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Elaboration and characterization of tubular supports for membranes filtration

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ABSTRACT

The use of ceramic membranes has many advantages, such as high thermal and chemical stability, pressure resistance, long lifetime, good resistance to fouling, and the ease of cleaning. Up to now, the production of industrial membrane supports uses a limited choice of materials. As a consequence, the price of ceramic membranes is high and a significant effort was provided in this last years in the membrane technology field in order to find new porous ceramic materials with clays and kaolins. These materials are in abundance and need lower sintering temperatures than metal oxide materials. In this work, the tubular supports for membranes filtration was manufactured from kaolin and lime extracted from limestone. The influence of the relative low sintering temperature ranging from 800 to 1,100˚C on the porosity, the average pore size (APS), a pore size distribution, and a strength of supports have been investigated. Additionally, the APS and the porosity values were about 8 μm and 47% for supports sintered at 1,000˚C. Besides this, three-point flexural strength values were ranged from 30 to 53 MPa for samples sintered at sintering temperatures situated between 1,000 and 1,100˚C, respectively.

Keywords: Anorthite; Membrane; Support

1. Introduction

Anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) is an important technical ceramic material that has good physical properties, such as a very low thermal expansion coefficient, low dielectric constant and loss, good thermal shock resistance, and high creep resistance at high temperatures. For these reasons, several studies were carried out to improve these properties in the past few years [1–4].

There is much current interest in the application of membranes in separation procedures because of their potential for the treatment of large quantities of wastewater [5]. The use of ceramic membranes has

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many advantages, such as high thermal and chemical stability, pressure resistance, long lifetime, good resistance to fouling, and the ease of cleaning [6,7]. Ultrafiltration (UF) and microfiltration (MF) operations are often used to remove particles, micro-organisms, and colloidal materials from suspensions [8].

Asymmetric membranes usually consist of a thin top-layer responsible for separating components, and a porous ceramic support with a single or multiple intermediate layers imparting the required mechanical strength to the composite membrane [6].

At present, the production of industrial membranes provides a limited choice of materials. As a consequence, the price of ceramic membranes is high, and a significant effort has been expended in recent years in the membrane technology field in order to develop new porous ceramic materials using inexpensive clays and kaolin. These materials are in abundance and may require sintering temperature lower than those for metal oxide materials [9,10].

In order to decrease the membrane cost and evaluate our natural resources, many works have been carried out using interesting Algerian raw materials [11–25]. Additionally, it should also be mentioned here that using ceramics (oxides) in this work and others [26] instead of metallic products [27,28] is well justified, particularly for used water filtration or purification.

Indeed, supports of membranes were manufactured from local raw materials, kaolin (Al_2O_3·2-SiO_2·4H_2O) and lime extracted from limestone ($CaCO_3$). Moreover, these raw materials have been selected on the basis of their natural abundance (low price), in one hand. On the other hand, the single anorthite phase presence is also another interesting factor. In fact, this phase is well recognized by the good physical and chemical properties of sintered products [1,29–31].

This paper describes the results of these efforts. More recently, a flexural strength of 87 ± 2 MPa was obtained for 100 wt.% Al_2O_3 samples sintered at 1,620˚C for 2 h [32], while nearly the same flexural strength value (87 ± 6 MPa) was also measured for compacts sintered only at 1,250˚C for 1 h, using the proposed process [33].

2. Experimental procedures

2.1. Characterization techniques

The total porosity and pore size distribution were measured by mercury porosimetry (Micromeritics, Model Autopore 9500). This technique is based on the penetration of mercury into a membrane's pore under pressure. The intrusion volume is recorded as a function of the applied pressure and then the pore size is determined.

The mechanical strength of sintered specimens was measured by the three-point bending method (universal LLOYD Instruments, LRX apparatus) using a span of 30 mm and a cross-head speed of 10 mm min^{-1}. All experiments were carried out on a series of at least 5 bar to report an average strength for each series, following the International Standard specifications.

Phase compositions of prepared samples were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) (Karlsruhe, Germany) with a CuKα radiation (λ = 0.154 nm) and an Ni filter, working voltage 40 kV, and working current 30 mA.

The microstructure of sample surfaces was observed using a SEM (HITACHI, JSM-6301 F) (Tokyo, Japan) working at 7 kV as an accelerating voltage. Before SEM observation, all samples were gold coated.

