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Silica porous membranes synthesis and characterization

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ABSTRACT

Membranes can be made by various methods and are generally classified as either organic or inorganic. In recent years there has been a growing interest in the use of inorganic membranes for several industrial and laboratory applications. This is because they offer many advantages over commercial organic membranes, the most important of which are: steam sterilizability, resistance to organic solvents, longer lifetime, with standing cleaning by bleaching, and oxidizing agents. For applications in ultrafiltration UF and reverse osmosis RO, the sol–gel process provides the technique for producing thin ceramic porous layers with controllable porosity on a wide range of chemically resistant macroporous substrates. In this work, we have used two sol–gel procedures for obtaining inorganic membranes: polymerization of molecular units (PMU) and destabilization of colloidal solutions (DSC). The first (PMU) concerns polymeric oxide gels made in our case from metal alkoxide $Si(OC_2H_5)_4$. Hydrolysis and polymerization reactions are very important for the properties of gel. The second process (DSC) is the destabilization of colloidal solution; we use peptization of hydrous metal oxide with an electrolyte. These colloidal solutions are then destabilized for instance by increasing the compounds concentration in the solution (by evaporation) thus gelation occurs. Thin membrane layer was deposited on a porous support. This is possible by infiltrating a low viscosity sol or by direct coating onto an ultrafiltration layer. Membranes produced using the two procedures were examined by X-ray diffraction, infrared spectroscopy, differential thermal analysis, nitrogen adsorption–desorption, and scanning electron spectroscopy. The control of sol–gel transition and thermal decomposition has allowed us the synthesis of silica membranes destined at separation, concentration, or purification of chemical species.

Keywords: Membrane; Inorganic; Porous; Sol–gel

1. Introduction

The development of porous ceramic thin layer is of prime interest for sensors or gas separation membranes working at high temperature [1–4]. Since the beginning

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of the 70s, the constraints imposed by the energy cost and raw materials have led to the optimization of the processing and recycling of industrial liquids and gas; as a result, there is a great demand in many fields for separation processes that are efficient and inexpensive [5–9], this is where filtration techniques find place. In the field of water and wastewater treatment, micro and ultrafiltration through an inorganic membrane are most promising technologies [1,10,11].

Ceramic membranes are emerging as an alternative to polymeric membranes for some applications due to their thermal, mechanical, and chemical characteristics [12–14]. Crossflow microfiltration and ultrafiltration are becoming of increasing interest to produce drinking water.

They can remove bacteria and clarify the water in a single step, so they can reduce appreciably the classic sequences of treatment processes.

There are currently several methods employed to fabricate inorganic membranes. Sol–gel process is especially appropriate to elaborate thin and porous layers, and a very useful way to produce ultrafiltration ceramic membranes [15–19]. In this study, the goal of our research is the use of sol–gel process to contribute to the synthesis of silica membranes.

2. Experimental

2.1. Synthesis

Silicate gels are synthesized by hydrolyzing tetraethoxysilane (TEOS) [$SiO(C_2H_5)_4$] used as precursor, chlorydric acid was employed as a catalyst, and ethanol as solvent. We have chosen the sol–gel process to obtain a gel and privileging at maximum of connection formation Si–O–Si.

The synthesis difficulty is to avoid precipitation; the idea is to use hydrolysis reaction in two steps. The scheme of preparation is illustrated in (Fig. 1).

At the functional group level, three reactions are used to describe the sol–gel process.

Hydrolysis

$$\text{Si–OR} + H_2O \leftrightarrows \text{Si–OH} + \text{R–OH}$$

Condensation

$$\text{Si–OR} + \text{HO–Si} \leftrightarrows \text{Si–O–Si} + \text{R–OH}$$

Alcoholysis: water condensation

$$\text{Si–OH} + \text{HO–Si} \leftrightarrows \text{Si–O–Si} + H_2O$$

The second method of preparation uses cecassol as a precursor and nitric acid as a catalyst.

The colloidal silica sol used is a commercial product cecassol containing 30% SiO_2 in aqueous solution, stabilized at pH 8. The effect of pH on the gel permits the establishment of the optimal working conditions for obtaining homogeneous sols with rapid gelation of the deposited films. The cecassol solution is dried at 80°C.

