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# A novel approach to the industrial preparation of mesostructured silica: Use of ion exchange resin and study of the effect of composition variables

E. Santamaría *, A. Maestro, M. Porras, J.M. Gutiérrez, C. González

*Department of Chemical Engineering, Faculty of Chemistry, University of Barcelona, Barcelona 08028, Martí i Franqués 1-11, Catalonia, Spain*

## HIGHLIGHTS

- New industrial fabrication process much more viable than the proposed synthesis for mesostructured materials until now.
- Use of acid ion exchange resins in order to obtain silica mesostructured materials.
- Influence of the composition variables (surfactant and precursor concentrations).

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## ABSTRACT

Structured mesoporous silica was successfully synthesized using ion exchange resin as proton source to avoid the use of HCl during the synthesis and preventing the ions being freed in the media. The material was obtained from sodium silicate solution, which acts as a silica source and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_{19}PO_{39}EO_{19}$ denoted as P84) was used as structure-directing agent. The influence of two composition variables was studied: the ratio of silica used and the ratio of surfactant. The obtained materials were characterized through, SEM, TEM, SAXS and nitrogen adsorption–desorption isotherms. The use of sodium silicate solution as silica source instead of TEOS or TMOS and the possibility to obtain a material through an ion exchange resin is important from an application point of view due to relative cheap raw materials and equipments. The process using the ion exchange resins has around 65% of efficiency respect to Si source, which is an important data not reported in other papers, and it must be considered when planning an industrial approach to obtain these structured materials.

## 1. Introduction

Since the discovery of the ordered mesoporous material by the “Mobil Research and Development Corporation” many surfactants have been studied as structure-directing agents to synthesize novel mesoporous molecular sieves with well-defined pore size (2–10 nm) and high surface area [1,2]. The surfactant aggregates as self-assembled templates to develop new mesoporous materials with a variety of textures and structures [3]. These porous materials have attracted attention because of the wide variety of applications they are suitable for, and are of special interest in the preparation of catalysts and drug delivery systems, for example [4–6].

However, before developing these applications it is important to tailor the pore size diameter. The most used route to obtain mesostructured materials is the Cooperative Self-Assembly (CSA) pathway [3,7,8]. In this route, formation of ordered mesoporous materials is determined by the interaction between precursor and surfactant molecules. When the concentration of surfactant is above its critical micellar concentration (CMC), it aggregates, depending on the experimental conditions, forming spherical micelles, rod-like micelles, etc. When a silica source is added, usually silicon alkoxide precursors like TEOS, and through a hydrothermal treatment at relatively high temperature, precursor and surfactant cooperate and condensate to form a material with an ordered structure. After the condensation, the surfactant can be removed by calcination, extraction, etc.

As reported by other authors [9–11] TEOS is quite expensive, and therefore its use represents a material cost disadvantage for producing mesostructured materials. Another flaw for TEOS in front of sodium silicate is the production of ethanol as a reaction sub product. Efforts have been devoted to reduce the cost in last decade by using inexpensive sodium silicate as a silica source to replace TEOS [12].

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* Corresponding author. Tel.: +34 679972602.
*E-mail address:* esthersantamaria@ub.edu (E. Santamaría).

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**Table 1**
List of the carried out experiments: specific surface area ($S_{BET}$), and pore diameter ($\phi$) as a function of the surfactant quantity and the sodium silicate amount.

| Experiment number | Water (W) (g) | P84 (S) (g) | Sodium silicate solution (SS) (g) | $S_{BET}$ ($m^2/g$) | $\phi$ (nm) |
|---|---|---|---|---|---|
| 1 | 30 | 0.25 | 2 | 168 | 7.14 |
| 2 | 30 | 0.40 | 2 | 289 | 4.13 |
| 3 | 30 | 0.50 | 2 | 485 | 5.37 |
| 4 | 30 | 0.60 | 2 | 211 | 4.42 |
| 5 | 30 | 0.75 | 2 | 90 | 11.44 |
| 6 | 30 | 1.00 | 2 | 95 | 15.43 |
| 7 | 30 | 0.50 | 1 | 536 | 4.36 |
| 8 | 30 | 0.50 | 3 | 456 | 5.40 |
| 9 | 30 | 0.50 | 4 | 278 | 5.23 |

