness of the support and $P$ the porosity of the support. If the Equations 2 and 3 are substituted in the Equation 1:

$$\%sc = l\rho/LP \tag{4}$$

With this equation the percentage of necessary solids content in a suspension to obtain a layer with a thickness $l$ can be estimated approximately.

In the first scheme, a suspension of $\alpha$-alumina with an average particle size of 3 $\mu$m ($Al_2O_3$-3 $\mu$m) (ZN-203, Martinswerk, Germany) with different solids content (30, 40 and 50 wt%) was prepared. By means of viscosity measurements the necessary amount of deflocculant (Dolapix CE64, Zschimmer & Schwarz, Germany) has been determined to get stable suspensions. To avoid the appearance of defects on this layer, two different binders have been added: a carboxymethylcellulose of low viscosity (Optapix C12G, Zschimmer & Schwarz, Germany) named as Binder1 and a carboxymethylcellulose of high viscosity (Optapix C1000G, Zschimmer & Schwarz, Germany), named as Binder2.

In both schemes, the last layer was deposited from a suspension of $\alpha$-$Al_2O_3$ (HPA05, Condea, USA), which has an average particle size of 0.5 $\mu$m ($Al_2O_3$-0.5 $\mu$m). Different solids content in this suspension has been studied (1, 2, 4 and 8 wt%). It has been studied through viscosity measurements, the necessary amount of deflocculant (Dolapix CE64, Zschimmer & Schwarz, Germany) and binder (Optapix C12G, Zschimmer & Schwarz, Germany) to get stable suspensions and layers. The obtained suspension was stirred for 1 h and an ultrasounds bath was used for the elimination of air bubbles.

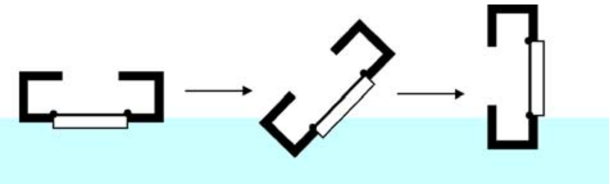

*Figure 1* Followed method for the deposition of the intermediate layers on supports.

In order to study sintering process, unsupported intermediate layers were obtained by slip-casting on plaster molds. The optimization of sintering temperatures was performed in an electric furnace on the unsupported layer.

The intermediate layers deposition was carried out by dip-coating from the suspension as shown in Fig. 1. Dipping was performed leaving one side of the support open in order to facilitate the exhaust of air. The samples were dried vertically at room temperature for 24 h and sintered later on.

The preparation of the top layer was performed via sol-gel process to obtain $\gamma$-$Al_2O_3$ membranes. For this, it has been followed the process developed by Yoldas [24, 25]. So it has started from an alcoxide (Aluminumtri-sec-butylate, Merck, Germany), which has been hydrolized totally with water above 90°C in a proportion of 2 liters of $H_2O$ per mole of alcoxide. The obtained precipitate was peptized with 0.07 moles of $HNO_3$ per mole of alcoxide. The suspension was maintained at reflux conditions for 16 h and at 90°C. A boehmite sol 0.5 M plus an amount of 33 wt% of polyvinylalcohol (Optapix PAF 35, Zschimmer & Schwarz, Germany) was prepared. The deposition of this membrane on the multilayer system consists in three necessary dipping procedures: deposition of the membrane by dipping for 45 s, a first reparation by dipping for 30 s and a second reparation 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 gel was calcined at 600°C (kept for 3 h) at a rate of 60°C/h in an electric furnace.

## 2.2. Characterization

Mercury porosimetry with a Micromeritics Autopore II 9215 porosimeter was used for the determination of the pore size and porosity of the supports and unsupported intermediate layers.

The viscosity of suspensions was measured with the aid of a Brookfield DV-I viscometer.

