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New Inorganic Ultrafiltration Membranes: Preparation and Characterisation

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SUMMARY

The 'sol–gel' process allows the preparation of thin microporous layers. We have used this technique to obtain an inorganic membrane. The experimental conditions for the preparation of a stable sol from boehmite powder, suitable for casting onto a porous substrate, have been studied.

Different aluminium oxide phases during the thermal treatment are observed. The characteristics of the membrane as a function of the sintering temperature are reported. At 500°C, the mean pore radius is 2·5 nm and the thickness of the layer 3 μm.

1 INTRODUCTION

In separative processes, the use of inorganic membranes instead of organic membranes offers numerous advantages viz:

—high temperature and pressure resistance i.e. no compression of the membrane,
—corrosion and abrasion resistance,
—insensitivity to bacterial action,
—steam sterilisable,
—longer life-time.

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Pressure-driven membrane filtration processes can be divided into different fields according to mean pore diameter:

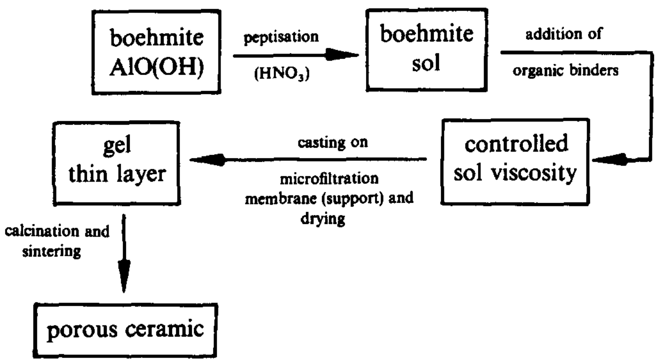
Separation process	*Reverse osmosis*	*Ultrafiltration*	*Microfiltration*	*Classical filtration*
Mean pore diameter (nm)	0·1 → 1	1 → 10^2	$10^2 \rightarrow 10^4$	$>10^4$
Range of application	Separation of ions and molecules	Separation of macromolecules	Separation of particles Sterile filtration–clarification	

Membranes must be from 1 to 10 μm thick, if a high flux is to be obtained through them. It is also important to obtain a very narrow pore size distribution, in order to have very good selectivity. The above processes are used for separation, concentration or purification in various industries, for example, dairy, food, pharmaceutical, textile, chemicals, and water. The sol–gel process is specially important for the preparation (at lower temperatures than used for normal sintering) of porous ceramics, in thin layers with a very narrow pore distribution.[1-3] By means of the sol–gel process, we have obtained a new generation of alumina ultrafiltration membranes.

2 MATERIAL PREPARATION

2.1 Experimental

The different steps of the preparation process oan be summarised as follows:



2.2 Materials

—Boehmite Pural SB (Condea chimie, FRG)
—Nitric acid (Normapur), specific gravity 1·33
—Polyvinyl alcohol (Rhodoviol 25/140 Rhône-Poulenc, France)

2.3 Formulation

The choice of boehmite powder as the precursor has been determined by the porosity properties of this particular variety.[4–6] Following previous studies of alumina gels,[7,8] we have chosen nitric acid as electrolyte for its ability to dissolve the boehmite particles and at the same time to modify their surface charge. Boehmite powder has been added to acid solutions of different pH. Results of these experiments are described in Fig. 1, which shows that boehmite gels are only obtained for solutions of pH < 1·1 ('% Boehmite' is the percent in the final gel or suspension and M(g) is the mass of boehmite added to 25 g or 2 *m* nitric acid).

To obtain a homogeneous sol, we carried out many experiments, in the light of which the following experimental conditions were defined: a suspension of 18 g of boehmite powder in 34·5 g of distilled water, peptisation with 12·5 g of 2 M nitric acid and mixing with an organic binder solution.

This second phase of the preparation gives a sol, which is applied homogeneously to a porous ceramic support. The sol viscosity allowed it to

