Effects of the calcination temperature and the load of sodium carboxymethyl cellulose in the synthesis of novel bentonite ceramic foams

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Abstract

Novel ceramic foams were obtained by the replica method, using bentonite as alternative raw material and polyurethane sponge as template, where the latter also controls the distribution of the pore size of these ceramics. The synthesis of the ceramics was carried out using slurries of bentonite clay with different percentages of sodium carboxymethyl cellulose as a binder, and evaluating different calcination temperatures. The effect of these factors on the textural and morphological properties of the ceramic foams was studied. The porosity measured by mercury intrusion showed that the total porosity of the ceramic foams decreases as the calcination temperature increases. Furthermore, a small quantity of porosity is generated after the burnout of the binder during the calcination step. This porosity is given by pore sizes from 0.05 to 3 μm and it was increased with the amount of the binder that was increased, which was also confirmed by scanning electron micrographs. The characterization of bentonite clay, polyurethane, coated polyurethane sponge and ceramic foams was also complemented with thermogravimetric analysis, nitrogen adsorption at 77 K, and mechanical strength measurements.

Keywords: ceramic foams, bentonite, replication process, calcination temperature, sodium carboxymethyl cellulose.

1. Introduction

Ceramic foams are highly porous materials (40-90%), with low densities due to their porosity, which could be open or closed depending on the synthesis method. Nowadays, these materials are used in a wide variety of applications depending on their type of porosity. Ceramic foams with closed porosity or isolated pores are generally used as thermal insulating materials. On the other hand, ceramic foams with open porosity, where their pores are interconnected, show great permeability to gas or liquid flows [1]. The great permeability to flow is the main reason why the development of open ceramic foams has attracted the attention, since it can be used in applications that require working with materials with open porosity.

The most used technique to synthesize ceramic foams with open porosity is the *replica method,* which was introduced by Schwartzwalder *et al.* in 1963 [2], where the final material obtained is a positive replica of the template. According to this method, a polymeric sponge (template) is impregnated with a ceramic suspension (slurry) by immersion of the sponge into this slurry. The chosen polymer is usually polyurethane (PU) with open porosity. In order to get the morphology of the pores of the polyurethane sponge structure in the ceramic foam, a partial slurry removal inside of its structure is necessary. After the removal of this excess of slurry and subsequent drying, a thermal treatment is needed in order to eliminate the polymer and provide enough mechanical strength to the final ceramic [3-5]. Ceramic foams obtained by this method exhibit interconnected pores by filaments (struts) similar to a network structure, providing high permeability [1, 6]. These materials also have low thermal conductivity and low specific heat. All these properties have contributed ceramic foams to be suitable materials for a variety of applications. Some of these applications are catalyst supports [7], adsorbents [8], molten metal filters [9], industrial hot gas and diesel engine exhaust filters, gas burners, thermal insulators [5] and other new applications as porous implants [10].

Ceramic foams that are already commercially available or under study are obtained from different materials as cordierite, mullite, silicon carbide, alumina, zirconia and some of their composite systems [5]. Another possibility is by using clays, which appears to be an interesting alternative raw material due to its high availability and low cost. In the synthesis of ceramic foams by the replica method, clays have been used as a necessary additive to improve the rheology of the slurry. Nevertheless, there are recent works about ceramic foams synthesized from clays as main raw material by the replica method.

Wen *et al.* synthesized ceramic foams from a kind of natural clay that is composed of montmorillonite and illite (70%) and silica (30%). Organic templates with different cell sizes were used to obtain ceramic foams with open porosity. Those ceramic foams showed 1.6 MPa of compressive stress to ceramics with 2.2 cm of cell size. In addition, it was found that their compressive stress decreases as the cell size of the ceramics increases [11].

Muhamad Nor *et al.,* used a ceramic powder consisting of clay (10%), quartz (30%), kaolin (40%), and feldspar (20%). That work was focused on the effect of ceramic slurry density on the properties of ceramic foam. As a result, they found that an increase in the ceramic slurry density enhances the mechanical strength of the ceramic foam as well as its density; consequently, it makes the foam denser [12].

Yang *et al.* developed a processing route for the preparation of silicate ceramics with unique pore structures, which consisted of combining freeze casting with the replica method, using kaolin as unique raw material. When applying this combining method of synthesis, ceramic foams showed homogeneity in their porous microstructure. However, the disadvantage of these materials was that they exhibit low mechanical strength [13].