Our approach is based on the CSA method where sodium silicate and P84 cooperate to form the mesostructure based on an electrically $S^0I^0$ assembly pathway, where $S^0$ is a nonionic surfactant (P84) and $I^0$ represents the electrically neutral silicic acid. Silicic acid was formed from sodium silicate through the use of an ion exchange resin, which was reported before by Alexander [13] who obtained monosilicic acid at pH 3 from sodium metasilicate. Other studies shown that the use of ion exchange resins is an easy method to produce colloidal silica with an homogeneous nucleation rate [14,15]. However, the use of ion exchange resin has not been reported for the formation of ordered mesoporous materials..

The great advantage of the $S^0I^0$ pathway [16,17] is that it relies on H-bonding between $S^0$ and $I^0$ and circumvents charge matching constraints. Consequently the pathway affords more fully cross-linked framework structures in comparison to mesoestructures formed through electrostatic $S^+I^-$ and $S^0(H^+X^-)$ pathways [18].

In CSA method, an acid is added to the solution, usually HCl in order to reach pH $\leqslant 2$ [19,20] to improve the condensation reaction, because in the range of pH 2–4 the silica polimerization is very slow [21]. The $Na^+$ cations from the sodium silicate remain free in the media so they must be removed washing the material with ethanol: HCl mixtures. By means of an ion exchange resin the use of HCl during the synthesis is not required because the resin is previously charged with $H^+$ and these cations are changed with the $Na^+$ cations freed by the sodium silicate. And excess of resin is used in order to ensure that all the $Na^+$ are removed from the media. Therefore the resulting material does not need to be washed.

The chance of using ion exchange resins to produce mesostructured silica opens the door to a new industrial fabrication process which seems more viable than the proposed synthesis proposed until now.

In this work, the influence of the composition variables (surfactant and precursor concentrations) on the specific area, as well as on the pore diameter was studied in order to determine the most favorable conditions to obtain mesostructured materials using a cation exchange resin as a source of $H^+$.

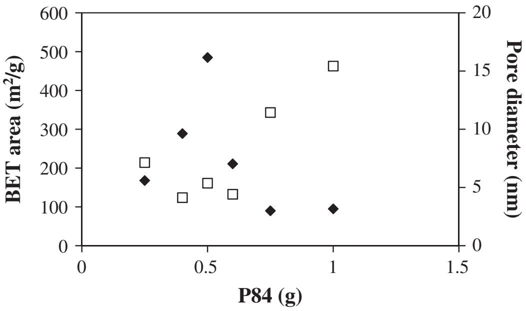

**Fig. 1.** Specific surface area (black points) and mesopores diameter (white squares) as a function of the quantity of surfactant for 30 g of water and 2 g of sodium silicate.

## 2. Materials and methods

### 2.1. Materials

The triblock copolymer of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) Pluronic P84, $(EO)_{19}(PO)_{39}(EO)_{19}$ was supplied by Sigma Aldrich. Sodium silicate solution ($Na_2O \sim 10.6\%$ and $SiO_2 \sim 26.5\%$) was used as a silica source and was supplied by Sigma Aldrich. Sodium hydroxide (>98%) and HCl (37%) were purchased from Panreac. Deionized water was used in all samples. All chemicals were used without further purification. Ion exchange resin Amberlyst 15 with a total capacity $\geqslant 1.7$ mmol/mL and particle size of 0.355–1.18 mm supplied from Merck was used in all the experiments.

