Some considerations to optimize the synthesis procedure and the structural quality of mesostructured silicas

Verónica R. Elías [a,b], Mónica E. Crivello [a], Eduardo R. Herrero [a], Sandra G. Casuscelli [a,b], Griselda A. Eimer [a,b,*]

[a] Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional (UTN), Facultad Regional Córdoba (FRC),
Maestro Lopez esq. Cruz Roja s/n, C. Universitaria, 5016 Córdoba, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

ABSTRACT

Two methods for the preparation of highly ordered MCM-41 silica are discussed. The quality of the structure was optimized by adequate stirring of the reaction mixture containing low concentration of surfactant, followed by heating at 70 °C for 3 h under stirring. Besides this energetically favorable procedure allowed to obtain structures very stable upon calcination. The role of the ethanol and the hydroxide source in the synthesis process is also analyzed.

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1. Introduction

Nanotechnology will be one of the fields that will contribute the most to scientific and technological development along the 21st century. Nanostructured inorganic, organic or hybrid organic–inorganic materials present the ability to assemble and organize inorganic, organic and even biological components in a single material. This feature represents an exciting direction for developing innovative multifunctional advanced materials presenting a wide range of novel properties besides allowing an integration and miniaturization of devices.

Soft chemistry-based processes (i.e., chemistry at low temperatures and pressures, from molecular or colloidal precursors) clearly offer innovative strategies to obtain tailored nanostructured materials. The mild conditions of sol–gel chemistry provide reacting systems mostly under kinetic control. Therefore, slight changes of experimental parameters (i.e., pH, concentrations, temperatures, nature of the solvent, counterions) can lead to substantial modifi-

cations of the resulting supramolecular assemblies and give rise to solids with very different structures and properties [1,2]. Moreover, although the resulting nanostructures certainly depend on the chemical nature of their organic and inorganic components, they also rely on the synergy between these components. Thus, the tuning of the nature, the accessibility and the curvature of the hybrid interfaces are a key point for the design of new nanostructured materials.

The use of supramolecular assemblies (surfactant micellar aggregates) as structure directing agents in soft chemistry-based silica gelation processes resulted in the discovery of a new family of mesoporous silica compounds (M41S) [3–10]. These solid phases are characterized by a regular structure of mesopores (2–10 nm) with sharp pore size distribution, a high specific surface (up to 1500 m^2/g), a specific pore volume (up to 1.3 mL/g) and a high thermal stability. The M41S family includes a bidimensional hexagonal phase (MCM-41), a cubic phase (MCM-48) and several lamellar phases. These materials are potential candidates for a variety of promising applications in many fields: catalysis, optics, electronics, photonics, sensors, membranes, separation, sorption, biological applications (drug delivery, immobilization and recognition), etc. [11–16]. Particularly, the hexagonal packed array of unidirectional large channels in MCM-41 offers unique opportunities

to be used as 'host porous structure' allowing the preparation of new nanostructured composite materials [17–19].

It is possible to synthesize M41S materials under a variety of concentration of surfactants and conditions [5,6,20–23]. At high concentrations of surfactant, it has been proposed that micellar aggregates are formed in solution, around which the silicate source polymerizes [5,6]. However, these materials can also be formed in mixtures with as little as 0.5 wt% of surfactant, which indicates that at these low concentrations a cooperative templating process may be in operation [20,24–26]. This self-assembly process is also sensitive to factors such as temperature, stirring and heating time, reactives nature and presence of cosolvents in the solution. Thus, finding a quick and easy method of synthesizing a particular mesostructure of this M41S family offers a significant advantage to the use of these materials. Other authors have made some efforts in this sense [27–28]. In this report, the preparation of a series of mesoporous silicas has been investigated in order to furnish more information about the influence of different synthesis conditions on the formed mesostructure. As part of these studies, the role of both the alkalinity source (supplied via alkali metal hydroxides or quaternary ammonium cation hydroxides) and the ethanol in the synthesis process was also discussed.

2. Experimental

The mesoporous silica materials were obtained by two different synthesis procedures (methods **A** and **B**). Following the first method, based on that reported previously by us to synthesize Ti-MCM-41 [29–30], 20 wt% solution of cetyltrimethyl ammonium bromide (95%) (CTABr) in water (previously heated at 35–40 °C to dissolve the surfactant) and 70% of the tetraethylammonium hydroxide 20 wt% aqueous solution (TEAOH) were added dropwise to tetra-ethoxysilane (98%) (TEOS) under stirring at room temperature and stirring was continued for 3 h. The remaining TEAOH and the water were further added dropwise to the milky solution and stirring was continued for 20 min. The pH of the resultant gel was 11.45 and the molar composition was as follows: TEAOH/Si = 0.30, CTABr/Si = 0.4, water/Si = 60. This gel was heated in a Teflon-lined stainless-steel autoclave under autogeneous pressure at 100 °C for 0–7 days. Sometimes, ethanol was used as solvent of CTABr in place of water.