Sooksaen and Karawatthanaworrakul used natural clays and alumina powder as raw materials. Open-cell polyurethane sponges with different pore sizes were used as templates for ceramic slurries. They found that the composition and pore size of the sponge template strongly affected the physical properties and mechanical strength of the synthesized porous ceramics [14].

Besides these works, the use of bentonite clay as the main raw material to synthesize ceramic foams by the replica method has not been reported. In this work, ceramic foams synthesized by the replica method using sodium bentonite clay as the unique raw material were actually obtained. On the other hand, as it is known, some additives are necessary in order to control the rheology of the ceramic slurry. For natural clays, sodium silicate and sodium carboxymethyl cellulose (Na-CMC) are the most used as deflocculating and binder, respectively. Na-CMC is a polymeric compound, soluble in water that provides strength to the green body by forming bridges between the particles. Also, it avoids the collapse of the structure during the calcination process of the coated PU sponge [15, 16]. Due to the fact that Na-CMC is an organic compound, it leaves porosity after its elimination during the calcination step. Based on this, the ceramic foams were synthesized using sodium bentonite clay as raw material, where the percentage of Na-CMC and the effect of the calcination temperature on the final materials were studied. These materials were characterized by thermogravimetric analysis, nitrogen adsorption at 77 K, mercury intrusion, mechanical strength measurements and scanning electron microscopy.

2. Experimental Procedure

2.1 Synthesis of ceramic foams

The synthesis of the ceramic foams was carried out by the replica method [2]. First, the bentonite and Na-CMC powders were homogenized in a horizontal mixing for 1 hour (h). Then, these powders were added to distilled water under constant stirring. Afterward, sodium silicate was added to obtain ceramic slurries with densities of 1.1 g/cm^3.

The PU sponge was cut into dimensions of 50 mm x 50 mm x 50 mm. In this study, the density of the ceramic slurries was maintained at 1.1 g/cm^3, where the slurries were prepared with 16-17.5% of bentonite with respect to the total weight of clay and water, and 0.4-1.7% of sodium silicate with respect to the weight of the clay. The impregnation step was carried out by the immersion of the PU sponges into the ceramic slurry, where consecutive compressions and expansions were made in order to replace the air in the sponges with the slurry. Then, the excess of slurry was removed after 0.5h of the impregnation process by compression of the coated sponge between two parallel sheets. The coated PU sponges were dried at room temperature by approximately 24h on a flat surface. Finally, thermal treatment was performed in an oven (Nabertherm Mod: N200/14), first to eliminate the PU sponge and Na-CMC, and then to obtain enough mechanical strength of the ceramic foams, where the maximum temperature reached was called the final calcination temperature (T_C).

Synthesis of ceramic foams at different calcination temperatures

With the aim of choosing a suitable final calcination temperature to synthesize ceramic foams, four different TC (650, 850, 950, and 1050°C) were studied, using one percent (1%) of Na-CMC with respect to the weight of the clay in the ceramic slurry. The thermal treatment applied was: i) from room temperature to 650°C at a heating rate of 1°C/min, with intermediate isothermal steps of 1h at 80°C and 650°C, with the purpose of slowly eliminating the water and organic materials (PU sponge and Na-CMC) respectively; and ii) from 650°C to TC for 1h at a heating rate of 5°C/min.

Synthesis of ceramic foams with different percentages of Na-CMC

In order to study the effect of Na-CMC in the synthesis of ceramic foams, the calcination temperature was fixed at 950°C (as explained above), and four ceramic slurries with Na-CMC at different percentages (0.1, 0.5, 1, and 2) were used. Thermal treatment of the samples was performed with a heating rate of 1°C/min until reaching 700°C, and was held at this temperature for 1.5h to slowly eliminate the water from the OH- of the clay. Finally, the samples were heated at the same heating rate up to 950°C with a hold time of 4 h.