The study of the quality of supported intermediate layers were performed using the permeability method developed by Uhlhorn *et al.* [26–28] and later by Conesa [29], which can be summarized as follows:

The gas flow equation through a membrane is given by:

$$\frac{NRT}{\nu \Delta P} = \frac{k_o}{L} + \frac{B_o P_m}{L \eta \nu} \tag{5}$$

where $N$ is the gas flow per unit area, $R$ the gas constant, $T$ the temperature, $\Delta P$ the pressure difference, $\nu = \sqrt{\frac{8RT}{\pi M}}$ the mean molecular velocity, $M$ the gas molecular weight, $k_o = \frac{2\varepsilon}{3\tau} r_p$ the term corresponding to Knudsen diffusion, $\varepsilon$ the porosity, $\tau$ the tortuosity, $r_p$ the pore radius, $L$ the membrane thickness, $B_o = \frac{\varepsilon}{8\tau} r_p^2$ the term corresponding to viscous flow, $P_m$ the mean pressure and $\eta$ the 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:

$$F = \frac{N}{\Delta P} \tag{6}$$

Substituting the Equation 6 in the Equation 5 is obtained a first degree equation:

$$F = a + b P_m \tag{7}$$

where $F$ is the permeability, $a$ is a constant corresponding to Knudsen diffusion, $b$ a constant representing viscous flow and $P_m$ the 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 [30] ($\phi < 10$ nm [31]). 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 [30] yielding a pressure dependence on the permeability.

Starting from the obtained data of $a$ y $b$, the pore radius can be estimated from:

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

where $\eta$ is the viscosity of the gas (in this case $N_2$), $R$ the gas constant, $T$ the temperature and $M$ the molecular weight of the gas.

The surface of the intermediate layers has been examined by light reflected optical microscopy. The thickness and microstructure of the layers was measured with a Hitachi Field Emission Scanning Electron microscope.

# 3. Discussion

## 3.1. Supports

Depending on the particle size used for the preparation of the support, the total processing of the system will change. Starting from large pore sizes, the permeability will be high, but the processing will result in more intermediate layers before the deposition of the toplayer. On the other hand, one support with small pore size will have low permeability, but the processing of the total system will be simpler.

In the first scheme, $Al_2O_3$-75 $\mu$m was used and at a sintering temperature of 1700°C provides a pore size of around of 10 $\mu$m. However, the bending strength

TABLE II Mechanical strength of $Al_2O_3$-75 $\mu$m as a function of additive and sintering temperature

| wt% additive | Pressing (MPa) | Sintering temperature (°C) | Bending strength (MPa) |
|---|---|---|---|
| 0 | 125 | 1700 | 3.4 |
| 5% $Al_2O_3$-6 $\mu$m | 125 | 1700 | 5.0 |
| 15% $Al_2O_3$-6 $\mu$m | 125 | 1700 | 8.7 |
| 5% $Al_2O_3$-2 $\mu$m | 125 | 1700 | 5.6 |
| 10% $Al_2O_3$-2 $\mu$m | 125 | 1700 | 7.6 |
| 5% $Al_2O_3$-2 $\mu$m | 125 | 1750 | 6.4 |
| 5% $Al_2O_3$-0.5 $\mu$m | 125 | 1700 | 6.0 |
| 10% $Al_2O_3$-0.5 $\mu$m | 125 | 1700 | 9.7 |
| 15% $Al_2O_3$-0.5 $\mu$m | 125 | 1750 | 13 |
| 2% colloidal $SiO_2$ | 125 | 1650 | 39 |
| 2% colloidal $SiO_2$ | 50 | 1500 | 28 |
| 2% colloidal $SiO_2$ | 50 | 1650 | 30 |

