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Elaboration and Properties of Zirconia Microfiltration Membranes

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Abstract

The main objective of this work is the preparation of ceramic supports and membranes for microfiltration application. The supports were prepared by using clay and calcium carbonate mixtures as starting materials. The choice of these raw materials is based on their natural abundance. These powders were mixed with certain organic additives to obtain a conveyable paste ready for extrusion in order to fabricate a porous tubular configuration with highly uniform porous structure. Microfiltration zirconia membranes were deposited on the tubular supports, using slip-casting process. It was found that the average pore size of the membrane and its thickness were about 0.16 µm and 25 µm, respectively. Moreover, the fabricated membrane was tested with distilled water with cross-flow microfiltration process. Results showed a good retention of turbidity, conductivity and Total Dissolved Solids (TDS) in permeate.

Keywords: Supports; Membranes; Porosity; Ceramic

1. Introduction

The specific properties of ceramic membranes which have attracted the attention of academic and industrial scientists are: long-term stability at high temperatures [1-3], resistance to severe environments, resistance of high pressure drops, inertness to microbiological degradations, and easy cleaning and catalytic activation.

Asymmetric membranes usually consist of a thin top-layer responsible for separating, and a porous ceramic support with single or multiple intermediate layers imparting the required mechanical strength to the composite membrane [4]. However, a membrane support provides mechanical strength to a membrane top-layer to withstand the stress induced by the pressure difference applied over the entire membrane and must simultaneously have a low resistance to the filtrate flow [1,5]. A significant effort was then provided these last years in membrane technology field in order to find out new porous ceramics materials at low price [6]. This study is related to the development of ceramic supports using Algerian natural materials, whereas the top layer was made from zirconia (ZrO_2). This is because of their attractive properties such as its excellent chemical resistance, refractory character, oxygen ionic conductivity and polymorphous nature [7]. It has been widely used for several practical applications.

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2. Experimental procedures

2.1. Analysis of the raw materials

In this study, the supports were prepared using clay and calcium carbonates. The chemical composition of clay given in weight percentages (wt%) of oxides is given in Table 1. The quantitative analysis of these calcium carbonates showed that the purity of this raw material is about 99.6%.

Table 1. Chemical composition of clay using fluorescence XRD analysis.

Oxides	Al_2O_3	SiO_2	MnO	MgO	CaO	F_2O_3	TiO_2	I.L
wt. %	37.27	43.69	0.41	0.06	0.38	0.64	0.09	17.46

2.2. Preparation of support materials and membranes

The prepared plastic paste is based on a mixture of clay (74 wt%), calcium carbonate (21wt%) and organic additives (2.5 wt% of Amijel derived from methylcellulose (Dow Chemical Company), (2.5wt%) of methocel derived from starch (Cplus 12072, Cerestar)) with a progressive addition of water. The tubular support is then obtained by extrusion of the prepared ceramic paste. After extrusion, the wet support is set on rollers to obtain a homogenous drying at room temperature. Finally, a thermal treatment was carried out in a programmable oven at different final temperatures.

For preparing a microfiltration layer with zirconia powder, a deflocculated slip was obtained by mixing 10 wt% of ZrO_2, 30 wt% of PVA (12 wt% aqueous solution) and water (60 wt%). The deposition of the slip on the support was performed by the slip casting method [6]. The deposition time was between 2 and 5 minutes. After drying at room temperature for 24 h, the microfiltration layer was sintered at 1050°C for 1 h.

3. Results and discussion

3.1. Phase identification

X-ray diffraction was used to identify the formed phases. In clay plus calcium carbonate, heated at different temperatures, the main observed phases were: mullite ($3Al_2O_3.2SiO_2$), anorthite ($CaO.Al_2O_3.2SiO_2$) and gehlenite ($2CaO.Al_2O_3.SiO_2$) as shown in Fig. 1. For samples sintered at 1150°C. The main dominant phase appearing at this temperature is gehlenite while at 1250°C the main dominant phase is anorthite; its content increased with increasing temperature.