Our first concern is to pass from the powder suspension to colloidal solution; for that, we have used destabilization of colloidal solutions (DSC) procedure.

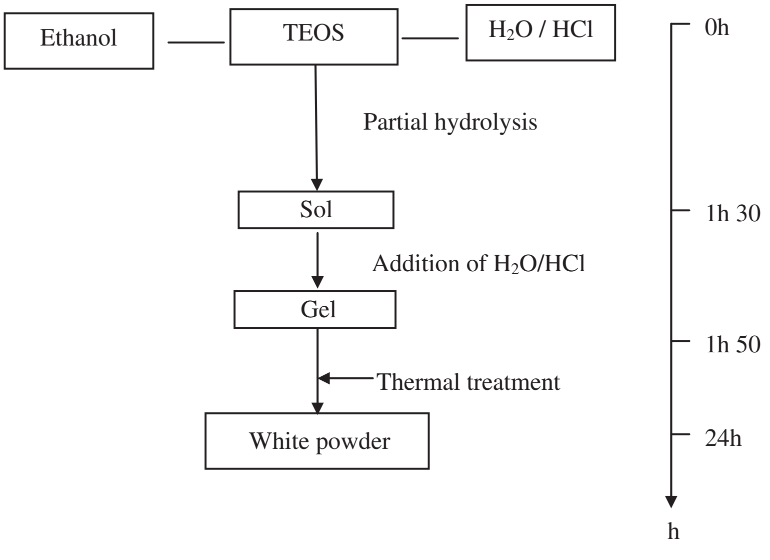


Fig. 1. Preparation of SiO_2 powder by PMU procedure.

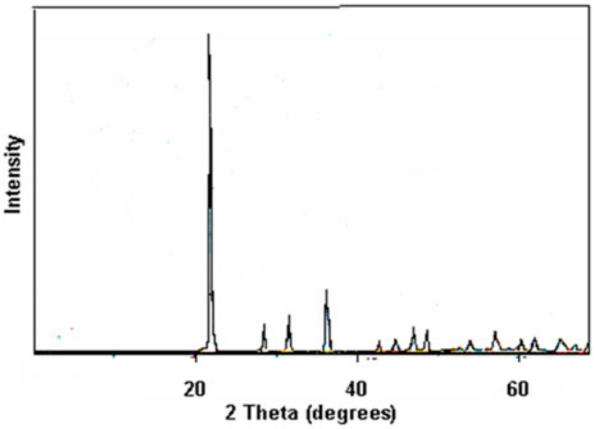
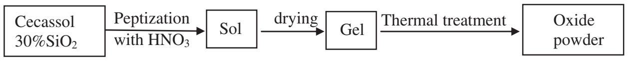


Fig. 2. XRD spectra of SiO_2 powder obtained with PMU and treated at 1,300˚C.



Preparation schemes of SiO_2 by DSC procedure.

2.2. Instrumentation

X-ray powder diffraction data were obtained using Philips Pw 1830 diffractometer with Cu Kα radiation (λ = 1.54 A°).

The FTIR spectra of samples were obtained using the KBr wafer technique. N_2 adsorption isotherms were recorded on a Micromeritics ASAP 2010 automated sorption analyzer. The samples were outgassed at 150˚C before the analysis. The Barret–Joyner–Halende (BJH) method was used to determine pore size.

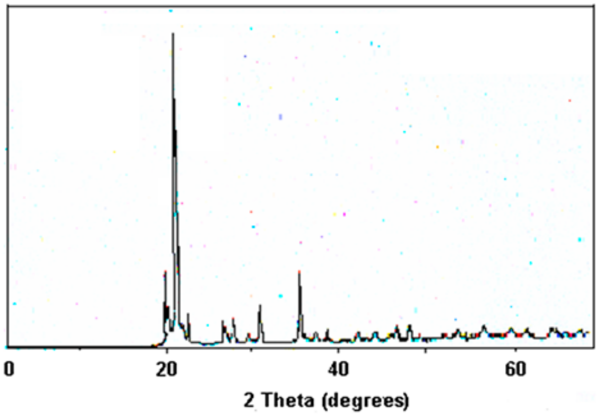


Fig. 3. XRD spectra of SiO_2 powder obtained with DSC and treated at 900˚C.