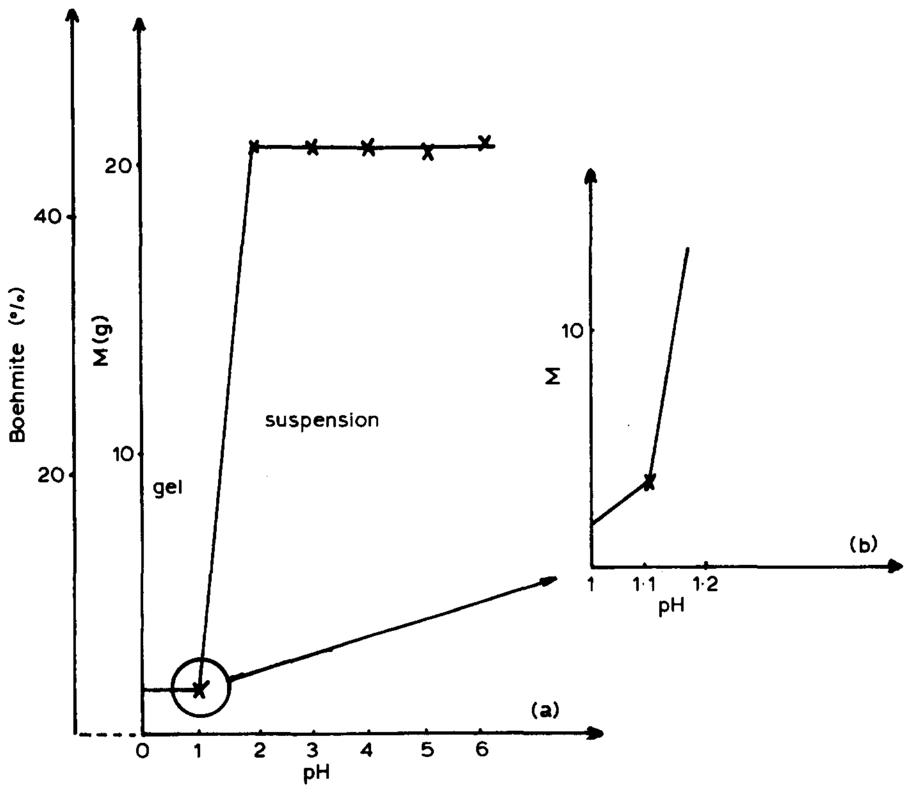


Fig. 1. Peptisation of Pural SB as a function of pH.