3. Characterization

The morphology of the PU sponge and the ceramic foams were studied by scanning electron microscopy (SEM) (LEO 1450VP equipment). For this analysis, the samples were coated with gold as the conductor material. The textural properties of the bentonite and the ceramic foams were studied by nitrogen adsorption - desorption at 77 K in a manometric measurement unit (Quantachrome Instruments, AUTOSORB-1MP). These samples were previously degassed for 12h at 100°C for the bentonite, and 200°C for the ceramic foams. In addition, the evaluation of textural properties of the ceramic foams was complemented by mercury intrusion (Micromeritics AUTOPORE III 9410 equipment). Thermogravimetric analysis (TGA) of the bentonite, the PU sponge, and a coated PU sponge were carried out on a Shimadzu TG-51 analyzer, in air atmosphere with a flow of 50 cm^3/min and using a heating rate of 10°C/min from room temperature up to 1000°C.

The mechanical strength analysis was carried out in a Com-Ten Industries Series 94 VC unit, where the ceramic foams with dimensions of 14 mm x 12 mm x 8 mm were submitted to compression stress.

3.1 Materials

Commercial PU sponge with open porosity and density of 24 kg/m^3 was used as template material in the synthesis of ceramic foams. Figure 1 shows the morphology of the PU sponge, which is an open three-dimensional network structure formed by dodecahedral cells. Struts of the cells and their triangular junctions are also indicated (shown with rectangles and triangles, respectively). Moreover, it is observed that few faces of the cells are covered with a thin sheet of PU (shown with arrows) giving a small amount of closed porosity. On the other hand, the interconnectivity of the open network structure of the PU sponge (shown with a circle), with pore sizes in the range of 50 – 800 μm can be easily noticed.

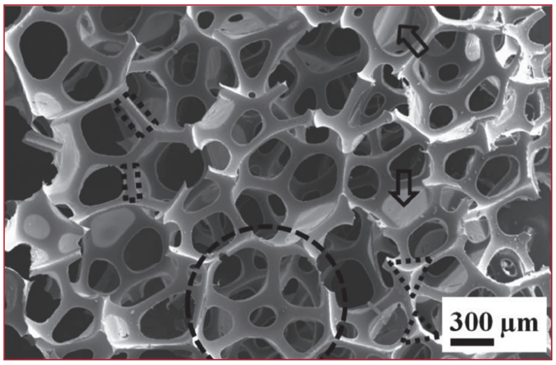

Figure # 1. Scanning electron micrograph of the PU sponge.

The Na-CMC used was a commercial binder (Parafar-Drogueria Saporti). Bentonite powder with particle size < 75 μm was used as raw material, whose chemical composition (in wt.%) was: 61.6% SiO_2, 15.3% Al_2O_3, 1.9% Fe_2O_3, 4.2% MgO, 0.7% CaO, 2.4% Na_2O, 0.5% K_2O and 0.01 % MnO. Figure 2 shows the nitrogen adsorption–desorption isotherm at 77 K of the bentonite sample, exhibiting typical isotherm of montmorillonites. According to the IUPAC classification [17], this isotherm exhibits a type II adsorption isotherm with a type H3 hysteresis loop associated to aggregates of particles with laminar structure. Low contribution of the micropores is observed from the small amount of nitrogen adsorbed at low relative pressures. The abrupt increase in the amount that was adsorbed at high relative pressures suggests the presence of larger mesopores and/or macropores, which could be formed in the aggregates of particles of the clay. From adsorption data, the specific surface area (S_{BET}) of the bentonite was obtained by the Brunauer, Emmett and Teller method [18] obtaining a value of 35 m^2/g.

The pore size distribution (Figure 2, inset) of the bentonite was obtained by using the NLDFT model with the kernel for N_2 adsorption at 77 K on silica with cylindrical pore geometry [19]. This distribution presents a maximum around 13Å, which correspond to the interlaminar space between the natural clay layers of the bentonite.

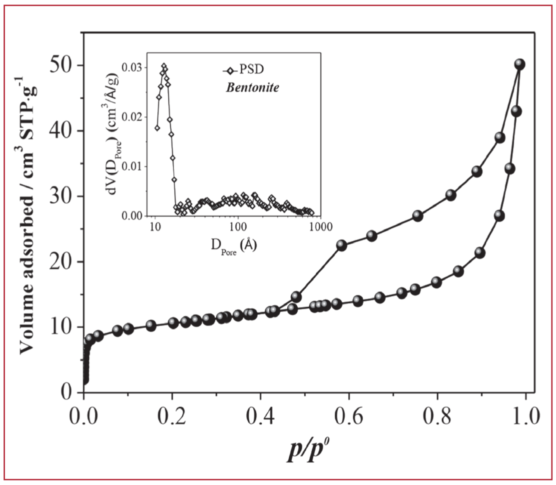

Figure # 2. Nitrogen adsorption–desorption isotherm at 77 K of the bentonite sample and its corresponding pore size distribution.