2.2. Analysis of the raw materials

In this study, the supports were prepared from domestic kaolin (DD3) and calcium oxide extracted from calcium carbonates obtained, respectively, from Guelma and Constantine regions in Algeria. The chemical composition of kaolin is given in Table 1. The majority of the used powder (81 wt.%) consists of SiO_2 and Al_2O_3, where the main impurities are CaO, MnO, and Fe_2O_3. The chemical composition of $CaCO_3$ given in wt.% of oxides is shown in Table 2. The majority of the used (99.7 wt.%) consists of CaO. The particle size distributions of the used raw materials were illustrated in Fig.1. The kaolin powder, obtained by a calcination of the finely ground mineral coal at 520˚C, shows particle size distribution less than 20 μm (Fig.1(b)). The particle size distribution of the calcite powder is also less than 20 μm (Fig. 1(a)).

Table 1
Chemical composition of kaolin (DD3) (wt.%), using fluorescence XR analysis

Oxides	(wt.%)
Al_2O_3	37.27
SiO_2	43.69
I.L	17.46
CaO	0.38
MgO	0.06
MnO	0.41
Fe_2O_3	0.64
TiO_2	0.09

Table 2
Chemical composition of calcium carbonates $CaCO_3$ (wt.%), using fluorescence XR analysis

Oxides	wt.%
P_2O_5	0.003
Al_2O_3	0.088
SiO_2	0.145
CaO	99.692
K_2O	0.007
SrO	0.013
Cl	0.037
SO_3	0.011

2.3. Supports elaboration

For preparation of anorthite supports, the kaolin (DD3) is properly crushed, then calcined at 520˚C for 1 h to be later sieved at 200 μm. After that, an amount of about 20 wt.% of calcium oxide powder is added. In order to improve the properties that facilitate the synthesis, some organic materials have been added, such as 4 wt.% methocel as a plasticizer and 4 wt.% amijel as a binder. This mixture must be continuously mixed with water so as to obtain a plastic paste. For good dispersion of water in the paste, this mixture should be covered in a plastic case for at least 12 h. After that, an extrusion technique is used to form some tubular samples. For good drying of these tubular samples, they are placed at room temperature on rotating aluminum rolls. In these studies the dried tubular samples were sintered at various temperatures ranging between 800 and 1,100˚C following this program:

$$25^{\circ}C \xrightarrow{2^{\circ}\,C/min} 250^{\circ}C\ (2\ h) \xrightarrow{5^{\circ}\,C/min} 800-1,100^{\circ}C\ (3\ h)$$

In order to eliminate the added organic materials and to avoid formation of microcracks during the sintering of the samples, the initial rate of heating was chosen to be 2˚C/min.

The main steps of the processing route for anorthite tubular supports preparation used in this work are shown in the following diagram (Fig. 2).

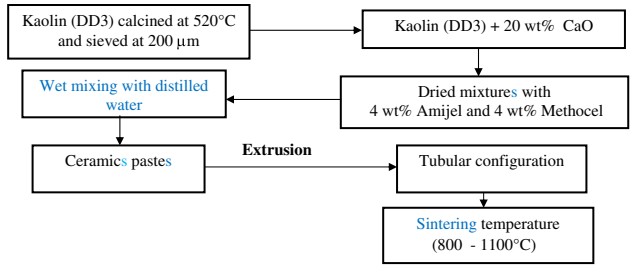

Fig. 2. The main steps of the processing route for tubular supports preparation.

3. Results and discussion

3.1. Phase identification

Phase identification is of great importance before any support and membranes fabrication, because the