### 2.2. Methods

#### 2.2.1. Ordered mesoporous silica material preparation

First of all, water and surfactant were mixed and kept under stirring at 50 °C to ease the melt of the surfactant until a clear solution was obtained. Then 100 g of an ion exchange resin were added to the water and surfactant solution. Later on, a sodium silicate solution ($Na_2O \sim 10.6\%$ and $SiO_2 \sim 26.5\%$) was added drop by drop. The resulting slurry was stirred, so the $Na^+$ of the sodium silicate solution substituted the $H^+$ on the exchange sites of cation resin. The 100 g of resin provided an excess of exchange sites in order to assure the complete removing of $Na^+$ from the solution. The pH was measured and it was stable after 15 min approximately, indicating that the ion-exchange was complete. The slurry was filtered in order to separate the ion exchange resin from the liquid. The filtered liquid, which did not have condensated silica yet, was placed in an oven at 100 °C during 24 h in order to allow the silicate condensation producing a white precipitate that corresponds to the ordered mesoporous material.

After that, the material was filtered and dried up and calcined at 550 °C during 5 h in order to eliminate the residual surfactant. The final look of the material was a white colored powder.

After the material preparation the resin was washed with water, and treated with a NaOH (1 M) solution to solve the remaining silica. After that and previously at each experiment the resin was regenerated with $H^+$ using HCl (1 M) solution. Finally, the resin was washed again with deionized water.

#### 2.2.2. Characterization

*2.2.2.1. Scanning electron microscopy (SEM).* SEM (HITACHI S-4100 with carbon-coated operated at 15 keV) was used to observe the morphology of the samples.

*2.2.2.2. Transmission electron microscopy (TEM).* The samples were examined by TEM (JEOL JEM-2100 microscope with the acceleration voltage of 200 kV). In order to prepare the sample for TEM analysis, it was suspended in ethanol by 5 min sonication. The suspension was dropped onto a copper grid coated with carbon film and dried at room temperature.

*2.2.2.3. SAXS measurements.* Small-angle X-ray diffraction scattering (SAXS) measurements were used to determine the type of liquid crystal phase. Measurements were performed in a Hecus X-ray Systems GMBH Graz, equipped with a Siemens Kristalloflex 760 (K-760) generator. Temperature of the samples was fixed by a Peltier Anton Paar (25–300 °C) controller. Radiation wavelength was 1.54 nm.