4. Results and discussion

Ceramic foam synthesized at different calcination temperatures

Figure 3 shows the TGA analysis of the bentonite, the PU sponge, and the PU sponge coated with the slurry of 1% of Na-CMC. For the bentonite, a total weight loss of about 15% was observed, related to the loss of physisorbed and reticular water present in this clay.

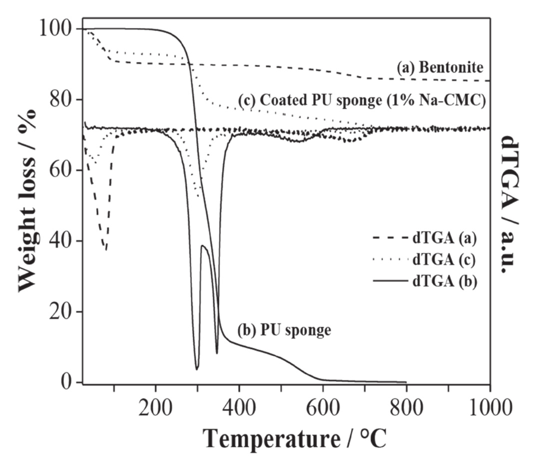

Figure # 3. TGA and differential thermogravimetric (dTGA) data of: a) bentonite, b) PU sponge, and c) PU sponge coated with ceramic slurry (1% Na-CMC).

The PU sponge starts to lose weight after reaching a temperature of 200°C due to a possible condensation of OH present in the PU composition. After 300°C, the main weight loss can be associated with the outflow of various gaseous products during the decomposition of the PU, such as CO_2, NH_3 and O=C=N. Other loss is observed at approximately 350°C, which could be related with CO and the production of some light hydrocarbons. At temperatures higher than 650°C, the PU disappears completely, in agreement with previous reports [20, 21] and the decomposition process ends with the loss of all volatile material. For this reason, the calcination temperatures shown in this work are from 650°C to higher values.

Based on the observed results for the bentonite and the PU sponge, it is possible to deduce the behavior of the coated PU sponge. It presents a first weight loss of approximately 7% at temperatures lower than 100°C. This first loss corresponds to the evaporation of water between the particles and the physisorbed water on the bentonite. The second weight loss, at about 300°C, is due to the PU decomposition associated with the loss of some gases as CO_2, CO and NH3. The last weight loss, between 650 and 700°C is due to the loss of water from the hydroxyl groups (OH) of silicate layers of the montmorillonite present in the bentonite. From this point up to 900°C, a tiny weight loss is observed after the sintering process starts.

The ceramic foams that are synthesized at the different calcination temperatures and are shown in Figure 4 are positive images from the PU sponge. The color change that is observed among them could be associated to the formation of different phases (i.e. iron oxide phases) as the calcination temperature increases.

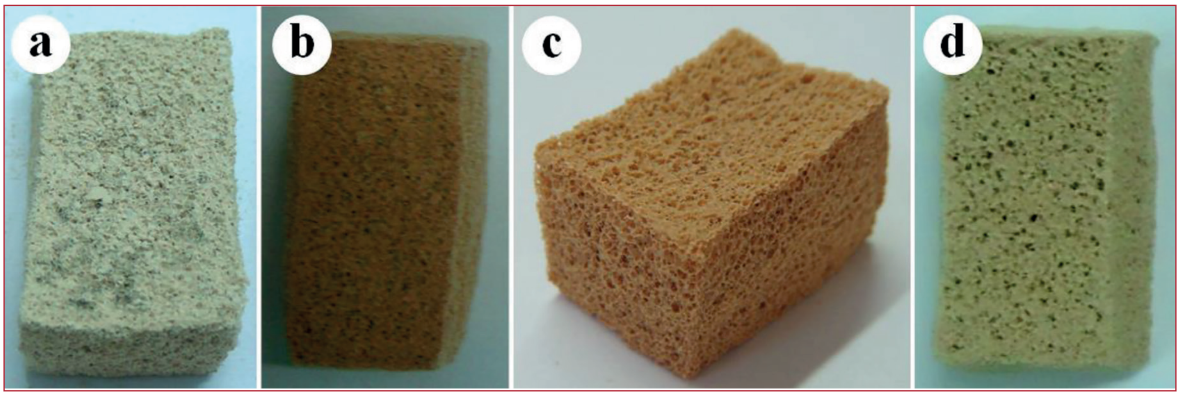

Figure # 4. Ceramic foams synthesized at final calcination temperatures of: a) 650°C, b) 850°C, c) 950°C and d) 1050°C.