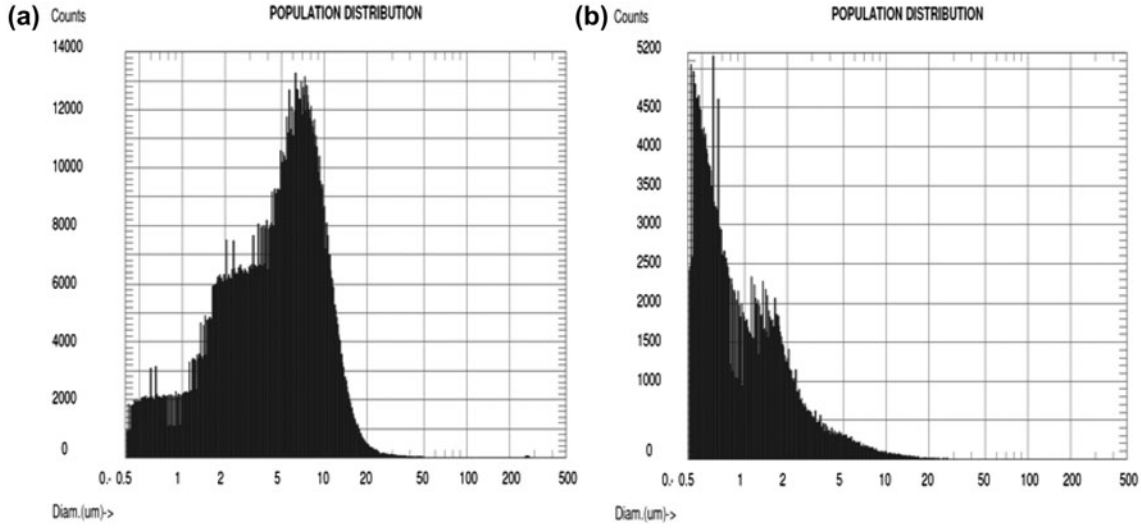

Fig. 1. Particle size distribution of powders used in this work. (a) calcite powder and (b) kaolin powder (DD3).

presence of certain phases may limit their application for water filtration only, rather than acid filtrations or gas separations. The formed phases mentioned below are chemically stable in acids. The objective of this section is to prepare porous anorthite phase supports, but a relatively well sintered (strong necks or bridges formation).

The XRD spectra for samples sintered at different temperatures (Fig. 3) show that all spectra diffraction peaks belong to the anorthite phase. It has also been noticed that an evolution in the number and diffraction peaks intensity with the increase in the sintering temperature. This may explain clearly the role of the heat-treatment temperature in the crystallization and sintering of anorthite-based supports. Moreover, a careful examination at these XRD spectra, one can remark that fortunately there are no any free CaO traces. This result is a good confirmation of the large application domains of these elaborated anorthite-based supports. One of the main objectives in this subsection is to find out the appropriate amount of CaO composing the final mixture to obtain an anorthite phase alone. This is why CaO is added at a particular proportion (20 wt.% CaO) into kaolin then the mixture is sintered at different temperatures. It should also be noticed that CaO used in this work instead of $CaCO_3$ was activated according to a proposed process well detailed elsewhere [13].

3.2. Pore characterization

For the development of high-quality supports, the following properties are of major importance: pore size distribution, total porosity ratio, mechanical properties, and chemical stability.

According to the previous results, there is a relationship between porosity ratio, pore sizes, sintering temperatures, and mechanical properties [30,33]. Since porous supports should resist the applied pressure during solution filtrations, a higher mechanical strength is also of great importance.

As shown in Fig. 4, porosity (%) and APS behave oppositely as a function of sintering temperatures. Both curves may be divided into three distinct stages.

For example, the porosity (%) decreases from 48 to about 37 when sintering temperature increased from 800 to 1,100˚C, while APS increased from 1 to 8 μm at the same sintering temperature interval. This decrease in porosity (%) and the increase in APS values may be due to a better sintering.

However, the pore characterization may be divided into three main categories [33]. These consist of the total porosity, APS, and the modal of pore size distribution. The pore size distribution modal may also be classified into three distinct modals: single or Gaussian distribution, bi-modal and multi-modal pore size distributions. The single (mono) modal of pore size distribution (SMPSD) is generally obtained for samples having a uniform pore size distribution. When pore volume (%) is plotted against pore size, the curve is characterized by a single peak. However, the bi-modal of pore size distribution is characterized by two different or overlapping peaks. This means that there are two classes of pore size distribution. Finally, the multi-modal of pore size distribution is characterized by the presence of more than two distinct or overlapping peaks.