TABLE III Mercury porosimetry of the $Al_2O_3$-6 $\mu$m, $Al_2O_3$-3 $\mu$m, $Al_2O_3$-0.5 $\mu$m at different sintering temperatures

| | $Al_2O_3$-6 $\mu$m | | $Al_2O_3$-3 $\mu$m | | $Al_2O_3$-0.5 $\mu$m | |
|---|---|---|---|---|---|---|
| $T$ (°C) | Pore diameter ($\mu$m) | Porosity (%) | Pore diameter ($\mu$m) | Porosity (%) | Pore diameter (nm) | Porosity (%) |
| 900 | – | – | – | – | 84 | 43 |
| 1000 | – | – | – | – | 95 | 41 |
| 1100 | – | – | – | – | 90 | 38 |
| 1200 | – | – | – | – | 95 | 29 |
| 1300 | – | – | – | – | 100 | 17 |
| 1400 | – | – | 0.8 | 41 | 56 | 0.5 |
| 1450 | 1.2 | 40 | 0.8 | 39 | – | – |
| 1500 | 1.2 | 37 | 0.8 | 38 | – | – |
| 1550 | 1.1 | 37 | – | – | – | – |
| 1600 | 1.2 | 36 | – | – | – | – |
| 1650 | 1.2 | 33 | – | – | – | – |

of this support is very low (Table II). With this particle size, the sintering temperature must be higher to get a good bending strength. To increase the mechanical strength at lower sintering temperature, it has been neccesary to add materials with particle size smaller than the particle size of the alumina. This study has been performed with the addition of materials such as $Al_2O_3$ with a particle size of 6, 2 and 0.5 $\mu$m and with colloidal $SiO_2$. In Table II it can be observed that when the particle size of the added material is lower, the mechanical strength is better. The colloidal $SiO_2$ allows to decrease the sintering temperature to 1500°C and to provide good mechanical properties. So, an amount of 2 wt% colloidal $SiO_2$ has been added. The samples have been sintered at 1650°C for 2 h using a heating rate of 300°C/h, obtaining supports with an average pore diameter of 10 $\mu$m and a porosity of 32%.

In Table III the data of pore size and porosity obtained by mercury porosimetry of the support of $Al_2O_3$-6 $\mu$m (2nd scheme) are shown. It can be seen that while the pore size does not suffer variations in the studied interval of temperature, the porosity decreases when the temperature increases. In all cases the pore size distribution is very narrow. It has been optimized the sintering at 1500°C for 2 h at a rate of 300°C/h. As a result, the support has an average pore diameter of 1.2 $\mu$m and a porosity of 37%.

## 3.2. Intermediate layers

The deposition of the intermediate layers was performed by dipping the support in a suspension. The amount of deflocculant necessary to get stable suspensions was studied.

Following the first scheme, to obtain an intermediate layer of 0.8 $\mu$m of pore diameter, a suspension of $Al_2O_3$-3 $\mu$m with a 75 wt% solids content was prepared. In Fig. 2 the viscosity curve is shown and it has been seen that at least an amount of deflocculant of 0.1 wt% with respect to solids content is necessary. Using a dipping time of 60 s (enough time to assure a total saturation of the pores of the support) the layer has been deposited. In this layer the pore diameter calculated by permeability is 0.2 $\mu$m. This result is not in accordance with the mercury porosimetry data of pore diameter for this layer (0.8 $\mu$m, Table III). This difference is produced because permeability measurements are not valid to calculate high pore diameters (in this case around of 0.8 $\mu$m), since the contribution of the Knudsen diffusion to the permeability is almost nonexistent across the layer. However the calculation of the pore size by permeability is useful for the characterization of the layer, since the reproducibility of this result can be evaluated. In this case, this calculation presents very low reproducibility, showing the existence of layers with cracks. Therefore, the addition of a binder is necessary to obtain an intermediate layer without defects. The presence of the binder will affect the amount of necessary deflocculant to stabilize the suspensions. A carboxymethylcellulose of low viscosity (Optapix C12G, Zschimmer & Schwarz), named as Binder 1, was used to increase the stability of the layer. Now, the corresponding viscosity curve with a 1 wt% binder (Fig. 2) shows that an amount of 0.75 wt% of deflocculant with respect to solids content is necessary to stabilize the suspension.

