

Evaluation of the Influence of Microwaves in the Structure of Silica Gels

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In this work we studied the influence of microwaves in the pore structure of silica gels obtained via sol-gel polymerization process. We analysed the feasibility of replacing conventional heating by microwave heating during drying. Structural parameters such as specific volume of pores (V_p), specific surface area (S_p), average pore size (r_p) and the bulk and true densities were measured. X-ray diffraction confirmed the obtention of a completely amorphous structure for the gels. Some characteristics of silica gels were evaluated by thermogravimetric analyses (TGA), differential thermal analyses (DTA) and Fourier transform infrared spectroscopy (FTIR). We observed that microwave drying is a feasible process to yield controlled pore nanostructures. The gels obtained via microwave heating presented average pore size of 1.2 nm, specific surface area of 112 m²/g and specific volume of pores of 0.06 cm³/g. The gels obtained via conventional heating presented average pore size of 1.3 nm, specific surface area of 748 m²/g and specific volume of pores of 0.49 cm³/g.

Keywords: *structure, sol-gel and microwave*

1. Introduction

The microwave processing makes possible to heat both small and large pieces very rapidly and uniformly, to efficiently remove volatile constituents (binders, moisture, etc) from thick sections. The absorption of microwave energy varies with the composition and structure of different phases, being possible the selective heating¹⁻³.

Microwave heating is fundamentally different from conventional heating processes. In the microwave process, heat is generated internally within the material, instead of originating from external heating sources. As a result of this internal and volumetric heating, smaller thermal gradients are created in microwave-processed materials than in materials processed by conventional heating, reducing cracking during drying⁴.

Another advantage of microwave heating is that the treatment time can be considerably reduced, which in many cases represents a reduction in the energy consumption as well⁴.

Sol-gel is a low temperature method using chemical precursors that produces ceramics and glasses with better purity and homogeneity than high temperature conventional process. One major characteristic of sol-gel process is a large

variety of pore structures (average pore size, pore size distribution, surface area, porosity, etc) that occur during processing and in the final product. The control of pore structures in every stage of the process is of great interest, since controlling the pore structure is very important in order to achieve specific physical properties of products, such as index of refraction and capacity of adsorption^{5,6}.

A major concern in the production of monolithic dried gels is the prevention of cracks during aging and drying steps. As the solvent escapes from within the gel or as the pore size changes during these processes, stresses are introduced into the silica network which may cause fracturing^{7,8}.

Microwave processing has promising results when used for drying and densification of sol-gel silica^{4,9,10}. The liquid precursor is removed by means of the electromagnetic field associated to the microwaves. It was observed that microwaves affect not only the surface area and porosity but also adsorption isotherms¹⁰.

Mesoporous material has been prepared in very short crystallization time using microwave heating. Using microwave radiation during synthesis provides a way to control the crystallinity of gels according to the selection of syn-

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thesis parameters¹¹. Dense, foam-free, optically transparent gel-derived silica monoliths were produced using microwave energy. The heating produced by microwave energy allowed high heating rates, fast dehydration and rapid densification¹².

The exact way in which the microwave radiation affect the structural parameters of sol-gel materials are still unclear. It is important that the effect of microwaves in materials properties becomes well understood in order to make this process a reliable and practical technology for industrial applications. Thus, the goal of this work is to study the influence of microwaves in the structure of silica obtained by sol-gel method during drying.

2. Experimental Procedure

The chemical precursor used in the fabrication of silica gels was tetramethyl ortosilicate (TMOS, Aldrich Corp.). Nitric acid was used as catalyser. Porous silica obtained via conventional heating was aged and dried inside conventional open to air oven (model 315SE, FANEN). Porous silica obtained via sol-gel polymerization process was aged and dried using open to air microwave oven (MDS 2100, CEM).

Structural characteristics of silica gels were obtained using nitrogen adsorption-desorption analyses. The equipment used was an Autosorb-1 (Quantachrome). The average pore radius (r_p) was estimated from $r_p = 2 V_p / S_p$, where V_p is the specific pore volume and S_p is the specific surface area¹³. The data on true density (ρ_t) were obtained from helium pycnometry experiments, using Pycnometer Multivolume (model 1305, Quantachrome). Bulk density measurements were carried out using two different methods: mercury pycnometry and nitrogen adsorption-desorption analyses. The metric properties used for geometric description were volume fraction of pores (V_v) and the surface area density (S_v). These properties were obtained by nitrogen adsorption-desorption analyses. The connectivity of pores per unit volume (G_v) was evaluated using a cylindrical model developed by Vasconcelos^{6,14}. In that model, the expression used to evaluate the genus is obtained through correlating of the metric properties S_v and V_v , as follows⁶:

$$G_v = \frac{S_v^3}{(32\pi V_v(1 - V_v))} + 1. \quad (\text{A})$$

The thermal behavior of the gels was evaluated using thermogravimetric analyses (TGA-50, Shimadzu) and differential thermal analyses (DTA-50, Shimadzu). Fourier transform infrared spectroscopy (DRFTIR) was carried out using an equipment FTIR Paragon - 1000 (Perkin - Elmer) with the software Spectrum for Windows 1.0.