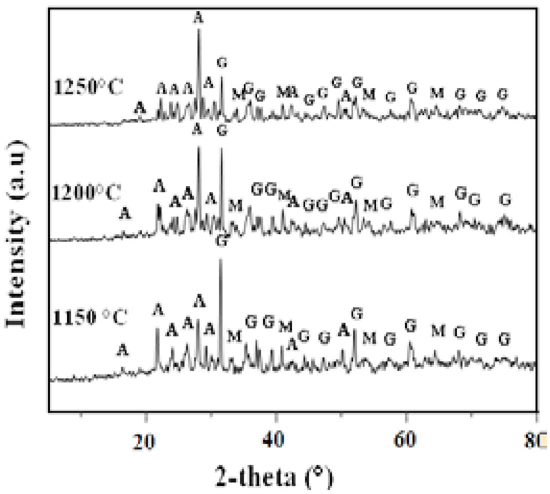

Fig. 1. XRD spectra of samples sintered at different temperatures for 1 h. A: Anorthite; G: Gehlinite; M: Mullite

3.2. Supports characterization

The sintering temperature is an important parameter which controls the pore diameter of the support but also its mechanical resistance [8]. The thermal expansion depends also on the heating treatment. Therefore, the best properties of the final support are achieved by adjusting the sintering conditions.

The porosity measurement and the average pore size have been carried out for supports sintered at different temperatures for 60 minutes. The obtained results are illustrated in figure 2. As expected, this figure shows, generally, that there is an increase in average pore size when the sintering temperature is increased. For example, supports sintered at 1150°C had an average pore size of around 1.39 µm, whereas it was 4.89 µm for supports sintered at 1300°C.

A typical curve of the porosity measurement of samples shows that there are three different stages (Fig.2). Following initial decreased sharply of the porosity, a state of constant porosity is reached for samples sintered at temperatures ranging between 1200° and 1250°C. Afterwards, the porosity increased sharply for samples sintered at 1300°C. This behavior is due to the decomposition of gehlenite, which leads to the formation of crystalline phases such as anorthite.

In the range of sintering temperature (1150-1250°C), the pore size and the porosity were acceptable. For example, the supports which were sintered at 1150°C had a porosity ratio of ≈ 54% and an average pore size of about 1.4 µm. On the other hand the supports which were sintered at 1250°C had a porosity ratio of about 52% and an average pore size of about 3.4 µm.

Fig. 3 shows the scanning electron microscope images of the cross section of the ceramic membrane tube. The morphology of the section suggests that the absence of macro defects and a good pore size distribution are a key condition leading to a good quality supports.

Considering Fig. 4 which presents a modal of pore size distribution for samples sintered at different temperatures for 1 h, it is almost single (mono) modal of pore size distribution or homogenous pore size distribution.

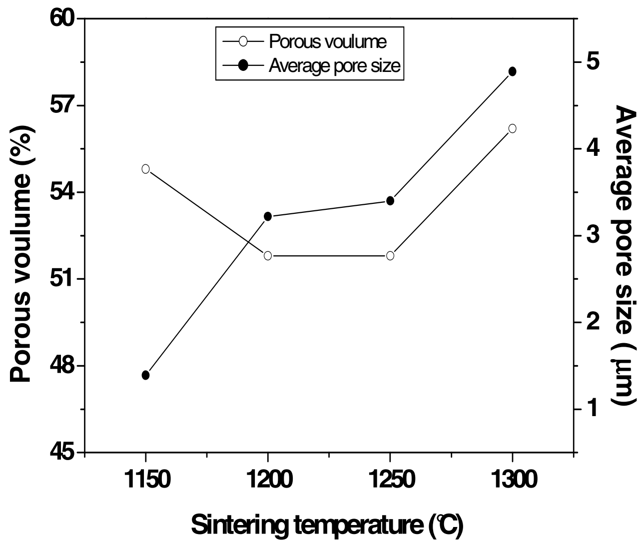

Fig. 2. Porous volume (%) and average pore size vs. sintering temperature.