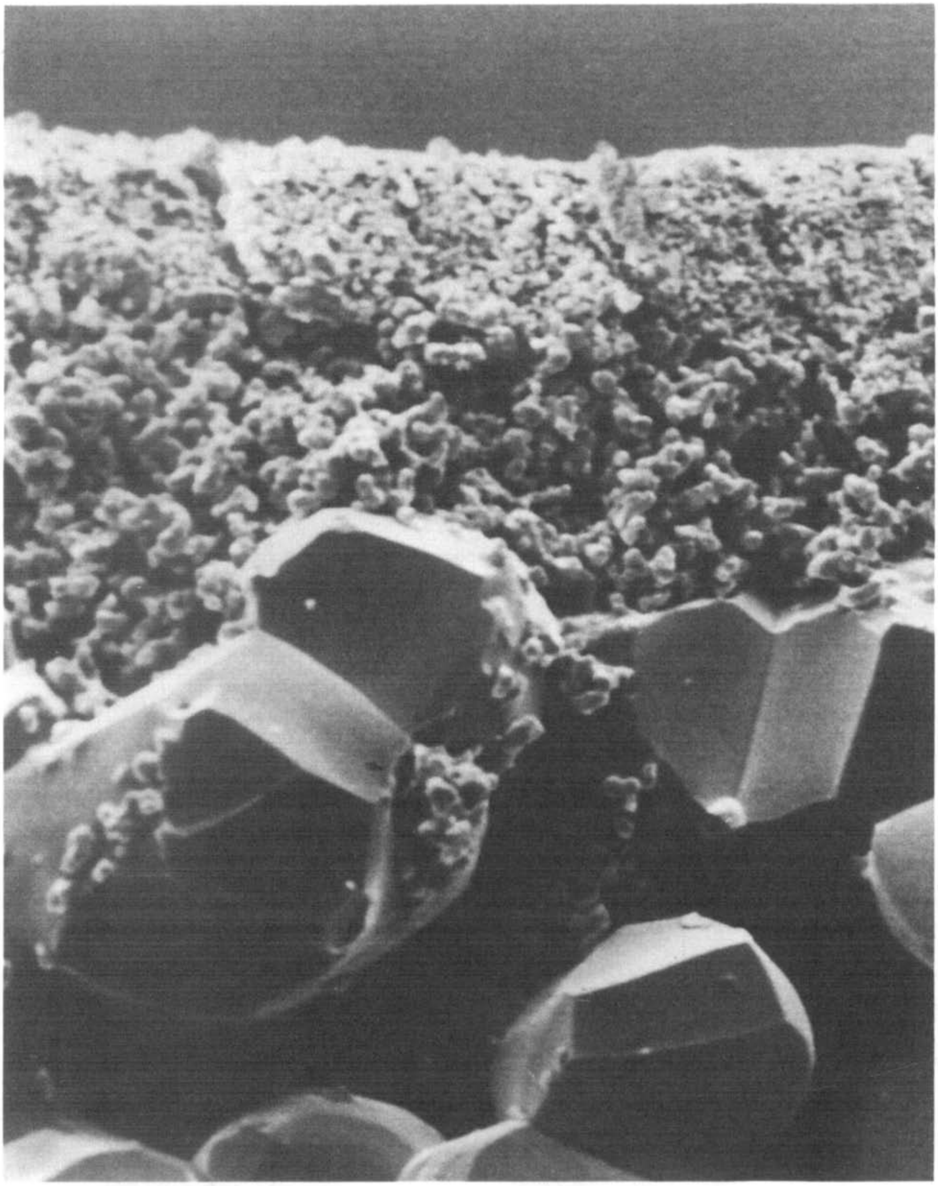


Fig. 2. Scanning electron micrograph of microfiltration membrane (Ceraver S.A.).

form a layer of regular thickness before the liquid was absorbed by the support. The organic binder plays a double role;[9] on the one hand it allows the adjustment of the sol viscosity (as a thickener) and on the other hand it protects the thin alumina layer from cracking during the sol–gel transition at the drying phase. The protection by the organic binder of the future ceramic layer should last until the first stage of the thermal treatment. Despite the fact that the organic binder should be soluble in the solvent used (i.e. dilute acid), it must also be stable to a relatively high temperature, and burn off gradually without leaving ash or tar. Rhodoviol 25/140 which is polyvinyl alcohol, fulfils these requirements. Simply concentrating the solution allows the adjustment of its viscosity; we have employed a 12 weight % solution.

A systematic study of the parameters, acid and organic binder quantity and concentration, boehmite powder quantity, order of introduction of the different components and stirring time, allowed us to determine the following definitive formula (in weight %): Pural SB 18%, water 34·5%, and 2 M nitric acid 1·5% (mixture A). This mixture was stirred vigorously for 6 h before the addition of mixture (B) (Rhodoviol (12%), 33·5%; 2 M nitric acid, 12·5%).

During stirring of mixture A in order to limit the suspension thickening due to the division of the alumina particles into even smaller particles, and to compensate for evaporation, 20% water was added before incorporating mixture B. After mixing together A and B solutions during 0·5 h, a homogeneous and translucent colloidal solution was obtained, which was passed through a 40 μm sieve. Its viscosity was 80 mPa s and increased regularly until gel formation about 12 h later.

2.4 Description of the porous support

The alumina support used in this study as a base of the thin layers was a microfiltration membrane (Ceraver S.A.[10]). This membrane was a cylindrical tube, internal diameter 15 mm and external diameter 19 mm, length 250 mm and 750 mm and the membrane structure was non-uniform (see Fig. 2). Table 1 summarises the characteristics of the two layers.

The permeation rate for water of this microfiltration membrane is $2{\cdot}5\ m^3\ h^{-1}$ under a bar pressure. The sol coating on the internal layer of the tube was obtained by filling the tube and emptying after 60 s in a vertical position.

2.5 Drying and thermal treatment

The sol so applied was dried at 4°C during 48 h. This treatment improved considerably the fineness and homogeneity of the layer. Thermogravimetric

TABLE 1
Characteristics of Microfiltration Support

	External layer	*Internal layer*
Thickness	2 mm	15 μm
Mean pore radius	5 μm	0·075 to 0·2 μm

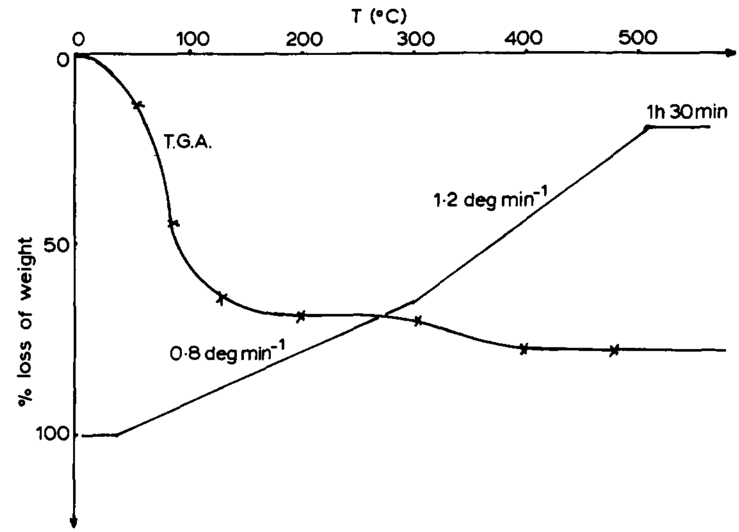


Fig. 3. Thermogravimetric analysis and program calcination of the alumina preparation (calcined at 500°C).