Following the method **B**, based on that proposed by Gallis et al. [31–32], CTABr was dissolved in water and 2 M sodium hydroxide aqueous solution (NaOH) (97%). After heating slightly (35–40 °C) to dissolve the surfactant, the TEOS was added. The ratios of the reactants were as follows: NaOH/Si = 0.50, CTABr/Si = 0.12, water/Si = 132, and sometimes TEAOH was used in place of NaOH. The resulting mixture (pH 11.25) was stirred at room temperature for 2–4 h. Then, this gel was heated at 70 °C under stirring in a closed flask or at 100 °C and 150 °C in a Teflon-lined stainless-steel autoclave. In both methods, the typical amount of TEOS used for the synthesis was 10 ml.

The final solid was then filtered, washed with distilled water and dried at 60 °C overnight. To remove the template, the samples were heated (heating rate of 2 °C/min) under N_2 flow up to 500 °C maintaining this temperature for 6 h and subsequently calcined at 500 °C under air flow for 6 h.

The materials were characterized by powder X-ray diffraction (XRD) and nitrogen adsorption. XRD patterns were collected in air at room temperature on a diffractometer using CuKα radiation of wavelength 0.15418 nm. Scans were performed between $2\theta = 1.5°$ and 7° at an interval of 0.01° and a scanning speed of 2°/min was used. The N_2 adsorption–desorption isotherms and surface area measurements were carried out at 77 K on a sorption equipment with an accuracy higher than 3% and a reproducibility

of +0.5%. Prior to the measurement the sample was outgassed for 12 h at 573 K to a residual pressure below 10^{-4} atm.

3. Results and discussion

3.1. Method **A**

3.1.1. Effect of the hydrothermal synthesis time

XRD spectra of calcined samples produced by method **A** with different hydrothermal treatment times at 100 °C and using water as solvent are shown in Fig. 1. As it can be observed, a mesostructure was formed without hydrothermal treatment. This sample exhibits an intense low-angle reflection peak at approximately 2.4° and other broader and less intense one between 4° and 5°, which is characteristic of mesoporous silicas. Moreover, the sample also shows a high surface area around 1400 m²/g typical of mesoporous materials (Table 1). A subsequent hydrothermal treatment of the gel appears to cause a partial collapsing of the pore array, giving rise to a notable decrease of the long-range order of the structure. In addition, the surface area of the samples decreases with the hydrothermal treatment up to a 50%, which is clearly correlated to the decrease in the structural order observed.

3.1.2. Effect of solvent

To examine the role of ethanol in our synthesis process, ethanol was used in place of water to dissolve the surfactant. Interestingly, this yielded a material with only a single broad peak in the diffraction pattern (Fig. 1) and lower surface area (Table 1). This result confirms that ethanol is involved at the silicate–surfactant inter-
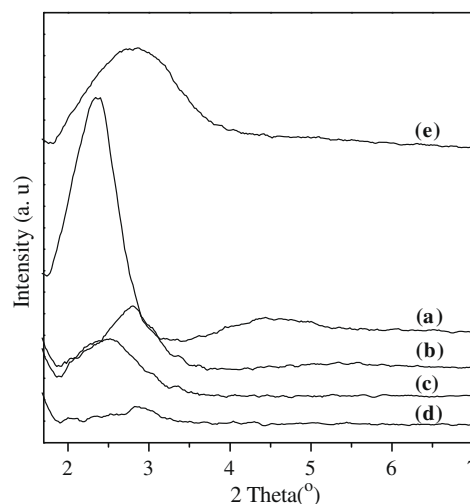
Fig. 1. XRD spectra of calcined samples prepared by method **A,** using water as solvent: (a) without hydrothermal treatment, (b) with hydrothermal treatment of 1 day, (c) 4 days, (d) 7 days and (e) using ethanol as solvent, without hydrothermal treatment.

Table 1
Surface areas of the samples synthesized by method **A**.