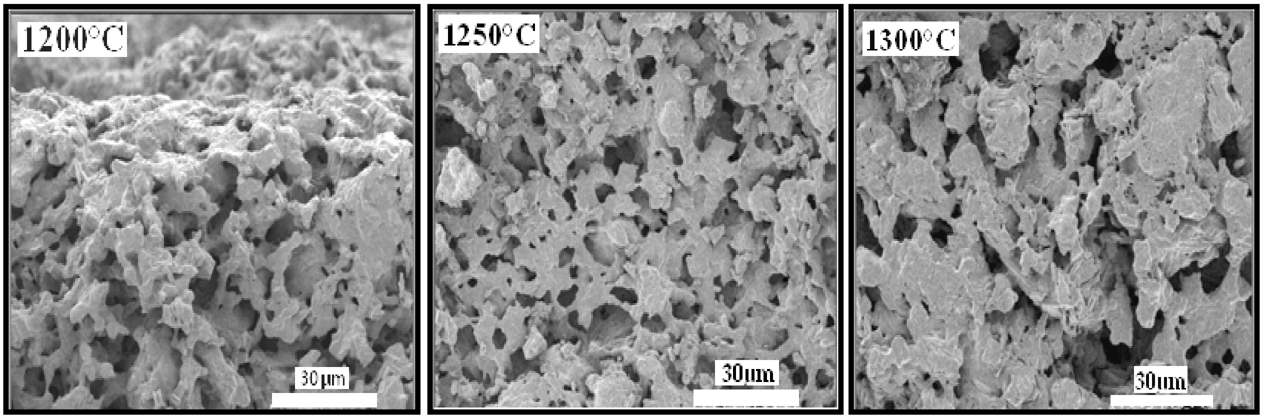

Fig. 3. SEM micrograph of the cross-section of supports in samples sintered at 1200°C, 1250°C and 1300°C for 1h.

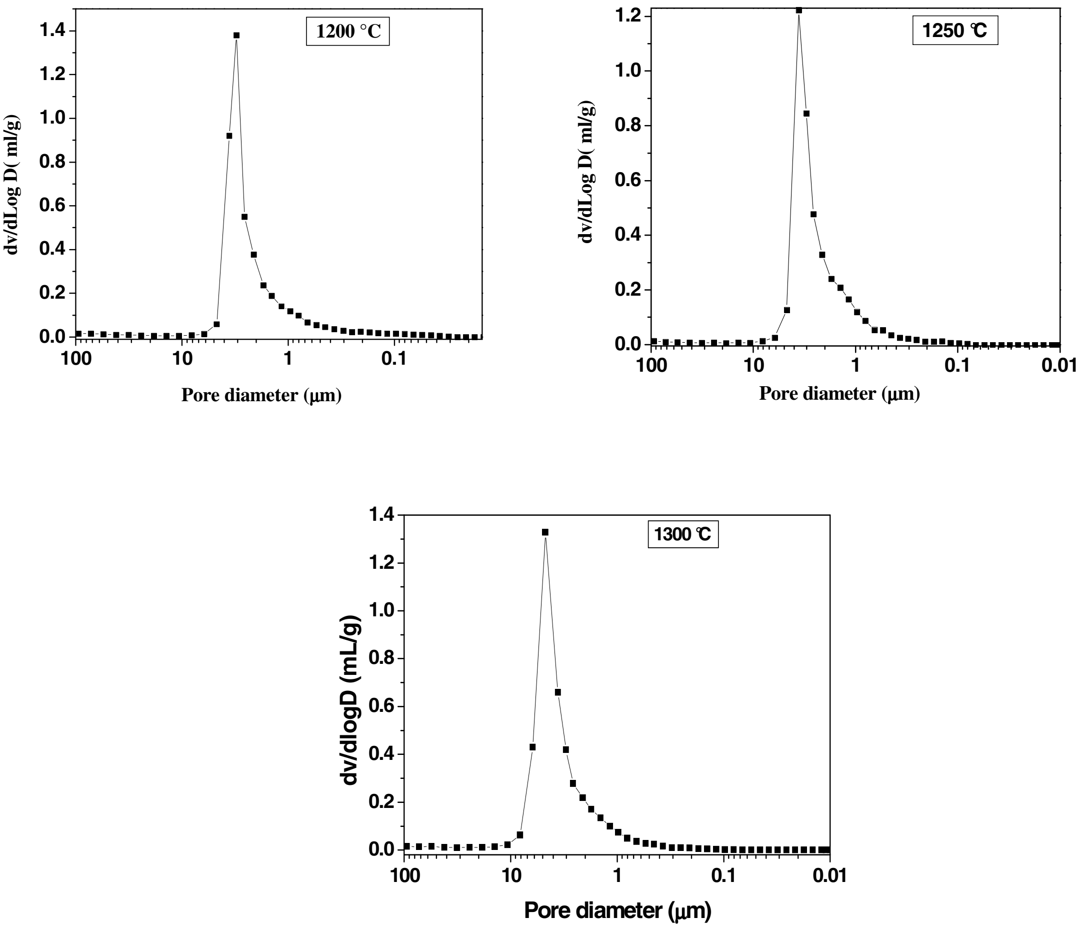

Fig. 4. Pore size distribution of samples sintered at 1200°C, 1250°C and 1300°C for 1h.

3.3. Membrane characterization

The layer made of zirconia was coated by slip casting on the prepared support (at 1250°C) using the suspended powder technique. After heating at a temperature of 1050°C for 1h, the ZrO_2 microfiltration membrane with mean pore diameter of 0.16 µm was obtained (Fig.5).