Subsequently it is necessary to fix the solids content of the suspension and the dipping time to get the adequated thickness. Since the particle size of the support is 75 $\mu$m, the maximum roughness produced by this grain size will have a value close to 100 $\mu$m. So, the necessary thickness to assure a total covering of the surface of the support, will be al least of 100 $\mu$m. To get this, it has been looked for the solids content of the

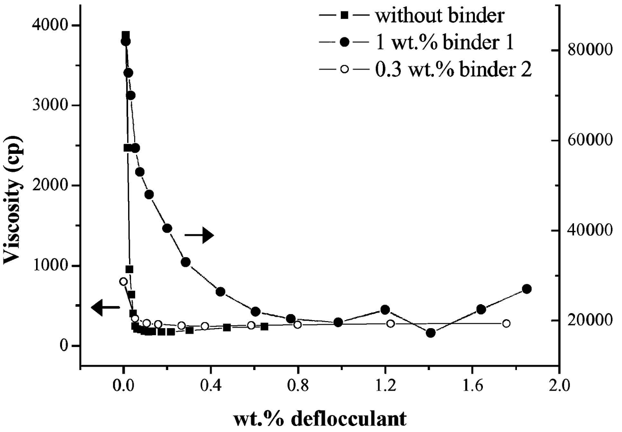

*Figure 2* Viscosity curves of a suspension of $Al_2O_3$-3 $\mu$m with a 75 wt% solids content without and with different binders.

suspension, which will provide a thickness of 100 $\mu$m approximately. Assuming that the porosity of the layer is of 40% (Table III), the density of the $\alpha$-$Al_2O_3$ 3.98 g/cm$^3$, the thickness and porosity of the support 2 mm and 32% respectively, and substituting in the Equation 4 is obtained a solids content of 25%. Since part of the particles of $\alpha$-$Al_2O_3$ are going to infiltrate into support is necessary to use a higher percentage. So, suspensions with solids content of 30, 40 and 50 wt% have been prepared. In Table IV it can be observed that with all these percentages of alumina is reached this thickness. The characterization by means of permeability of the supported layer indicates that at higher concentrations than 40 wt%, the radius pore remains constant (Table IV). This fact shows a defect-free layer.

If the surface of these intermediate layers is observed by means of an optical microscope, defects can be seen corresponding to non-covered areas. When the solids content is higher in the suspension, the possibility of appearance of these defects diminishes, as it can be seen in Fig. 3. In the Figs 3a and b is show an intermediate layer deposited from a suspension of 30 and 40 wt% solids content respectively, and areas of support not coated can be noticed. This was found by Redon *et al.* [32], who noted that the probability of appearance of not recovered areas, as well as the speed of growth of these areas, are inversely proportional to the viscosity (and as a result to the concentration of the suspension). These areas will cause defects in the next

TABLE IV Characteristics of suspension and layer prepared from $Al_2O_3$-3 $\mu$m

| Solids content (wt%) | Viscosity (cp) | Permeability (cm$^3$/s.dina).10$^6$ | Radius pore by permeability (nm) | Thickness by SEM ($\mu$m) |
|---|---|---|---|---|
| 30 | 9.3 | 4.84 | 287 | 290 |
| 40 | 15.7 | 4.04 | 155 | 450 |
| 50 | 36.5 | 3.08 | 163 | 680 |