analysis of the gel allowed the determination of a calcination program, taking into account loss of water and organic products (Fig. 3).

3 RESULTS AND DISCUSSION

We have studied the influence of the final calcination temperature on the crystalline structure of the membrane and on the value of the mean pore radius. Table 2 summarises the results of the X-ray diffraction study on the gel kept 1 h at the final temperature.

TABLE 2
Phases Observed after Thermal Treatment

Temperature (°C)	*25*	...	*400*	*900*	*1 100*	*1 200*
Structure			γ-Al_2O_3	θ-Al_2O_3		α-Al_2O_3
State	boehmite gel	←		crystalline solid		

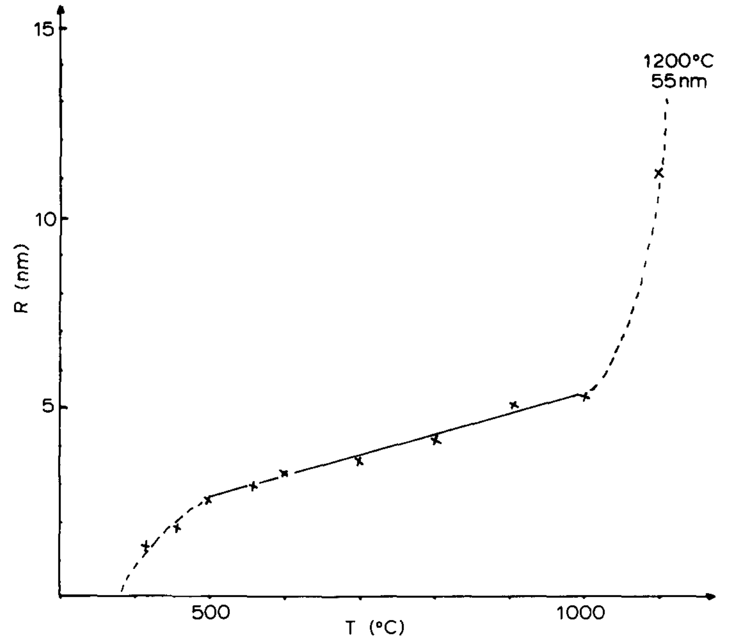


Fig. 4. Variation of pore radius as a function of sintering temperature.

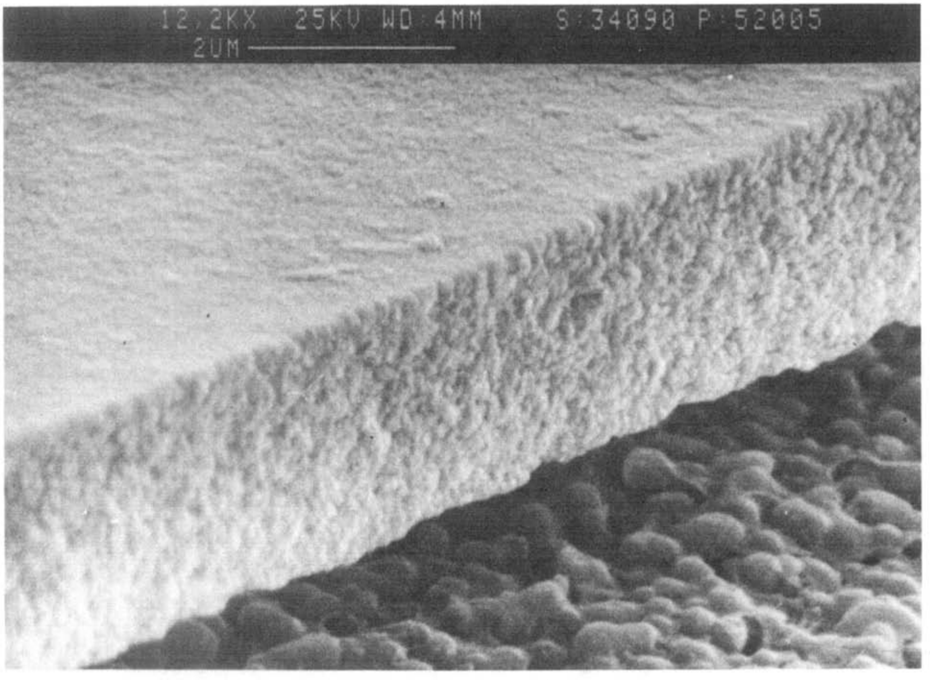


Fig. 5. Scanning electron micrograph of an ultrafiltration membrane (calcined at 540°C).