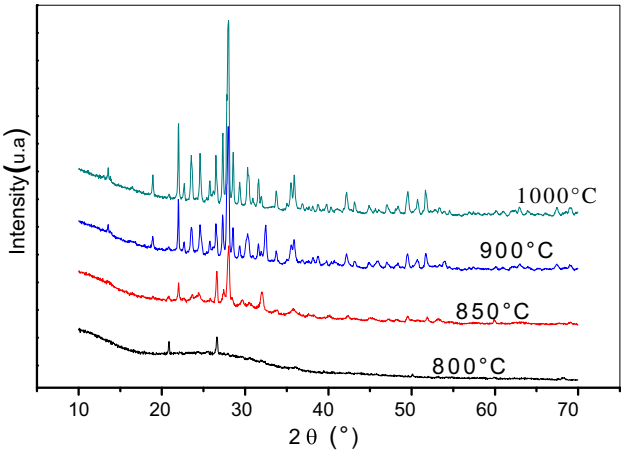

Fig. 3. The XRD spectra for samples sintered at different temperatures for 3 h.

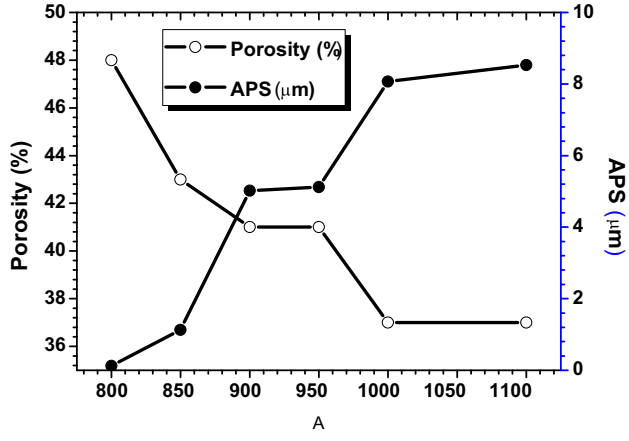

Fig. 4. Effect of sintering temperature on porosity (%) and APS of supports.

In this way, a typical pore size distribution anorthite support sintered at 1,000˚C is illustrated in Fig. 5. Fortunately, this curve shows clearly that the SMPSD for this support type. Additionally, the APS and Porosity (%) values for this prepared support were 47 and 5 μm, respectively.

The APS is also confirmed by a typical micrograph illustrated in Fig. 6. Finally, both APS and Porosity (%) values indicate that this kind of supports may be used as a substrate for the MF and/or UF membranes [33].

3.3. The flexural strength of supports

After pore characterization and phase identification of prepared samples, mechanical strength measurements are also of a great importance since porous supports should resist the applied pressure during solutions filtration.

A typical curve of the flexural strength of anorthite supports as a function of sintering temperature is shown in Fig. 7. This figure shows that the three-point flexural strength increases gradually from 22 to about 56 MPa for supports sintered at temperatures ranging from 800 to 1,100˚C, even though their total porosity ratios were all situated between 37 and 48%. Nevertheless, this curve may also be divided into three stages, as in the case of Fig. 4. The flexural strength increases slightly, as would be expected, during the first stage (800–900˚C). In fact this increase may be due to the decrease in porosity (%). Afterward, the flexural strength value of supports leveled (second stage) and increased sharply (third stage). The best flexural strength value (about 56 MPa) was achieved when anorthite supports were sintered at 1,100˚C.

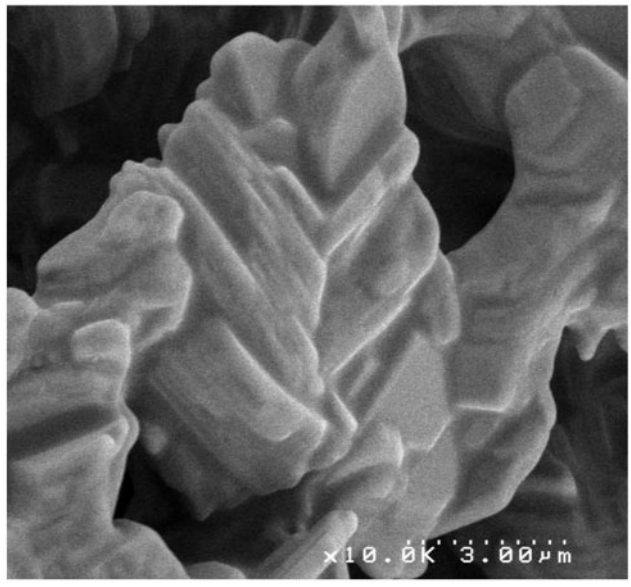

Fig. 6. SEM micrograph of supports sintered at 1,000˚C for 3 h.