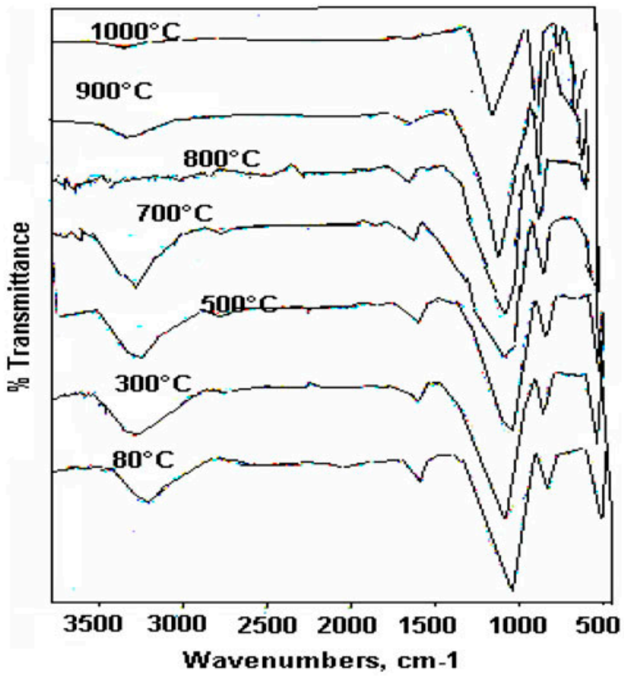


Fig. 4. Infra-red spectra of SiO_2 powders obtained with DSC and treated at different temperatures.

Scanning electron microscopy was used to characterize membrane morphology, that is, the thickness and homogeneity along the support.

3. Results

3.1. X-ray diffraction

The X-ray diffraction results in powders stem from the two sol–gel procedures (polymerization of molecular units, PMU and DSC) treated at different temperature are shown in figures (Figs. 2 and 3). In the case of DSC, we observe at temperature 900˚C a crystallization of cristobalite phase, while at temperature 1,300˚C a phase transformation into the crystalline cristobalite occurred in the case of PMU.

3.2. Spectroscopy absorption infra-red

Infra-red spectra were recorded for every powder obtained by the two sol–gel procedures (PMU and DSC) and treated at different temperatures (Figs. 4 and 5).

We notice in the two cases:

(a) Presence of bands at 470–800 cm^{-1} and 1,090 cm^{-1} characteristics of the connection vibrations Si–O–Si (ref).

(b) We observe that connection Si–O–Si is initially in the gel.

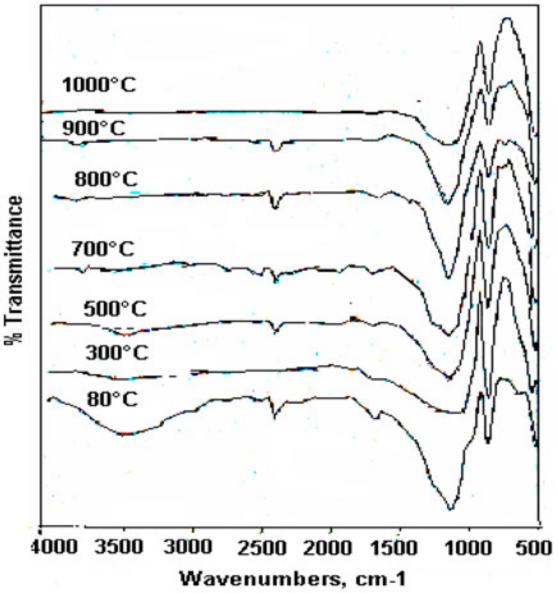


Fig. 5. Infra-red spectra of SiO_2 powders obtained with PMU and treated at different temperatures.

(c) Apparition of band at 630 cm^{-1} characteristic of cristobalite phase at temperature 900˚C for DSC procedure and above 1,200˚C for PMU procedure. These results confirm X-ray diffraction analysis.

Infra-red studies show that some OH groups remain in the membrane. The Si–OH groups may be characterized by an absorption band situated at 960 cm^{-1}. Dehydroxylation starts in the early stages of the thermal treatment and continues up to 700˚C. These OH groups are responsible for the membrane reactivity.

4. Textural characterization by nitrogen adsorption–desorption

4.1. Silica powder obtained with DSC procedure

N_2-sorption isotherms were recorded for 500, 600, 700, and 900˚C calcined samples which are shown in (Fig. 6).