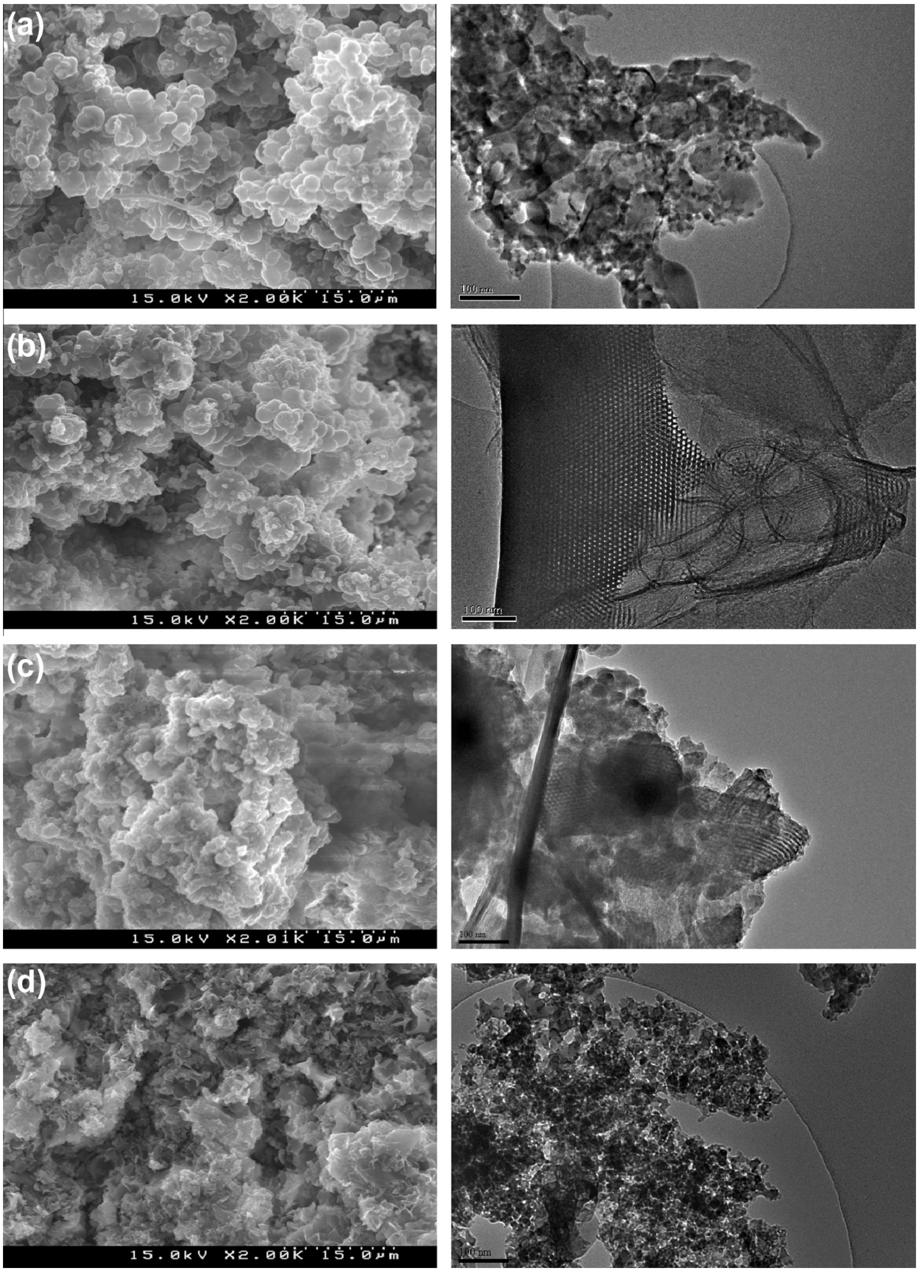

**Fig. 2.** SEM (left) and TEM (right) images for the obtained material using (a) 0.25 g of P84 (b) 0.50 g of P84 (c) 0.75 g of P84 and (d) 1.00 g of P84 and a constant weight of 2 g of sodium silicate solution and 30 g of water.

*2.2.2.4. $N_2$-sorption analysis.* The specific surface area, mean pore diameter and pore volume of the meso-macroporous silica materials were determined by $N_2$-sorption analysis using a Micromeritics Tristar 300 instrument at −196 °C. Prior to each measurement, the samples were degassed at 120 °C for 6 h. The specific surface areas were estimated by using BET method. The pore diameter and the pore size distribution were determined by the BJH method from the adsorption branch of the isotherm.

## 3. Results

A series of experiments have been carried out (Table 1) in order to study the influence of the different composition variables on the specific surface of the obtained materials, as well as their influence on the pore diameter. In order to find out the best rate water/surfactant/sodium silicate solution ratio (W/S/SS) the amount of water was kept constant and a set of experiments was carried out varying the surfactant weight and the amount of the sodium silicate solution. First of all, surfactant weight was changed from 0.25 to 1.00 g keeping constant the sodium silicate value in 2 g (Table 1). The same process was used to study the influence the weight of sodium silicate solution using 0.50 g of P84, corresponding to the best surfactant concentration found in the previous series of experiments (see Table 1).

The synthesis had around a 65% of efficiency, which means that the 65% of the used Si is incorporated in mesoporous material.