3. Results and Discussion

Table 1 presents the bulk density measurements from mercury pycnometry and nitrogen adsorption-desorption and also the true density obtained by helium pycnometry.

The data on bulk density obtained for conventionally heated samples by nitrogen adsorption-desorption analyses and helium pycnometry were smaller than the values obtained using mercury pycnometry. This difference can be a result of the errors associated with the determination of true density through helium pycnometry due to the difficulty to evaluate the real weight of samples, since can occur the presence of water molecules adsorbed in their surfaces e into their pores. The difference is only 8%, thus we used the estimated bulk density values to compare the samples properties. We observed that the bulk density is bigger for porous silica made via microwave heating.

The nitrogen adsorption-desorption isotherms for porous silica obtained via conventional and microwave heating are shown in Figs. 1 and 2, respectively. According to de Boer definition¹⁵, the isotherm obtained via conventional heating is type I isotherm, being characteristic of a microporous solid (pore radii ≤ 1.5 nm) and represent cylindrical pores opened in both extremities, in agreement with

Table 1. Values of bulk density (r_v) and true density (r_t) for porous silica obtained via conventional heating and microwave heating.

Material	r_t (g/cm ³)	r_v (Hg) (g/cm ³)	r_v (N ₂) (g/cm ³)
conventional	1.41 ± 0.05	1.22 ± 0.01	1.12 ± 0.02
microwave	1.82 ± 0.05	—	1.62 ± 0.06

(Hg): mercury pycnometry

(N₂): estimated from N₂ adsorption-desorption

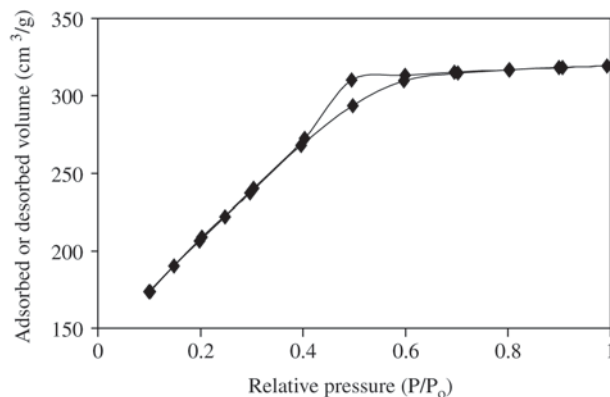


Figure 1. Isotherm of N₂ adsorption-desorption obtained for the porous silica via conventional heating.

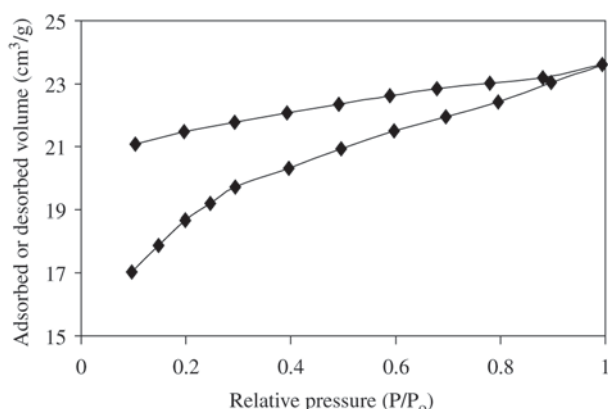


Figure 2. Isotherm of N_2 adsorption-desorption obtained for porous silica via microwave heating.

BET theory¹⁶. The isotherm obtained with microwave heating exhibited unusual shape⁴. This isotherm has a hysteresis in the region of low relative pressure. Analysing only the adsorption branch of the isotherm, we can observe that the microwave-processed gel also presents a microporous structure. The presence of the pronounced hysteresis can be a result of a high proportion of mesoporous and porous with complex geometries¹⁵.

Figure 3 shows the pore size distributions for silica gels obtained via conventional and microwave heating. The narrow pore size distribution observed is appropriate for using the silica gels in separation processes. For the porous silica obtained via microwave heating we observed a slightly broader pore size distribution, confirming the coexistence of micro and mesopores.