The isotherms of adsorption plotted for four samples show that the isotherms of desorption do not coincide with those of adsorption for all the temperatures. They are of type IV in the BET classification (Fig. 6). This can be explained by a capillary condensation characterized by the appearance of the phenomenon of hysteresis.

This textural study has permitted us the observations of surface area, porous volume and pore diameters according to the temperature.

In the domain of temperature 500–700˚C, applying BJH method to the branch of isotherm desorption shows an augmentation of pore diameters (Fig. 7). This can be explained by the removal of residual

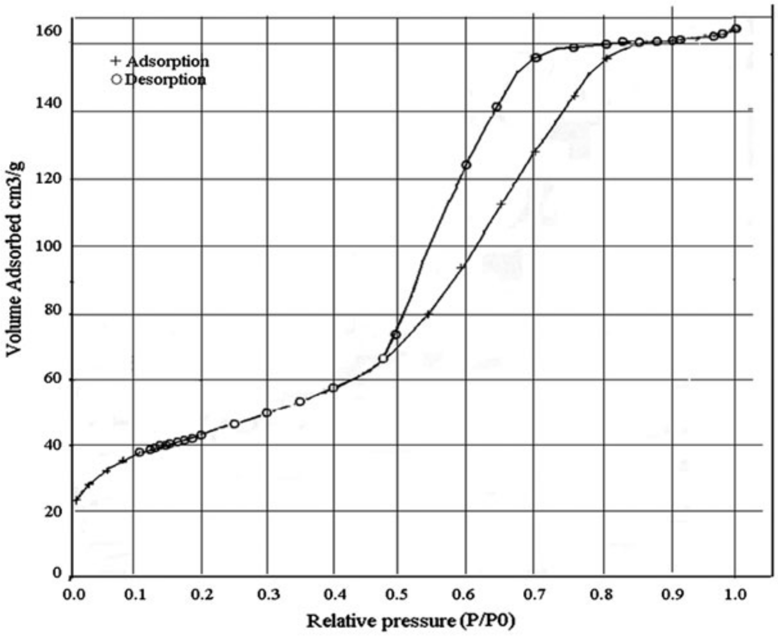


Fig. 6. Isotherm of adsorption plot of SiO_2 powder obtained from cecasol.

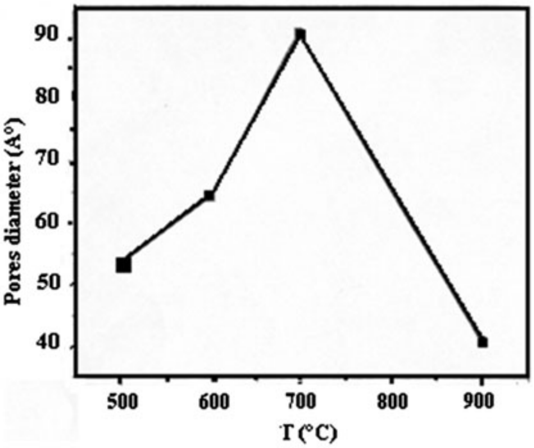


Fig. 7. Effect of temperature on pore area of SiO_2 diameters obtained with DSC.

water because the internal groups OH in the SiO_2 matrix migrate towards the surface under effects of temperature. Their elimination induces a widening of the pores.

In this interval of temperature, we observe a decrease of the surface area and porous volume (Fig. 8). We can explain these variations by widening of pores under temperature effect.

Over 700˚C, the diminution of surface area, porous volume, and diameter pores can be explained by the beginning of SiO_2 powder crystallization.

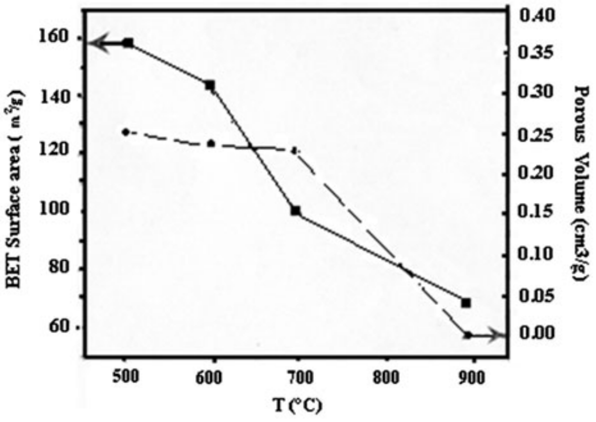


Fig. 8. Effect of temperature on surface and porous volume of SiO_2 obtained with DSC.