The mechanical strength measurement of the ceramic foams synthesized at 1050°C is shown in Figure 5. The curve exhibits a first maximum (at ≈ 0.1 mm/mm) related to the rupture of the ceramic. However, a second peak is observed (at ≈ 0.25 mm/mm), which could be related to a new contact zone of the ceramic foam due to the fact that the surface contact was not completely flat. Also, it could be associated with some dense zones produced by the filling of the cavities of the ceramic foam with their own detached material from the previous rupture. Similar mechanical strength analyses were performed on the others ceramic foams. Thus, it was found that the maximum stress values were 0.7 MPa, 0.06 MPa, and 0.03 MPa for the ceramic foams synthesized at 1050°C, 950°C, and 850°C, respectively. The ceramic foams synthesized at 650°C did not show an appreciable maximum stress. Therefore, as the final calcination temperature decreases, the ceramic foams lose mechanical strength. From these results, a final calcination temperature equal to or higher than 950°C should be used in order to synthesize ceramic foams with an intermediate mechanical strength.

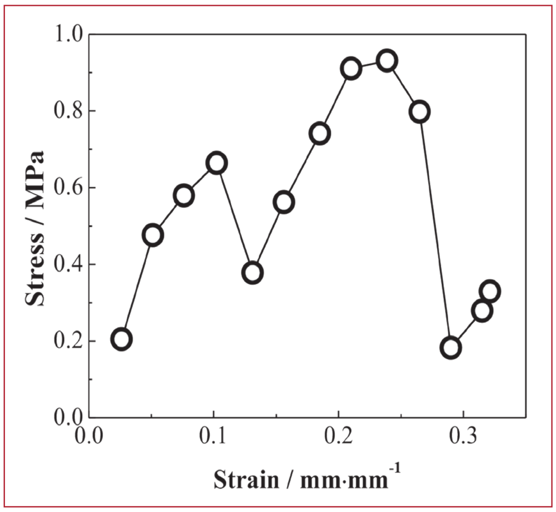

Figure # 5. Curves of stress-strain of the ceramic foam synthesized at 1050°C.

In order to study the meso-macroporosity of these ceramic foams, mercury intrusion-extrusion curves of the ceramic foams synthesized at different calcination temperatures were obtained and they are shown in Figure 6 a). A decrease in the cumulative pore volume is observed as the final calcination temperature increases. This result could be associated to the sintering densification process of the ceramic foams as the calcination temperature increases. On the other hand, it is also observed that most of the cumulative intrusion volume is present at low pressures (< 4 psia) indicating that the majority of the porosity of these ceramic foams is in the macropores range (higher than 50 µm). In addition, the ceramic foams synthesized at 650°C show a small increment in the cumulative pore volume at higher pressures (> 10^4 psia), due to the porosity in the mesopores range. These mesopores are from the bentonite porosity kept after the thermal treatment at this temperature. In Figure 6 b), it can be seen that all these ceramic foams present a unimodal macropore size distribution, with modal macropore size of around 200 µm.