Table 2 shows the data obtained for specific surface area of pores (S_p), specific volume of pores (V_p) and average pore radius (r_p) for porous silica fabricated via conventional and microwave heating. The silica gels obtained via microwave heating present specific surface area of pores and specific volume of pores quite smaller than for silica gels obtained via conventional heating. The microwave radiation has strong influence on silica gels structure. Silica gel processed by microwave heating has different pore structure, with smaller microporous area and high bulk density than the conventional-processed gel. This difference can be a result of radiation action on the sol-gel reactions kinetics, leading to a more condensed network.

Table 3 presents the data on volume fraction (V_v), surface area density (S_v) and genus (G_v) for the porous silica gels. We observed that G_v presented high values, in the order of magnitude of 10^{19} , for gel made via conventional heating, and G_v in the order of 10^{18} for gel obtained via microwave heating. The high pores connectivity of silica

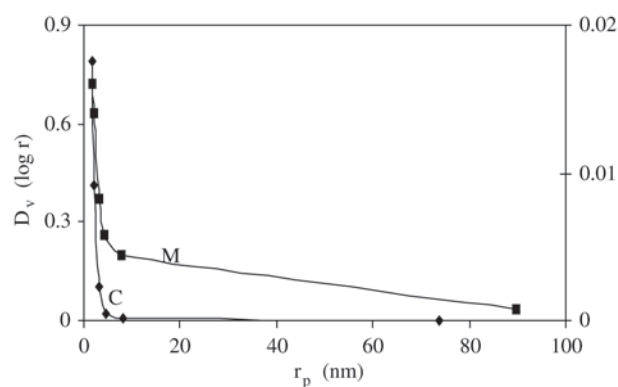


Figure 3. Pore size distribution for porous silica obtained via conventional (C) heating and via microwave (M) heating.

Table 2. Structural parameters of silica gels.

Material	S_p (m^2/g)	V_p (cm^3/g)	r_p (nm)
conventional	748 ± 37	0.49 ± 0.02	1.3 ± 0.07
microwave	112 ± 6	0.07 ± 0.004	1.2 ± 0.06

Table 3. Metric and topological parameters of silica gels.

Material	S_v ($10^6 cm^{-1}$)	V_v	r_p (nm)	G_v ($10^{19} cm^{-3}$)
conventional	10.5 ± 0.9	0.69 ± 0.06	1.32 ± 0.07	5.46 ± 2.3
microwave	2.0 ± 0.2	0.13 ± 0.01	1.24 ± 0.06	0.22 ± 0.09

gels show the feasibility of using these materials in separation or adsorption processes¹³.

The thermogravimetric analyses show that the porous silica obtained via conventional heating presented higher water content when compared with the water content of the porous silica obtained via microwave heating. The water content was approximately 36% for gel obtained via conventional heating and 15% for gel made via microwave heating. This result is related to the high specific surface area of pores for gel obtained via conventional heating when compared with the specific surface area of pores for gel obtained via microwave heating. Those high values favor the presence of silanol groups in that gel. Figure 4 exhibits the thermogravimetric curves for the porous silica obtained. We observed two different regions of weight loss for the gel obtained via conventional heating. The first region corresponds to temperatures below 150 °C and is associated to loss of structural water. The second region occurs at temperatures above 300 °C. For the gel obtained via micro-

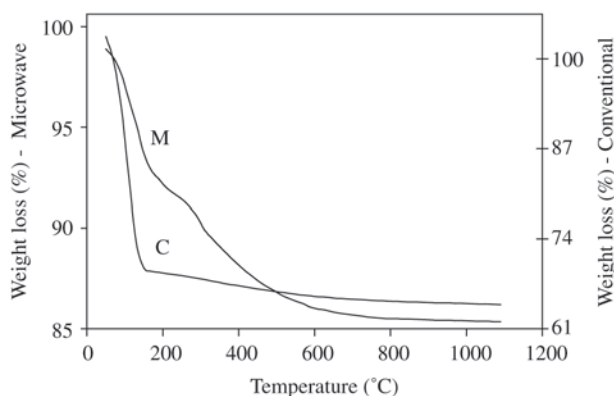


Figure 4. Thermogravimetric analyses of silica gels obtained via conventional (C) heating e via microwave (M) heating.

wave heating, Fig. 4 shows three different regions of weight loss: at temperatures below 180 °C and at temperatures between 230 °C and 300 °C, which corresponds the loss of structural water; and above 300 °C, which corresponds to simultaneous loss of carbon residues and also to the loss of structural water in the form of silanol groups.