### *3.1. Influence of the surfactant concentration*

Several experiments were been carried out in order to obtain the ratio of water/P84/sodium silicate in which it is possible to get mesoporous materials with ordered mesopores. These

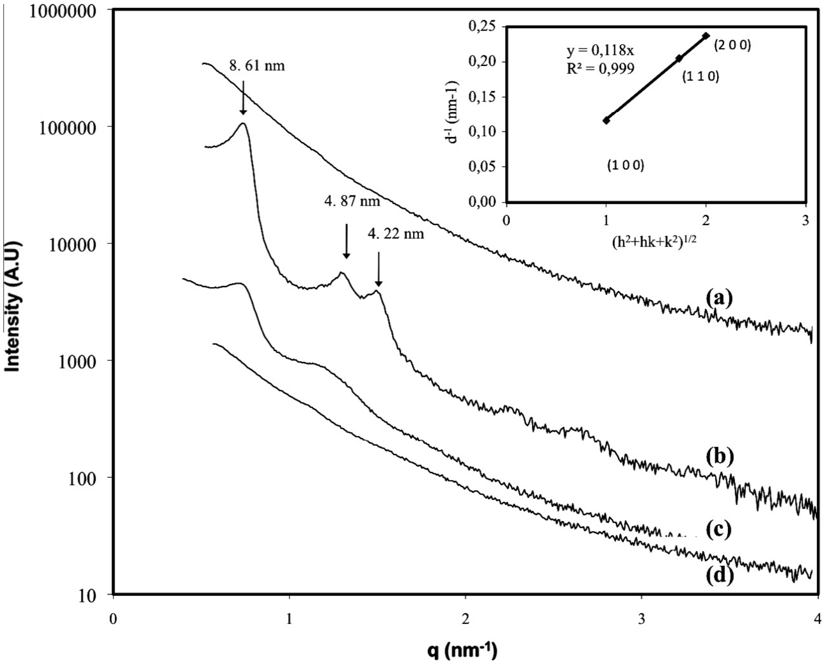

**Fig. 3.** SAXS pattern for the material with (a) 0.25 g of P84 (b) 0.50 g of P84 (c) 0.75 g of P84 and (d) 1.00 g of P84 and 2 g of sodium silicate solution. Indexing of SAXS peaks for the SAXS pattern of 0.50 g of P84.

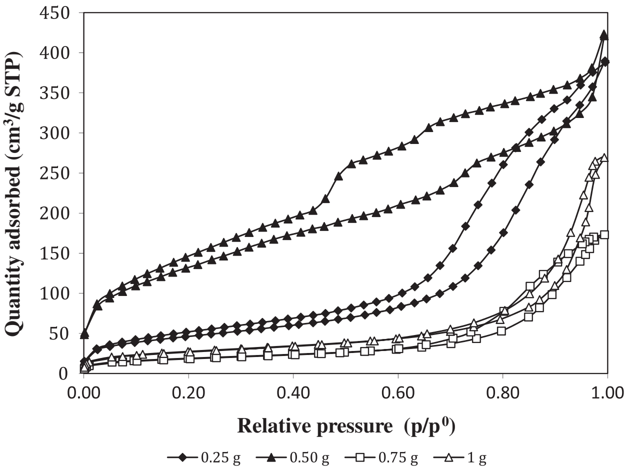

**Fig. 4.** Evolution of the nitrogen adsorption–desorption isotherm with the surfactant concentration a constant amount of 30 g of water and of 2 g of sodium silicate solution.

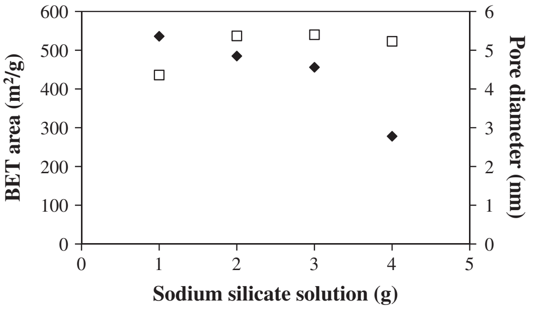

**Fig. 5.** Specific surface (black diamonds) and mesopores diameter (white squares) as a function of the weight of sodium silicate solution solution for 30 g of water and 0.50 g of surfactant.

experiments were been done using a constant quantity of sodium silicate solution of 2 g and 30 g of water, changing the weight of surfactant.