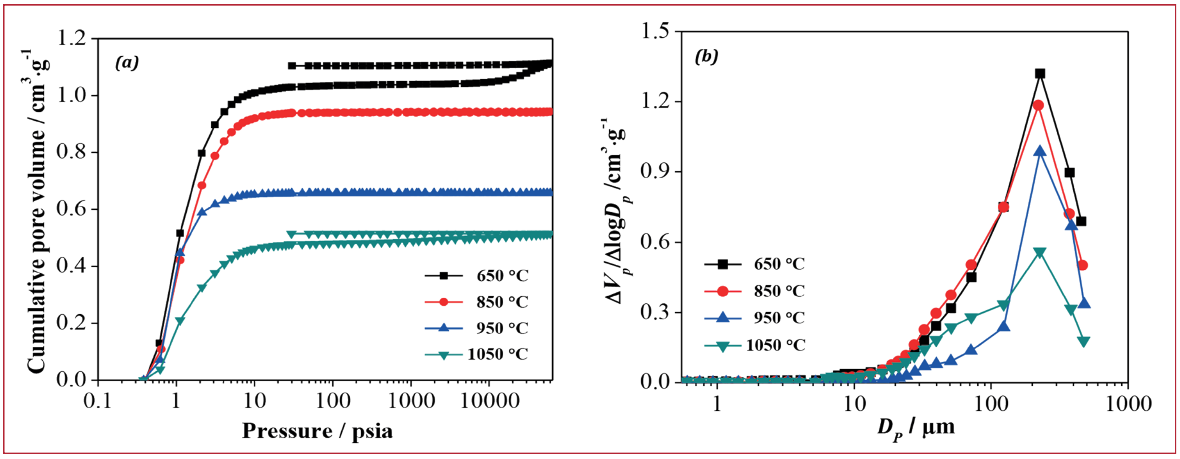

Figure # 6. Textural analysis by mercury porosimetry of the ceramic foams synthesized at different calcination temperatures: a) Mercury intrusion-extrusion curves, and b) macropore size distributions.

In Table 1, the textural properties of the ceramic foams obtained from mercury intrusion data are shown. These ceramics present a low apparent density (ρa) because they are lightweight materials, which is in accordance with their high porosities (> 50 %). The ρa increases as the calcination temperature increases due to the sintering densification process above mentioned. The decrease in the porosity with the increase in the calcination temperature could be understood as the decrease of the size of the cavities within the ceramic due to the approach between clay particles, which is responsible for the increase in the apparent density. On the other hand, it is observed that the skeletal density of these ceramics (ρs), which is the density of the solid matrix without porosity, remains approximately constant. This fact is because all these ceramics have the same bulk solid, which corresponds to the calcined bentonite without porosity.

Table # 1. Textural properties of ceramic foams obtained from mercury intrusion data.

Sample	ρa	ρs	Porosity
	g/cm^3	g/cm^3	%
CF_650	0.6	2.3	72
CF_850	0.7	2.2	67
CF_950	0.9	2.3	61
CF_1050	1.0	2.1	51

Ceramic foams synthesized with different percentages of Na-CMC

The chosen final calcination temperature was 950°C, in order to obtain an intermediate mechanical resistance from the ceramic, as mentioned above. Figure 7 shows the hollow struts created by the outflow of the gases during the decomposition of the PU sponge. The triangular form is due to the junctions of the PU, which interconnect the pores. Each triangular junction is shared with three pores of the PU. The pore sizes created by the struts are less than 50 μm.

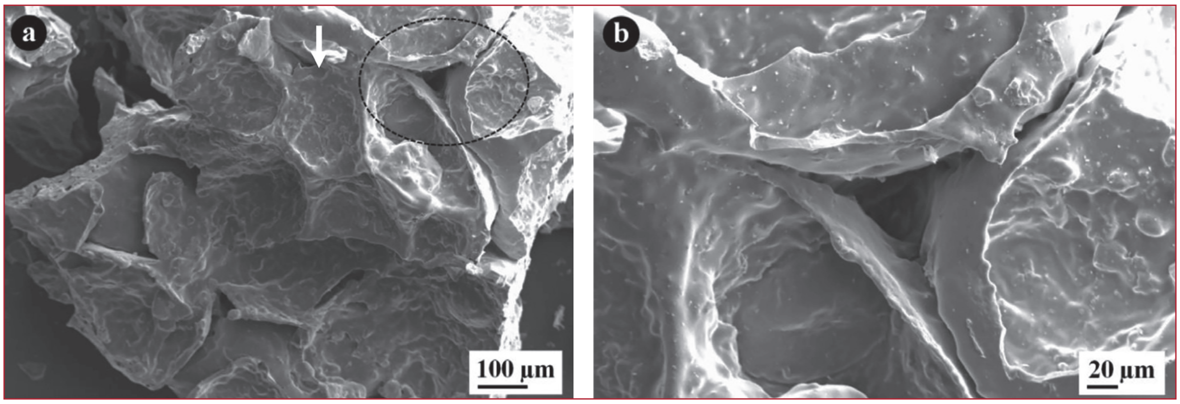

Figure # 7. Scanning electron micrographs of: a) ceramic foam with 2% Na-CMC, and b) enlargement of the zone in a) (strut).