Figure 5 shows curves of differential thermal analyses (DTA) for gels obtained via conventional and microwave heating. We observed an endothermic peak, which can be attributed to evaporation of molecular water adsorbed on gels surface. We noted that the endothermic peak intensity is bigger for the curve of gel obtained via conventional heating. The information obtained with differential thermal analyses (DTA) confirmed the results obtained by TGA. The porous silica obtained via conventional heating present higher water content when compared with the water content of the porous silica obtained via microwave heating.

With infrared spectroscopy it was possible to analyse the interactions involved and the structure of silica fabricated by sol-gel processing. The use of FTIR intended to verify the difference resulting from the variation of processing parameters for materials fabricated via conventional heating and microwave heating.

Figure 6 shows the spectra obtained for FTIR analyses of the porous silica fabricated via conventional heating and using microwave heating. In the region between 3700 cm^{-1} and 2700 cm^{-1} occurs the absorption corresponding to the presence of silanol groups (Si-OH) and water. In this region occurs a variety of absorption frequencies, due to the variety of structures and interactions involved.

The peaks located around 1970 cm^{-1} , 1860 cm^{-1} and 800 cm^{-1} are characteristics of Si-O-Si bonds of the silica network and these bonds appear in the spectrum of fused silica¹⁷. The peak at around 1630 cm^{-1} corresponds to the

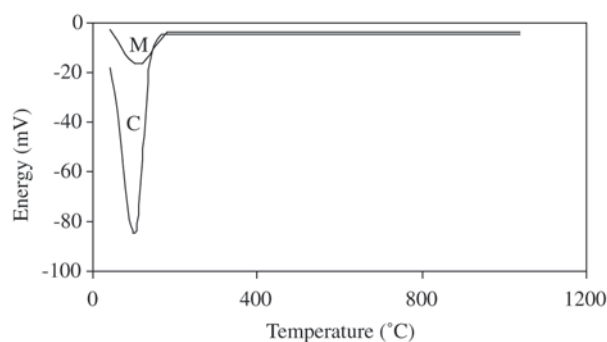


Figure 5. Differential thermal analyses of silica gels obtained via conventional (C) heating and via microwave (M) heating.

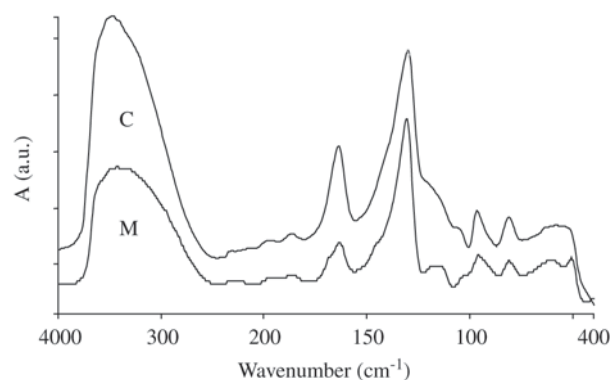


Figure 6. FTIR spectra of silica gels obtained via conventional (C) heating and via microwave (M) heating.

absorption for molecular water incorporated in the structure and tends to disappear after heat treatment at high temperatures. Differences in magnitude observed for peaks corresponding to molecular water and silanol groups (1630 cm^{-1} , 2700 – 3700 cm^{-1}) confirm the high proportion of water incorporated into the porous silica obtained via conventional heating, as determined by TGA analyses.

The absorption band between 1200 cm^{-1} and 1000 cm^{-1} corresponds to Si-O-(Si) stretching vibration associated to linear structures of glass network¹⁸. We observed that the spectrum of silica gels obtained via microwave heating presented this band at larger wavelengths. This represents a more branched network, with a larger proportion of Si-O-(Si) bonds associated to cyclic structures¹⁸. The peak at about 960 cm^{-1} corresponds to stretching vibration of Si-O(H) bonds and we can observe by Fig. 6 that this peak appears at a higher wavelength in the spectrum of gel obtained via microwave heating, indicating that this bond belongs to a more branched silica network. This result con-

firms that microwave radiation acts towards the increasing in the extension of polymerization reactions, leading to a more condensed network, with a higher bulk density, smaller surface area and pore volume, and a higher number of cross link than the conventional-treated gel.

4. Conclusions

Microwave radiation affects sol-gel materials structure, as was demonstrated by N_2 adsorption-desorption isotherms and density measurements. The gel obtained via microwave radiation presents higher density and smaller surface area than the gel obtained via conventional heating. Through the analyses of TGA, DTA and FTIR we observed that porous silica obtained via conventional heating presents higher water content than the gel obtained via microwave heating. According to FTIR analyses we observed that the silica obtained via microwave heating presents a more branched pore network than the pore structure of silica obtained with conventional heating.

Acknowledgments

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