In Fig. 1 a maximum can be observed for the material BET area corresponding to the ratio water/P84/sodium silicate W:30 g/S:0.50 g/SS:2 g. For the mesopore diameter a minimum seems to appear at this ratio. Fig. 2 shows SEM and TEM images for the materials. If the surfactant concentration was 0.25 g the material did not present ordered pores. It seems to indicate that there were not enough surfactant molecules to cooperate with the sodium silicate, and it condensated in an amorphous way. From TEM image for W:30 g/S:0.50 g/SS:2 g it can be appreciated the typical honey-comb arrangement of mesopores that indicates the hexagonal mesostructure of the obtained material.

For the materials synthesized using a surfactant ratio higher than W:30 g/S:0.75 g/SS:2 g, TEM images show zones with ordered mesopores and zones without ordered structure (TEM image for Fig. 2c). For a ratio of W:30 g/S:1 g/SS:2 g no ordination is observed. It seems that there exists an optimum around 0.50 g of surfactant. Above this value, the ordered zone is progressively lost and the mean pore diameter increases.

Through SEM it can be observed that the morphology of the materials is similar for all samples and independent of the pores structuration.

Fig. 3 confirms the structure for the obtained materials. SAXS pattern confirmed TEM images about the mesopores structure. For the 0.25 g and 1.00 g the patterns presented no peaks indicating they were disordered materials. For the material synthetized using 0.50 g of P84 in addition to a sharp peak at 8.61 nm, two peaks at 4.87 nm and 4.22 nm were detected on the SAXS pattern. The presence of these two peaks is suggests of a hexagonal organization of the channels. According to the Bragg's rule, the unit cell dimension ($a_0$), which is the sum of the pore diameter and the thickness of the pore wall can be deduced and it is about 8.74 nm for the experiment using 0.50 g of surfactant and 2 g of sodium silicate solution. The pore order was progressively lost while the surfactant concentration increased as the SAXS pattern shows for 0.75 g of P84. For this sample, two broad peaks can be observed.

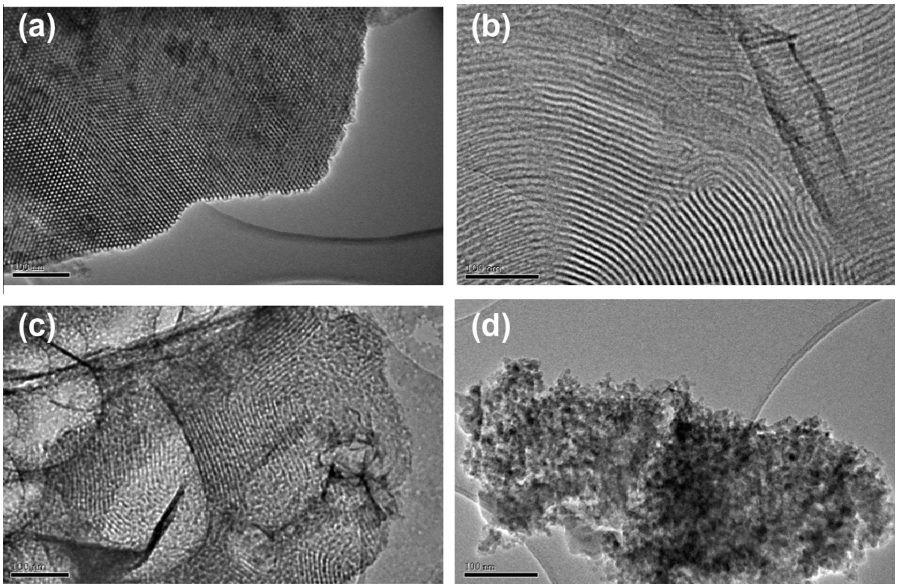

**Fig. 6.** TEM images for (a) 1 g of sodium silicate solution, SS (b) 2 g of SS (c) 3 g of SS and (d) 4 g of SS for constant weights of 30 g of water and 0.50 g of surfactant.