The adsorption isotherms of N_2 at 77 K for ceramic foams are shown in Figure 8, where a type III adsorption isotherm is exhibited. The fast increment of the amount adsorbed at high relative pressure indicates that these ceramic foams present larger mesopores and macropores. Although the ceramic foams have low specific surface area (S_{BET}), a small increase in the N_2 volume adsorbed is observed when the percentage of Na-CMC increases. This fact is related to the generation of some porosity due to the elimination of the Na-CMC.

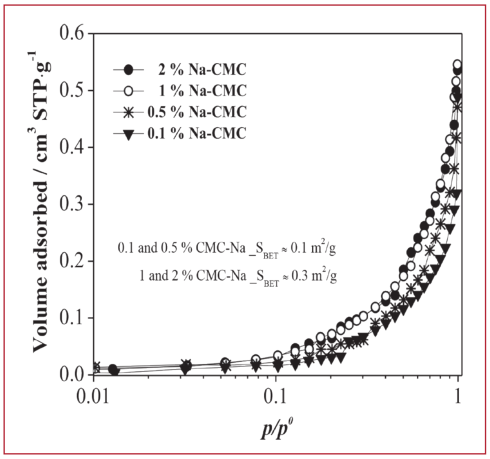

Figure # 8. Nitrogen adsorption isotherms determined at 77 K for ceramic foams.

Figure 9 shows the mercury intrusion curves of the ceramic foams. In order to study the influence of the Na-CMC on their porosity, this analysis is presented only for pore sizes less than 25 µm, due to fact that the pores sizes between 50 and 800 µm are given by the structure of the PU sponge, and the pores sizes between 25 and 50 µm correspond to the hollow struts.

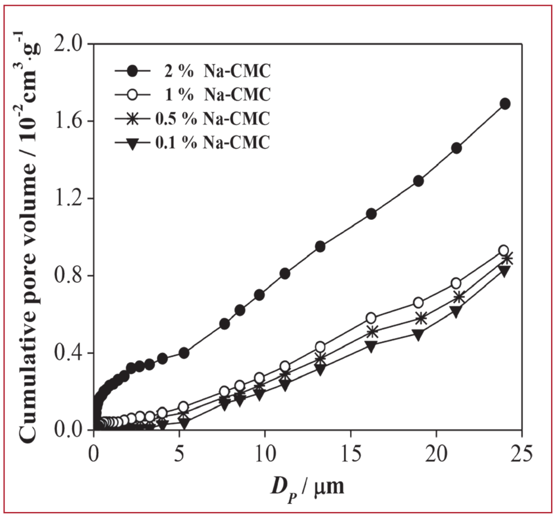

Figure # 9. Curves of cumulative pore volume obtained by mercury intrusion data on the ceramic foams.

The mercury intrusion curves show a correlation between the amount of Na-CMC and the accumulated pore volume (porosity due to the elimination of the Na-CMC during the firing), where a higher porosity is obtained when the Na-CMC amount increases. These results are in accordance with the behavior obtained by the nitrogen adsorption analysis.

The pore size distributions of the ceramic foams, obtained from mercury intrusion data, are shown in Figure 10. According to this figure and the previously shown results, it is possible to suggest that the Na-CMC generates porosity in the pore sizes ranging from 0.05 to 3 µm. However, the ceramic foam synthesized with 0.1% Na-CMC does not show this type of porosity in comparison to the other ones.

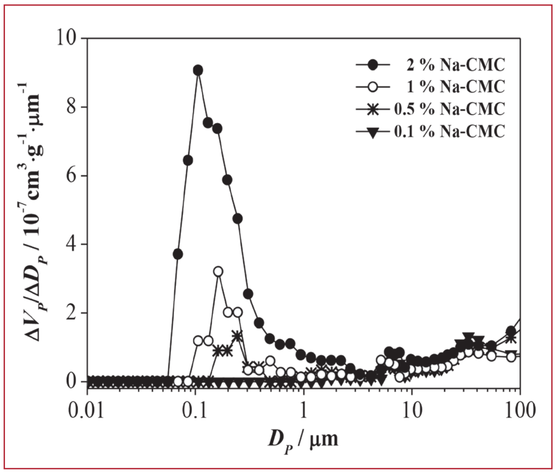

Figure # 10. Pore size distributions for the ceramic foams.