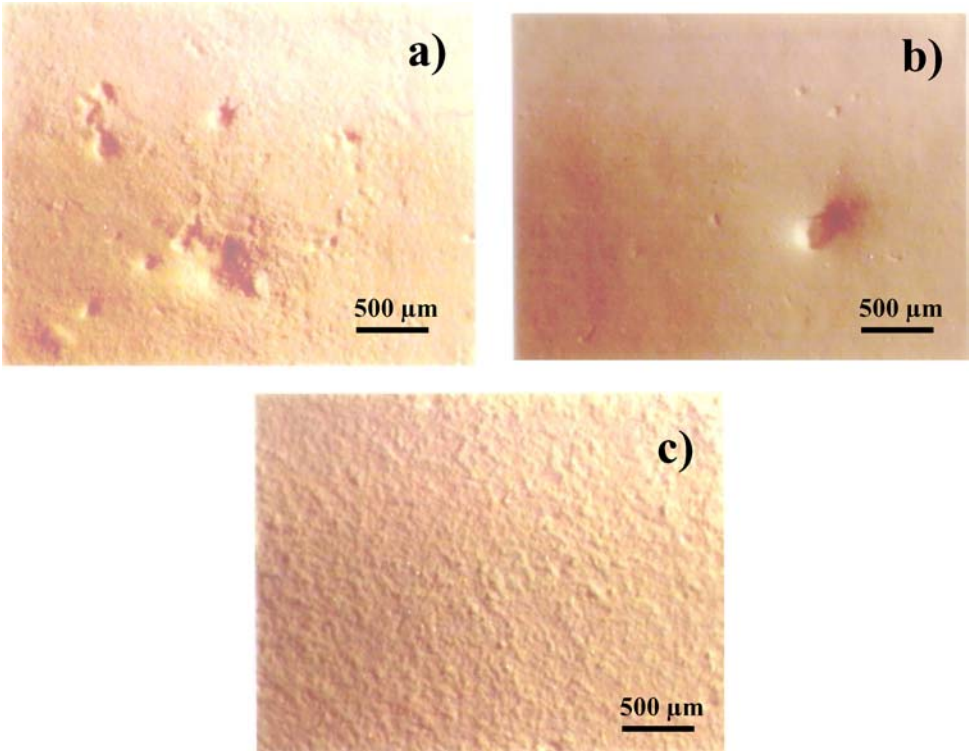

*Figure 3* Intermediate layer of $Al_2O_3$-3 $\mu$m deposited on a support $Al_2O_3$-75 $\mu$m from a suspension with a 30 wt% (a), 40 wt% (b) and 50 wt% solids content (c).

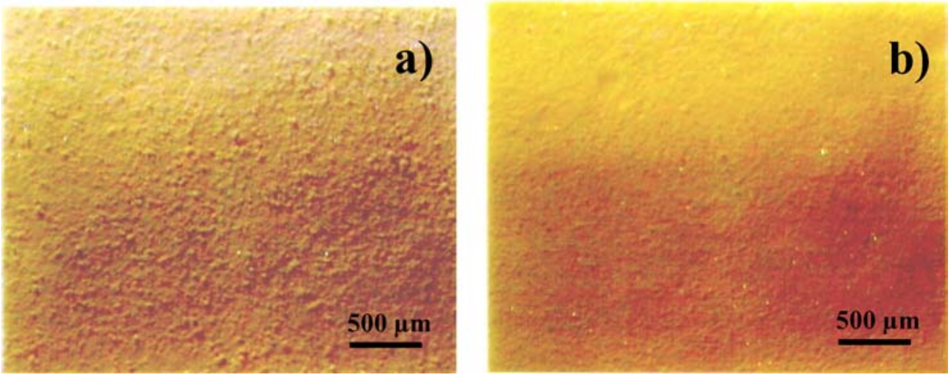

*Figure 4* Intermediate layer of $Al_2O_3$-3 $\mu$m with a 40 wt% solids content and 0.3 wt% binder 2 prepared by: high shear stirring (a), balls mill (b).

layer deposited on it. In Fig. 3c, these areas do not exist, however there is a big increase of the rugosity. This effect has been produced by an excess of binder in the suspension, since it is proportional to the solids content. Therefore the used binder is not valid to adjust the viscosity of the suspension, since the required quantity will cause the apparition of agglomerates in the suspension and as a consequence the quality of the surface will diminish. This problem has been solved using a binder which provides the same value of viscosity with less concentration. For that, a binder with a higher molecular weight was used, in this case a carboxymethylcellulose of high viscosity (Optapix C1000G, Zschimmer & Schwarz), named as Binder 2. Following the same previous procedure, the composition of this suspension was optimized. An amount of ligant of 0.3 wt% has been added. The viscosity curve corresponding to this suspension can be observed in Fig. 2. It can be concluded that it is neccessary an amount of 0.1 wt% with respect to solids content of deflocculant to get a stable suspension. If the surface of a layer with a solids content of 40 wt% is observed by means of an optical microscope, it can be found the apperance of aglomerates on the surface (Fig. 4a. This low concentration of binder does not justify the appearance of these agglomerates. To attempt the breaking of the agglomerates and obtain layers of high quality, ball milling was used instead of a high shear stirring in the preparation of the suspension, and it was observed that this last procedure is more effective in this case (Fig. 4(b)).