By contrast, the best flexural strength of kaolin + 15 wt.% doloma samples was about 41 MPa when they were sintered at 1,250˚C for 1 h [30], significantly lower than the best three-point flexural strength value obtained in this work (supports sintered at only 1,100˚C).

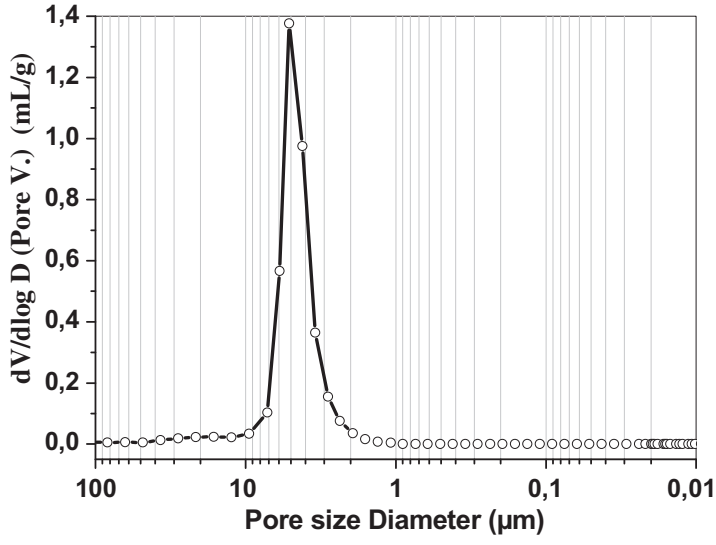

Fig. 5. Pore size distribution of supports sintered at 1,000˚C for 3 h.

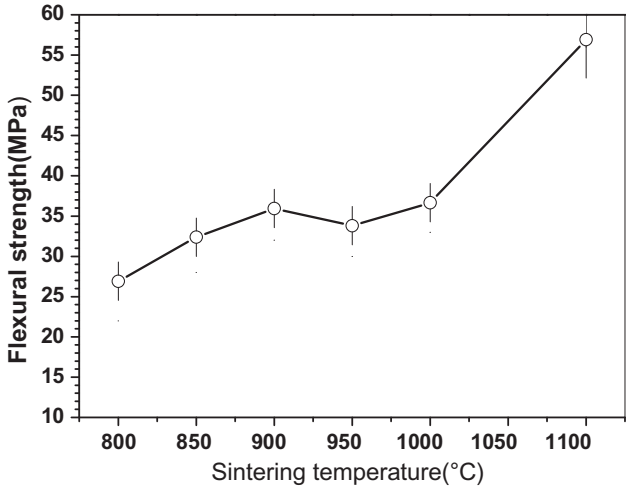

Fig. 7. Effect of sintering temperature on Flexural strength of supports.

One can compare the obtained flexural strength values using the present work with those reported by other studies carried out on mullite and anorthite-based ceramics and particular materials [33]. For example, the best flexural strength (56 ± 3 MPa), in this work was obtained for the anorthite support, sintered at 1,100˚C for 3 h.

Consequently, this flexural strength value is extremely higher than that reported by other works carried out on similar based ceramics [30,34,35].

This value (56 ± 3 MPa) is also significantly higher than those reported by Sarkar et al. [34] (40 MPa) and Dong et al. [35] (36 MPa) for their prepared membrane supports, although they have been sintered at relatively higher temperatures (≥1,450˚C).

Moreover, a flexural strength of 57 MPa was obtained for kaolin + 45 wt.% Al_2O_3 samples sintered at 1,450˚C [34], while nearly the same flexural strength value (56 ± 3 MPa) was also measured for compacts sintered only at 1,100˚C for 3 h. In fact, these interesting flexural strength values are of great importance for many porous membrane supports applications.

It should also be remarked that these mechanical properties are generally acceptable especially for MF and/or UF membranes applications.

4. Conclusions

In this work, anorthite tubular ceramic supports ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) have been prepared by using low cost local raw materials. These supports were formed by extrusion of a ceramic paste of kaolin and calcium carbonate mixtures. The supports sintered at 1,100˚C have pore diameters centered near 8 μm and 47% of porosity and flexural strength of about 56 MPa. These supports which have good characteristics can be selected as supports for MF and UF membranes.

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