These transformations are in accordance with those reported in the literature.[11] Figure 4 shows the variations of the mean pore radius determined by mercury porosimetry, as a function of the sintering temperature. The pore radius increases linearly for temperatures between 500°C to 1000°C, which corresponds to the field of the γ phase. Between 400°C and 500°C, the X-ray diffraction diagrams show a badly crystallised structure. Above 1000°C, the appearance of θ- and α-alumina is associated with a more marked increase in pore radius. Adjusting the final calcination temperature allowed the production from the same sol of mineral membranes with pore radius from 2·5 nm to 55 nm. As an example, Fig. 5 shows the morphology of a membrane calcined at 540°C. The homogeneity and small grain size can be seen. Figure 6 shows the graph of the porous volume (Vp %) as a function of the pore radius as well as the distribution graph $(\Delta Vp)/\Delta R$. This last function shows that the pore size distribution is very narrow, which is desirable if good selective separation is to be obtained.

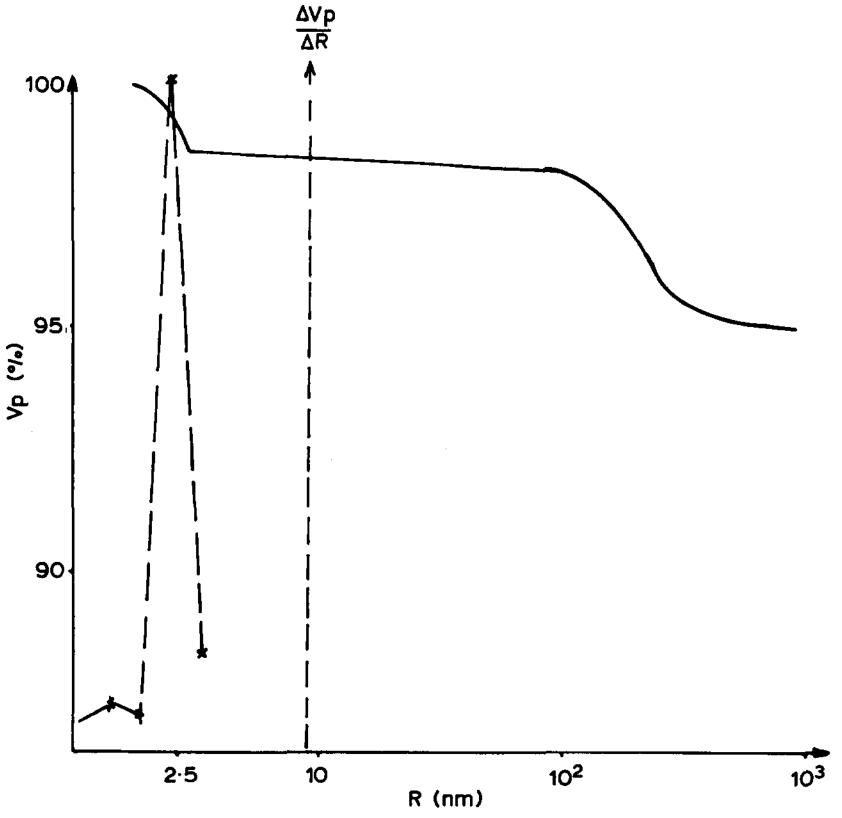


Fig. 6. $Vp\%$: Pore volume (full curve) and $(\Delta Vp)/\Delta R$: Pore distribution (dashed curve) as a function of pore radius for membrane calcined at 500°C.

4 CONCLUSIONS

This study has resulted in the preparation of an alumina mineral membrane using the sol–gel process. The experimental conditions for the preparation of the sol, and the production of the gel cast on a porous support are given. Variations in the thermal treatment have allowed variations in the pore radius from 2·5 nm to 55 nm to be obtained; with this technique a range of membranes can be obtained to cover the whole field of ultrafiltration.

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