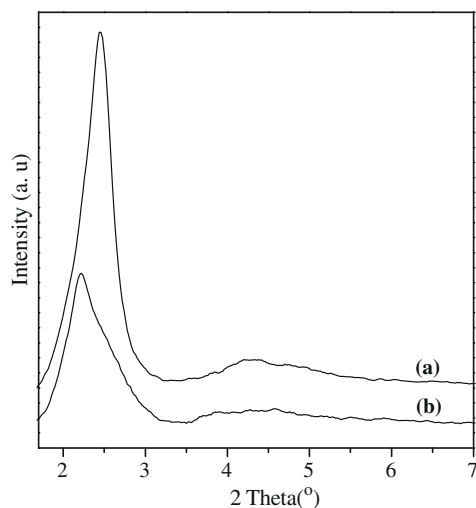| Hydrothermal treatments time (days)	Solvent	Area (m²/g)
0	Ethanol	1056 (5)
0	Water	1398 (6)
1	Water	1245 (6)
4	Water	1016 (5)
7	Water	817 (4)

The estimated deviations of the parameters are given in parentheses as uncertainty in the last digit.

face and plays an important role in the synthesis process affecting the phase produced and/or its structural order. Previous researches have shown that the self-assembly of the organic–inorganic structure can be modeled by the surfactant packing parameter $g = (V)/(a_0)(l)$ [24,33], where V is the total volume of the surfactant chain plus any solvent molecules between the chains, a_0 is the effective headgroup area at the organic–inorganic interface and l is the surfactant chain length. Small values of g stabilize more curved surfaces such as MCM-41 ($1/3 < g < 1/2$), while larger values stabilize structures with less curvature such as MCM-48 ($1/2 < g < 2/3$) and layers ($g = 1$). As it has been shown by Stucky et al., alcohol molecules with short alkyl chains (<4 carbons) tend to reside primarily in the outer shell of the surfactant micelle [24,26,34]. Thus, the addition of alcohols as solvents increases the effective surfactant volume, raising the value of g and causing transformation to a different phase. Therefore, the use of ethanol as solvent in place of water is expected to cause a structural distortion as well as the appearance of other phase or mixture of phases.

3.2. Method **B**

3.2.1. Effect of hydroxide source

On the other hand, Gallis and Landry [31] have reported the formation of well-ordered mesoporous phases from a synthesis mixture with low concentration of surfactant and NaOH as hydroxide source. Fig. 2 shows the XRD patterns of two calcined samples prepared by method **B**, where the reaction mixture (based on that of Gallis and Landry [31]) was stirred at room temperature for 4 h and then heated for 3 h at 100 °C in autoclave. NaOH or TEAOH were used here in order to analyze the influence of the hydroxide source on the synthesis process. Although both samples show a main diffraction peak between 2 and 2.5°, the sample prepared in presence of NaOH clearly exhibited a more ordered structure typical of the hexagonal MCM-41 phase. The surface of this mate-

rial was slightly higher (Table 2), which is in accordance with the higher structural ordering of the same. It has been reported that quaternary ammonium cations stabilize amorphous silica particles in aqueous solution [35]. Such bulky cations adsorbed onto particle surfaces provide steric stabilization, preventing aggregation upon collision. In an aqueous medium, silica species will acquire a negative surface charge due to dissociation of the surface silanol groups. Such a surface charge will cause organic cations in the surrounding solution to align along the particles surface, creating an electric double layer. This stabilizing barrier of bulky organic cations restricts the close approach of similar species or particles, so that the attractive potential between them could become insufficient to cause aggregation. This stabilization mechanism is not observed for systems where the alkalinity is supplied via alkali metal hydroxides, probably because the smaller size of the cations allows silica species to approach within distances where attractive interactions can occur [36]. Taking into account these comments, it can be thought that the presence of Na in our synthesis process is likely to allow to reach the optimum degree of silicate polymerization required for the formation of a well-ordered phase.

3.2.2. Effect of the stirring time and the subsequent thermal treatment

In order to improve the degree of ordering of the MCM-41 samples produced by our method **B**, both the stirring time at room temperature and the thermal treatment type of the reaction mixture were evaluated. Thus, Fig. 3 shows the XRD spectra of both calcined samples produced by stirring the reaction mixture at room temperature for 2–4 h and calcined samples obtained by the same preceding procedure followed by heating under stirring for 3 h at 70 °C. A notable improvement of the original structure, as determined by XRD, was achieved by heating the reaction mixture at 70 °C after an appropriate stirring at room temperature for 3–4 h. Moreover, this thermal treatment of the previously stirred mixture appears optimum to obtain a well-defined and well-ordered structure in contrast with a static heating at 100 or 150 °C in autoclave (Fig. 4). The better-defined structures synthesized by method **B** presented the higher surface areas (around 1500 m²/g) and a decrease in these values were again associated with less ordered phases (see Table 3).