Finally, in the micrographs of the ceramic foams shown in Figure 11, it is possible to observe that the quantity of pores generated by the removal of the binder increases as the Na-CMC amount increases. These results are in agreement with the previously discussed.

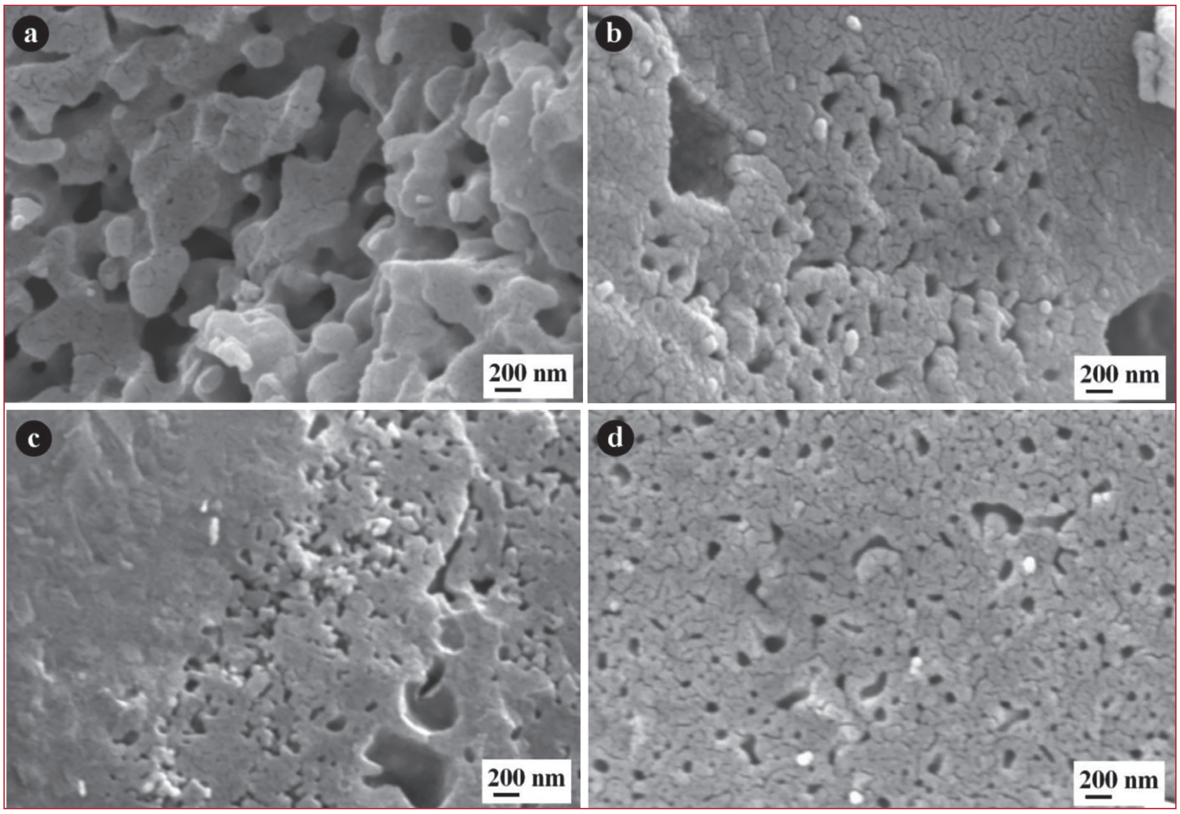

Figure # 11. SEM micrographs of the ceramic foams synthesized with: a) 0.1% Na-CMC, b) 0.5% Na-CMC, c) 1% Na-CMC, and d) 2% Na-CMC.

5. Conclusions

It is possible to obtain bentonite ceramic foams with high porosity by means of the replica process. By increasing the final calcination temperature, the total porosity of the ceramics is reduced and its mechanical resistance is improved. The mechanical resistance of the ceramic foams calcined at 950°C is twice than that obtained at 850°C, due to the sintering densification process. Hence, the lower calcination temperature of 950ºC is found to be appropriate in order to obtain a ceramic with a good mechanical resistance. The binder of sodium carboxymethyl cellulose generates porosity in the pore sizes ranging from 0.05 to 3 μm, and it increases as the amount of the binder was increased.

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