The sintering temperatures were studied from 1400°C (Table III), since at lower temperatures the bending strength is too low. The sintering was performed at 1400°C for 2 h at a rate of 200°C/h.

Finally, the preparation and deposition of the last layer (with a pore size of 0.1 $\mu$m) has been studied for both schemes. The evolution of the pore size and the porosity of the unsupported layer comes reflected in Table III. A sintering temperature of 1100°C for 2 h at a rate of 200°C/h has been chosen to get an intermediate layer with an average pore diameter of 90 nm and 38% of porosity. A narrow pore size distribution was obtained at this temperature (Fig. 5).

TABLE V Evolution of the permeability of the layer of $Al_2O_3$-0.5 $\mu$m with the percentage of solids in suspension

| Solids content (wt%) | Pore diameter by permeability (nm) | Permeability (cm$^3$/s.dina).10$^6$ |
|---|---|---|
| 1 | 142 | 4.29 |
| 2 | 96 | 4.77 |
| 4 | 104 | 2.44 |
| 8 | 98 | 1.07 |

By means of the corresponding viscosity curve it has been seen that 0.75 wt% of deflocculant with respect to solids content is necessary to get a stable suspension. To optimize the conditions of concentration of solids and dipping time, suspensions with different amounts of $\alpha$-alumina were prepared (calculated from Equation 4). The layer was deposited on supports of $Al_2O_3$-6 $\mu$m by dipping for 60 s. The evolution of the permeability of the last layer with the percentage of solids in suspension is shown in Table V. Comparing the pore sizes obtained by permeability of the last layer, it can be concluded that a solids content of 2 wt% is enough to obtain a free-defect layer, since a diameter pore size around of 100 nm is in agreement with the result obtained by mercury porosimetry (Table III). At lower solids content, the pore size is higher, truly corresponding to defects and not pore sizes. The permeability of the layer decreases as you increase the percentage of solids of the suspension, which indicates that the thickness increases. At dipping times higher than 60 s, small changes are observed in the pore sizes obtained by permeability, which shows that with a dipping time of 60 s, a total saturation of the pores of the previous layer is obtained.

The thickness of a layer obtained from 8 wt% solids content is 10 $\mu$m approximately. With this thickness a total coating of the previous layer is assured in the first scheme as much as in the second one. To increase the reproducibility of the measures, an amount of 1 wt% of

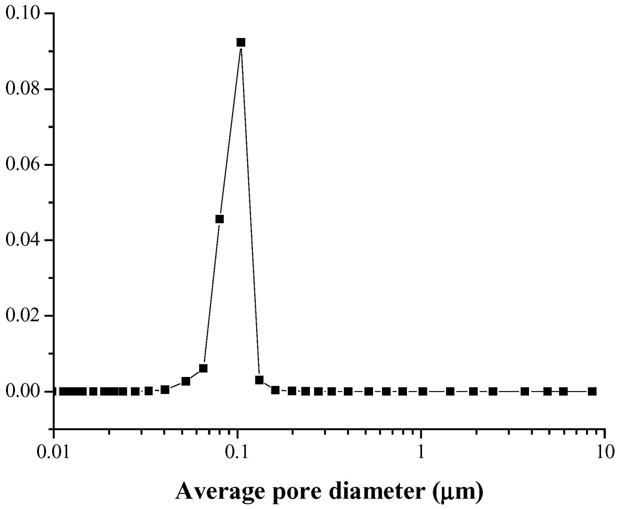

*Figure 5* Pore size distribution obtained by mercury porosimetry of the $Al_2O_3$-0.5 $\mu$m sintered at 1100°C.