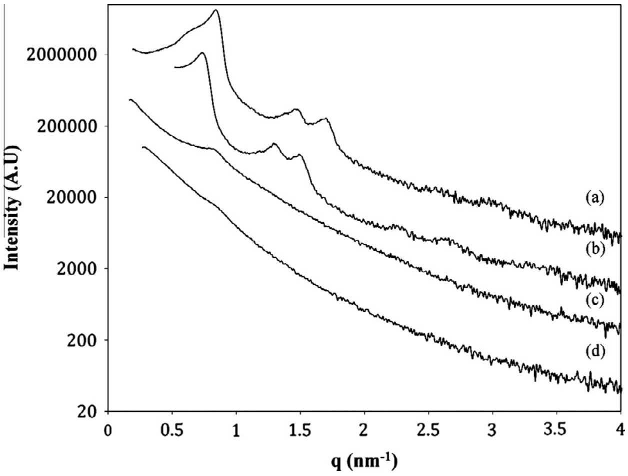

**Fig. 7.** SAXS pattern for the material with (a) 1 g SS (b) 2 g of SS (c) 3 g of SS and (d) 4 g of silicates, 30 g of water and 0.50 g of P84.

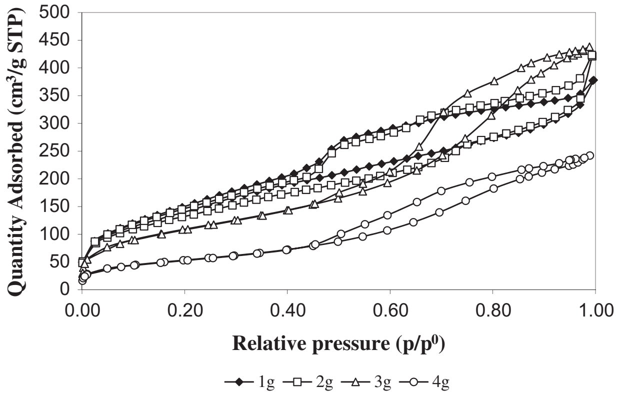

**Fig. 8.** Evolution of the nitrogen adsorption–desorption isotherm with the sodium silicate concentration for a constant amount of water of 30 g and 0.50 g of P84 .

For 1 g no peaks appear, indicating that the structure is completely lost, according to TEM images on Fig. 2.

According to the results, Schulz-Ekloff et al. [22] reported a poor hexagonal arrangement of the materials when the surfactant concentration was high with the polymerization of the silica source into solid amorphous silica. In our opinion, in order to obtain a hexagonal structure, polymerization should occur at condensation nuclei growing in one dimension, forming long cylinders that arrange in a hexagonal package. The number of condensation nuclei for the CSA route depends on the surfactant concentration. When the concentration of surfactant is high, at fixed sodium silicate and water, many condensation nuclei appear simultaneously and they probably cannot grow very much, and only short cylinders can be formed that cannot arrange in an ordered way.

Fig. 4 shows the evolution of the nitrogen adsorption–desorption isotherm with the surfactant ratio (W:30 g/S:0.25–1 g/SS:2 g). It can be observed that for the experiments with 30 g/0.25 g 2 g and 30 g/0.50 g/2 g the isotherm shape is like type IV, typical from the mesoporous materials, and for both hysteresis cycles are broader. The broader hysteresis loop the more presence the mesopores indicating an optimum around 0.5 g of surfactant, according to BET results. Moreover, TEM and SAXS data show that the most ordered structure was obtained when 0.5 g of surfactant was used.

### *3.2. Influence of the sodium silicate concentration*

Experiments were carried out in order to study the influence of the quantity of sodium silicate in the properties of the mesostructured materials. These experiments have been done using 30 g of water and 0.50 g, of surfactant corresponding with the specific maximum surface found in Fig. 1. The studied ratio was W:30 g/S:0.5 g/SS:1–4 g. The use of less sodium silicate was not possible due the low weight of material obtained.