4.2. Silica powder obtained with PMU procedure

We have plotted the isotherm adsorption for four samples obtained with PMU procedure at temperatures: 500, 600, 700, and 900˚C.

We notice the absence of capillary condensation (Fig. 9). The absence of hysteresis in these isotherms indicates either that the solid contains only micropores, or that the pores are tubular of constant section and closed at one extremity.

At temperature 600˚C, the isotherm is type III (Fig. 10). The appearance of hysteresis phenomenon in this case is probably due to the pore widening after the decomposition of organic products.

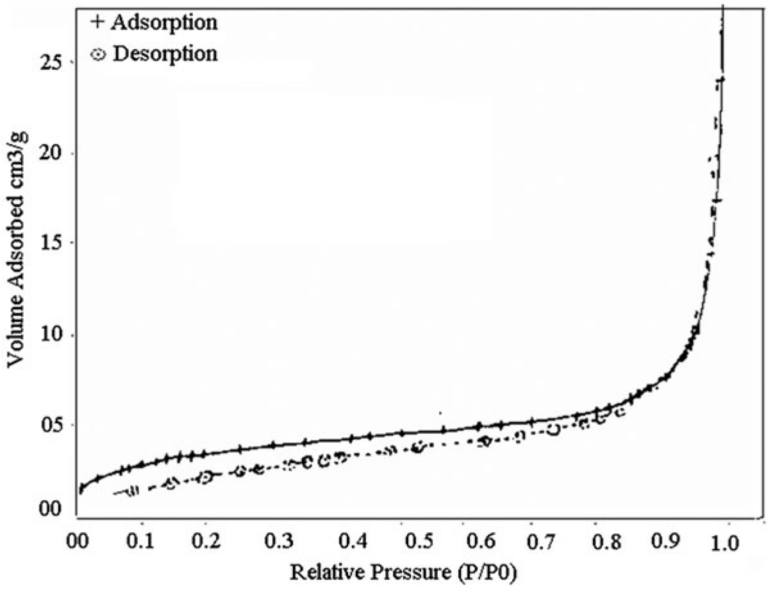


Fig. 9. Isotherm of adsorption plot of SiO_2 obtained from TEOS treated at 500˚C.

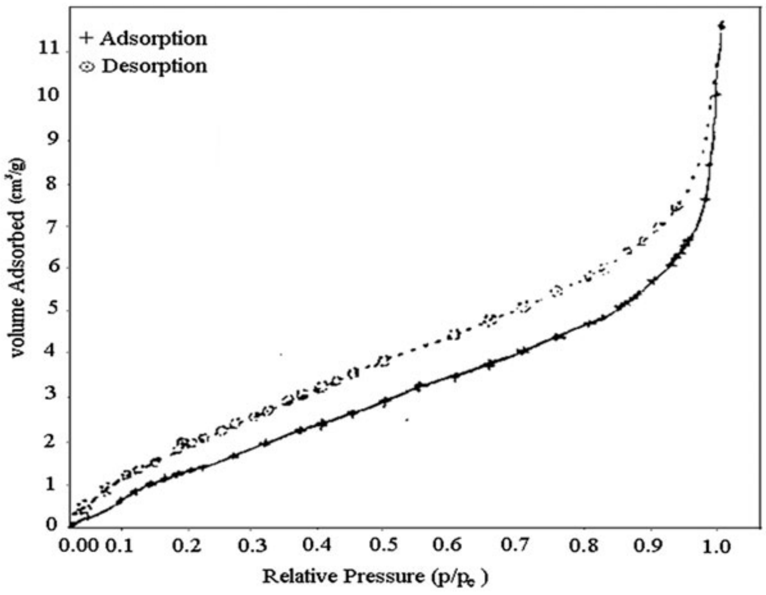


Fig. 10. Isotherm of adsorption plot of SiO_2 obtained from TEOS treated at 600˚C.