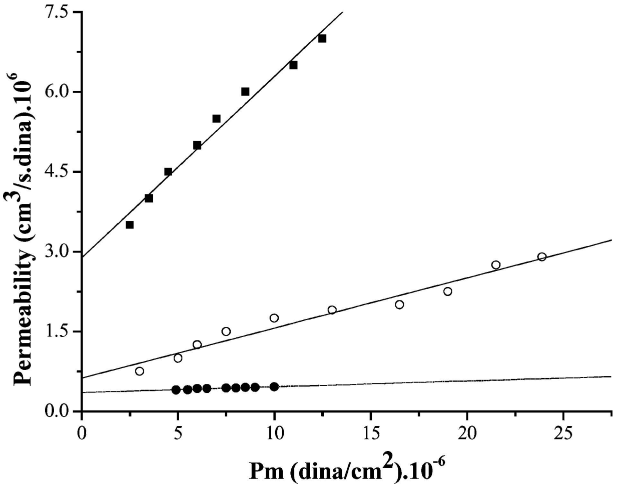

*Figure 6* $N_2$ permeability as a function of mean pressure for a layer $Al_2O_3$-0.5 $\mu$m deposited on a layer $Al_2O_3$-6 $\mu$m (○), on a layer $Al_2O_3$-3 $\mu$m (■) and a mesoporous membrane of $\gamma$-$Al_2O_3$ deposited on a layer $Al_2O_3$-0.5 $\mu$m (●).

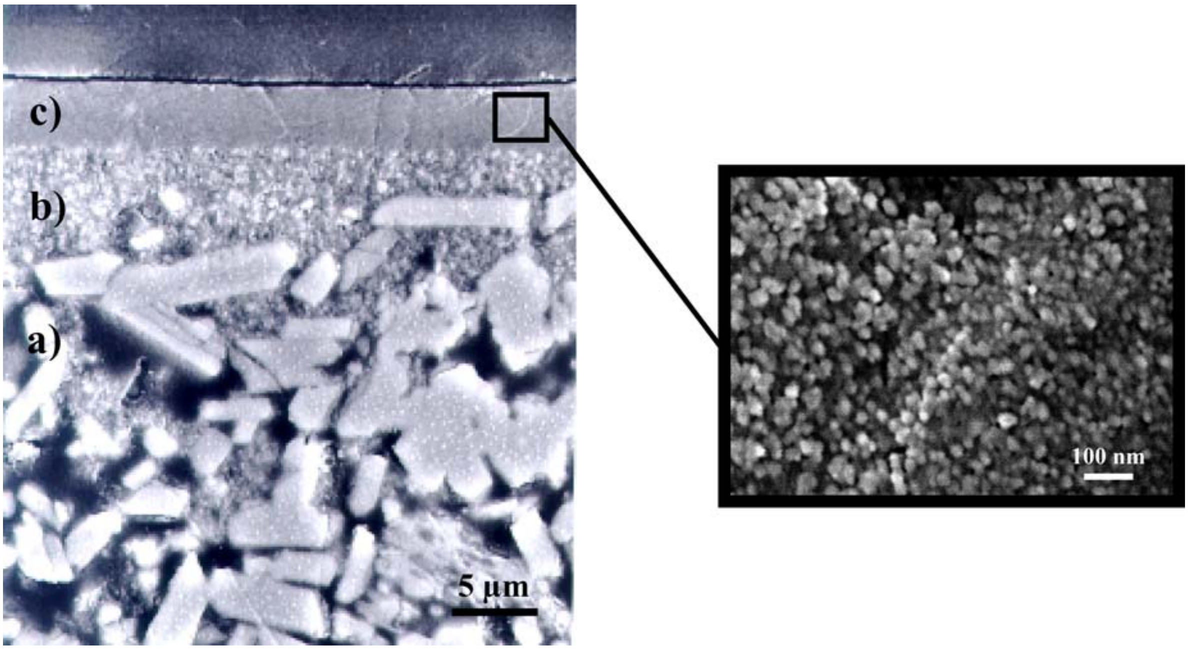

*Figure 7* Micrograph showing a multilayer system formed by a macroporous support of $Al_2O_3$-6 $\mu$m (a), an intermediate layer of $Al_2O_3$-0.5 $\mu$m (b) and a mesoporous top layer of $\gamma$-$Al_2O_3$ (c).