Fig. 6 shows a typical cross-section of a membrane consisting of a microfiltration layer coated on macroporous support. The membrane structure shows a good homogeneity, which is an important property for potential MF applications. The thickness of the microfiltration layer may be controlled by the percentage of the mineral powder added into the suspension and the coating time.

The MF membrane was first characterized by its water permeability. Fig. 7 shows that the water flux through the membrane measured as a function of time depends on the applied pressure. The average permeability is about 1000 $l/h.m^2.bar$. The characteristics of the effluent before and after filtration are presented in Table 2. The obtained results are very interesting; in fact a very important decrease of turbidity (about 100%) can be observed. The conductivity and TDS were reduced.

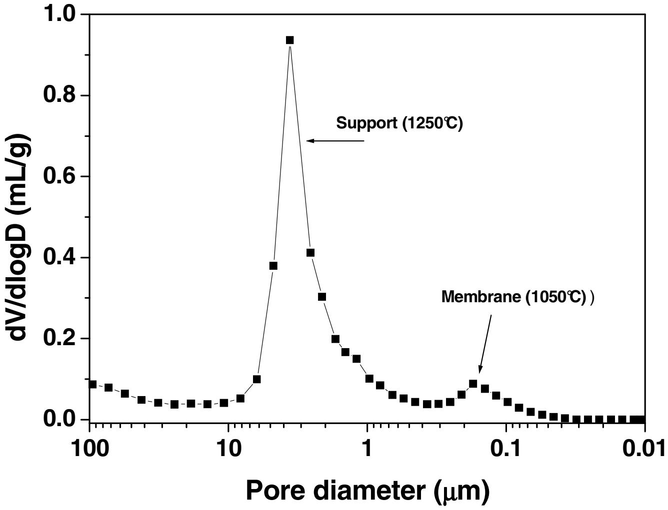

Fig. 5. Pore size distribution of support + membrane.

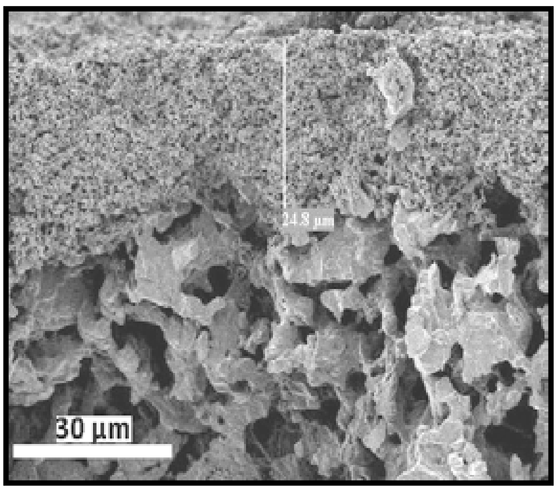

Fig. 6. SEM micrograph of the cross-section of both membrane and support

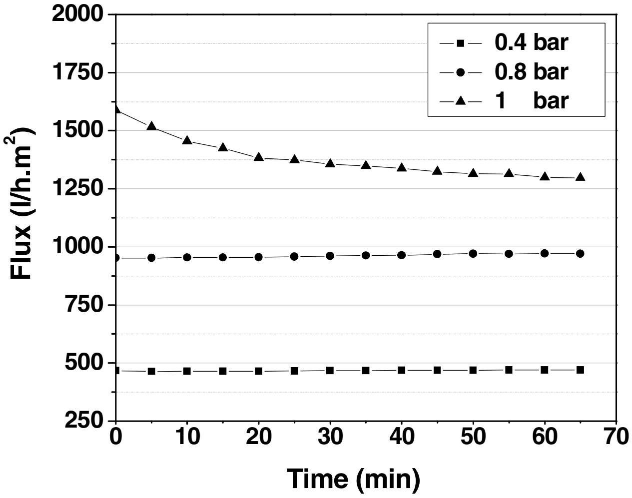

Fig. 7. Water flux as a function of time for 3 working pressure values.

Table 2. Effluent characteristics before and after filtration

Sample	Raw effluent	Permeate
pH	6.94	7.56
Turbidity (NTU)	161	1
TDS (mg/l)	196.3	181.4
Conductivity (µs/ cm)	383	353

4. Conclusions

The support for the coating membrane layer was fabricated by extrusion method. Microfiltration ceramic membrane was prepared by coating the ZrO_2 slurry on the inter support by slip casting method. The pore size of the MF membrane was 0.16 µm, and its thickness was about 25 µm. The results obtained enable to conclude that the fabricated membranes could be used for cross-flow microfiltration of different application as a stable high flux with good quality was obtained using these membranes.

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