We notice an augmentation of surface area and porous volume with a temperature of 500 at 600˚C. This augmentation results probably from the progressive creation of small diameter in the SiO_2 matrix (Figs. 11 and 12).

Over 600˚C, the variation of specific surface, porous volume, and pore diameter are probably due to widening of pores after decomposition of organic ligands.

5. Deposits of thin porous layers

Porous tubular supports are very convenient for tangential filtration. The sol coating on the inner part of the tube is obtained by filling it, and then emptying it after standing in a vertical position. The water of the sol is absorbed by the porous structure of the support, and capillary action of the support takes place. The rate of water absorption is a function of sol viscosity.

The gel layer is obtained because the sol concentration action increases by absorption of water. Temperature considerably improves the fineness and homogeneity of the layer.

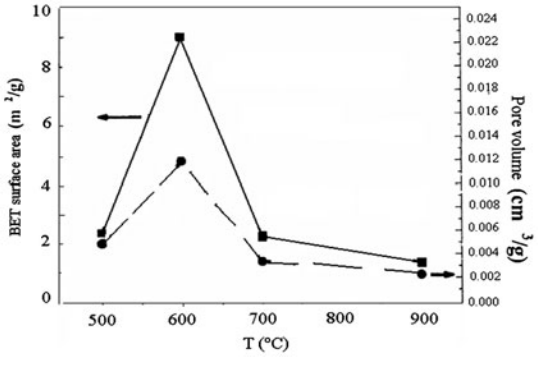


Fig. 11. Effect of temperature surface area and porous volume SiO_2 powder obtained from TEOS.

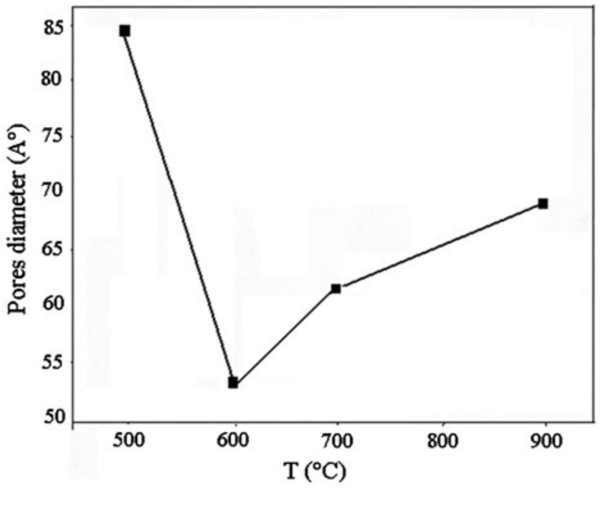


Fig. 12. Effect of temperature on average pore diameters of SiO_2 powder obtained from TEOS.

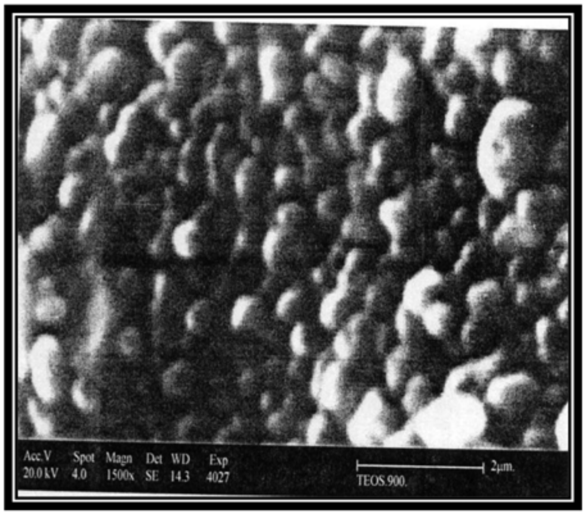


Fig. 13. Micrograph of the layer obtained with PMU treated at 900°C.