binder 1 with respect to solids content has been added. The amount of deflocculant was fixed at 0.75 wt% with respect to solids content in presence of these amount of binder.

The characterization by means of permeability of several membranes obtained starting from suspensions of $Al_2O_3$-0.5 $\mu$m with 8 wt% on supports of $Al_2O_3$-6 $\mu$m and $Al_2O_3$-3 $\mu$m can be observed in Fig. 6. The layers deposited on intermediate layers of $Al_2O_3$-6 $\mu$m possess lower permeability, since the capillary force produced by their pores is higher than the one produced by the layers of $Al_2O_3$-3 $\mu$m. This effect will cause a higher penetration of the particles into support and as a result the thickness will increase and the permeability will decrease. Both layers are defect-free, since the average diameter pore value obtained by permeability is around 90 nm. The obtaining of this pore size by means of the permeability is very important. This method is very sensitive to possible defects in the layer and a pore size of 90 nm obtained by this method indicates no pores sizes or defects bigger than 90 nm exist, obtaining a layer with a high quality. If the global permeability of both systems is compared, the system obtained by the first scheme shows also a higher permeability, although the total thickness of the system is higher than the second scheme. The explanation is that the previous layers and supports almost do not produce loss of pressure across the system because of their large pore size. So, the total permeability of the both systems comes determined by the last intermediate layer ($Al_2O_3$-0.5 $\mu$m). According to this conclusion, if a system very permeable is required, the most appropriate will be the obtained one by the first scheme ($Al_2O_3$-75 $\mu$m → $Al_2O_3$-3 $\mu$m → $Al_2O_3$-0.5 $\mu$m). However, the system obtained by the second scheme ($Al_2O_3$-6 $\mu$m → $Al_2O_3$-0.5 $\mu$m) has a cost-effective production better than the obtained one by the first scheme.

To check the validity of this ceramic system as support of mesoporous membranes, a $\gamma$-$Al_2O_3$ membrane has been deposited on the systems obtained by the first and the second scheme. This membrane must have an average pore size (assuming a slit-shaped pore) around of 4 nm according to studies carried out by different authors [33–35]. This membrane has also a porosity of 70%, so it is very difficult to deposit defect-free membranes of this type if the support is not of high quality [35]. In Fig. 7 the $\gamma$-$Al_2O_3$ membrane deposited on the ceramic system and a detail of this one are shown. This membrane has a thickness of 5 $\mu$m and a pore size obtained by permeability (Fig. 6) of 3.7 nm. The permeability as a function of the mean pressure shows an independent behavior of the pressure (transport by viscous flow is not produced). This result of pore size is in good agreement with the aforementioned results for defect-free membranes of this type and it has been obtained in $\gamma$-$Al_2O_3$ membranes deposited on both systems.

## 4. Conclusions

In this work the preparation of multilayer ceramic systems for deposition of mesoporous membranes is presented. Two different systems have been obtained and compared. The first one corresponds to a system with a support and two intermediate layers, and the second one to a support with one intermediate layer. In both cases, the last intermediate layer has an average pore diameter of 0.1 $\mu$m and a thickness of 10 $\mu$m. By measurements of $N_2$ permeability it has been proven that the second system has a higher permeability, therefore in a filtration procedure pressure losses through the second system will be smaller and the performance will be higher.

It has been shown that depositions of mesoporous defect-free membranes with very high porosities (70%)

may be obtained on both systems. It can be concluded that the structural characteristics of the last layer are suitable to deposit membranes of this type.

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