The more sodium silicate was added the smaller specific area the material had (Fig. 5). In all cases the materials presented ordered mesopores with diameters was between 4 and 6 nm.

Fig. 6 shows TEM images for the evolution of the materials when the sodium silicate ratio was increased. Using 1 g and 2 g of sodium silicate solution the materials presented a high ordered level, as SAXS patterns (Fig. 7a and b) supported. The patterns presented three peaks corresponding to a hexagonal pore arrangement. Fig. 6c shows the mesochannel of the material, but the SAXS pattern corresponding with this material only presented one broad peak, indicating that the order was partial. When 4 g of sodium silicate was used, no order was evidenced in the TEM image neither in SAXS pattern. It can be observed that an excess of precursor decreases the specific area of the material. This behavior was previously reported by Stébe et al. [23], when a nonionic fluorinated surfactant-based system was used according to these authors, when high amounts of precursor are used we can assume that only a part of the silica interacts with the surfactant to form the channel arrangement while the rest precipitates to form an amorphous silica phase.

Fig. 8 shows the evolution of the nitrogen adsorption–desorption isotherm with the sodium silicate concentration. It can be observed that the isotherms are very similar in shape, and the isotherm corresponding to 4 g of sodium silicate solution is below the others, because the specific surface area of the material is about 300 $m^2/g$ while the materials with less sodium silicate have specific surfaces areas around 500 $m^2/g$. Here again, we can conclude that the excess of sodium silicate precipitates in an amorphous way and, therefore, the more SS, the less proportion of structured mesopores is present in the sample, decreasing its surface specific area.

If results obtained in the study of surfactant concentration influence are combined with those where the sodium silicate concentration effect is studied, we could conclude that the most important factor, which determines the arrangement of pores, is the concentration of surfactant, which presents an optimum around 0.50 g in 30 g of water. If an excess of SS is used, it precipitates in an amorphous way, reducing the proportion of ordered structure in the sample. Table 1 seems to show that the concentration of surfactant is much more determinant than the ratio surfactant/sodium silicate solution, since experiments 6 and 7 have the same S/SS ratio and very different mean pore size. In experiment 6 the concentration of surfactant is too high, there are too many condensation nuclei and, therefore, they cannot properly grow in one dimension, as they are too close and disturb each other, preventing the one-dimensional growing. In experiments 1 and 9 the same S/SS ratio is used too, but in experiment 1 the amount of surfactant is too low, and probably the condensation nuclei are too diluted to arrange together in an ordered structure.

## 4. Conclusions

In this paper mesoporous materials have been obtained by CSA method, using sodium silicate as silica source. Since it is much cheaper than others used traditionally, like TEOS. Moreover, unlike TEOS, during polymerization of the silica the sodium silicate does not give off ethanol, which can break the network of mesopores losing the ordered arrangement. The most relevant point of this work is the use of an ion exchange resin to obtain mesostructured materials that prevents the presence of free ions in the media and, consequently, no washing is required. Moreover, the study of the influence of composition variables in the specific area and pore size shows that an optimum of surfactant concentration exists at fixed weights of water and silicate. In our opinion, above this optimum an excess of surfactant leads to the presence of too many condensation nuclei, that are too close from each other. The high concentration of these nuclei disturbs their one-dimensional growth, forming too short cylinders or just agglomerates that cannot arrange in an ordered way. Below this optimum, these nuclei seem to be too diluted to arrange together in a hexagonal configuration. The S/SS ratio has also an effect on the structure of the samples. A too low ratio, i.e. an excess of silicate, produces a decrease of the region with ordered mesopores and a decrease of specific area, probably due to the fact that only a part of the silicate cooperates with the surfactant, the rest being precipitated as an amorphous silica phase. If the S/SS ratio is too high, there is not enough silicate to form long cylinders, therefore only short ones form, resulting in a disordered structure.

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