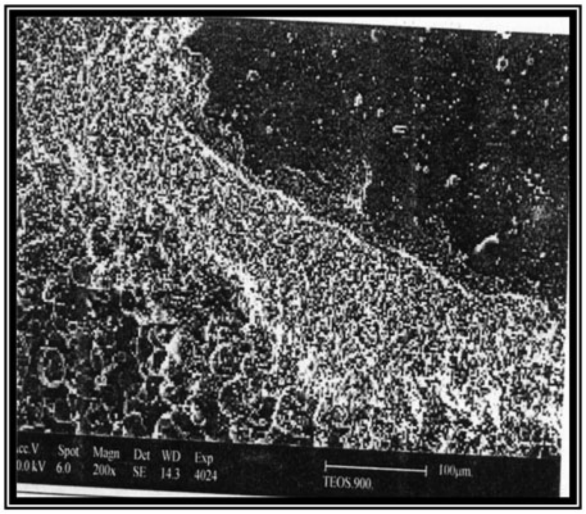


Fig. 14. Cross section of the layer obtained with PMU treated at 900°C.

The membrane deposit has been realized with a sol prepared with the two sol–gel procedures (PMU and DSC). The dried membranes were calcined.

Scanning electron microscopy observation showed homogeneous layers without cracking (Figs. 13–16).

It was found that the layer thickness could be varied at 900°C in the range 2–3 nm, respectively, for procedures PMU and DSC.

We obtain at temperature 900°C the pore diameter less than 50 nm for PMU and less than 90 nm for DSC procedures.

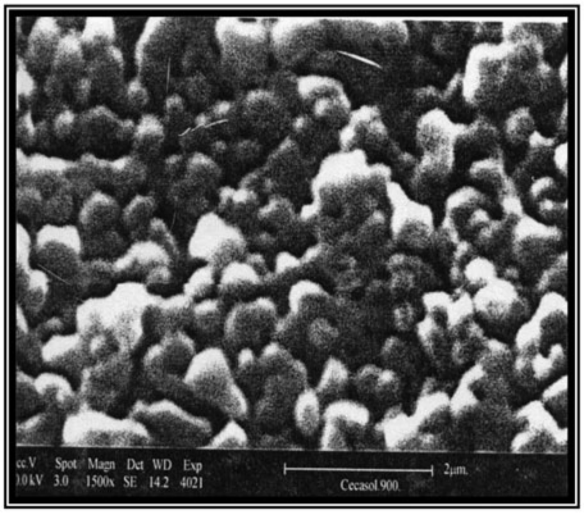


Fig. 15. Micrograph of the layer obtained with DSC treated at 900°C.

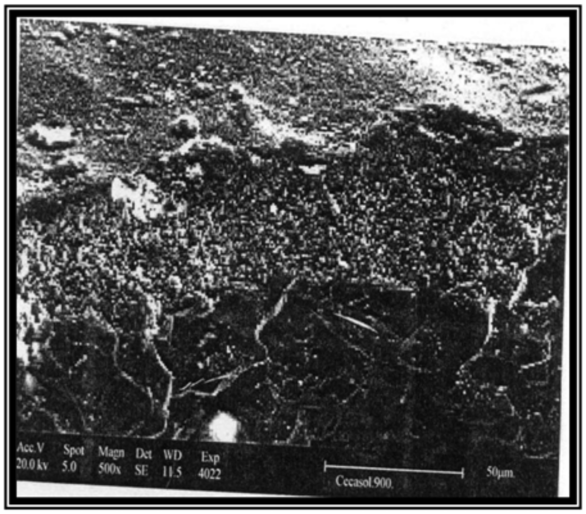


Fig. 16. Cross section of the layer obtained with DSC treated at 900°C.

6. Conclusion

We have chosen to study SiO_2 oxide for their interesting properties and the interest which may bring in the domain of inorganic membranes chemical and mechanical high resistance.

The synthesis of silica membranes using the two sol–gel procedures was investigated.

It was found that in the PMU process, a crystallization of cristobalite phase is at temperature 1,300°C, while in the DSC process the cristobalite is crystallized at 900°C.

In order to compare the results in both cases PMU and DSC and take into account the constraints imposed by the energy cost, the following experiments are below temperature 1,000°C.

The most important characteristics (pore diameter and porous volume) are determined using nitrogen adsorption–desorption. With the PMU process, we obtain a microporous silica membrane and with process DSC, we obtain mesoporous silica membrane. We notice that surface area, porous volume, and pore diameters according to temperature are related to structural changes in the two type of silica.

Scanning electron microscopy is used to characterize membrane morphology, that is, the thickness and its homogeneity along the support.

The use of these techniques has permitted us to obtain silica membranes which can be used in Ultrafiltration.

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