The N₂ adsorption and desorption isotherm and the pore size distribution of the optimized sample (synthesized by method **B**, applying an stirring of 4 h at room temperature followed by an stir-

Fig. 2. XRD spectra of calcined samples prepared by method **B** from a reaction mixture stirred at room temperature for 4 h and then heated for 3 h at 100 °C in autoclave: (a) NaOH as hydroxide source, (b) TEAOH as hydroxide source.

Table 2
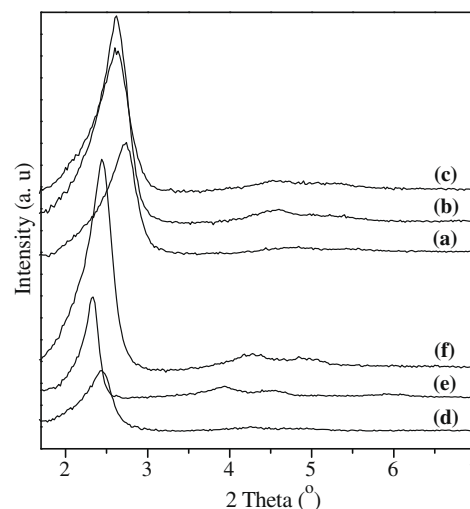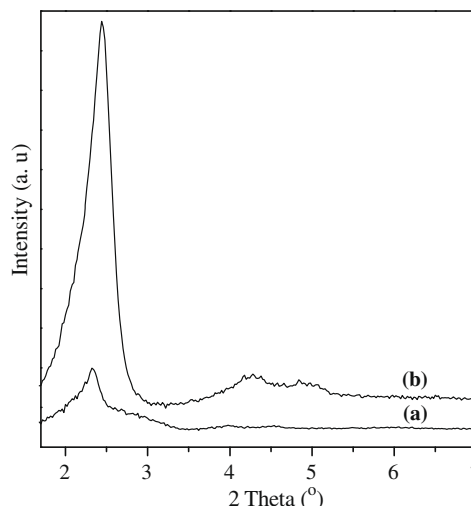Surface areas of the samples synthesized by method **B** using different hydroxide sources.

Hydroxide source	Area (m²/g)
NaOH	1390 (6)
TEAOH	1210 (6)

Fig. 3. XRD spectra of calcined samples produced by method **B** from a reaction mixture stirred at room temperature for (a) 2 h, (b) 3 h, (c) 4 h and from an identical mixture heated under stirring at 70 °C for 3 h after stirring at room temperature for (d) 2 h, (e) 3 h, (f) 4 h.
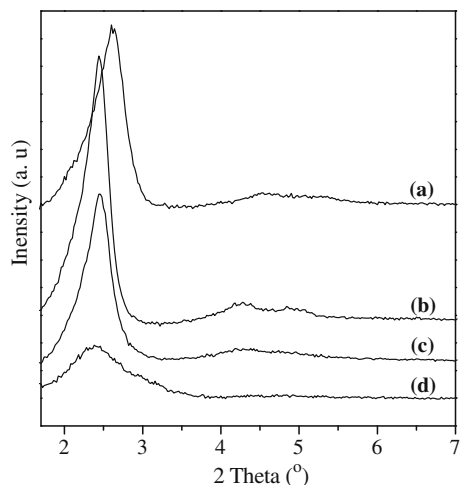
Fig. 4. XRD patterns of calcined samples produced by method **B** from a reaction mixture stirred at room temperature for 4 h: (a) without subsequent heating, (b) followed by heating at 70 °C for 3 h under stirring, (c) followed by heating at 100 °C for 3 h in autoclave and (d) followed by heating at 150 °C for 3 h in autoclave.

Table 3
Surface areas of the calcined samples synthesized by method **B**.

Stirring time (h)	Subsequent treatment	Area (m²/g)
2	Without	1295 (6)
3	Without	1350 (6)
4	Without	1310 (6)
2	Stirring 3 h at 70 °C	1110 (5)
3	Stirring 3 h at 70 °C	1400 (7)
4	Stirring 3 h at 70 °C	1480 (7)
4	3 h Autoclave 100 °C	1290 (6)
4	3 h Autoclave 150 °C	1070 (5)
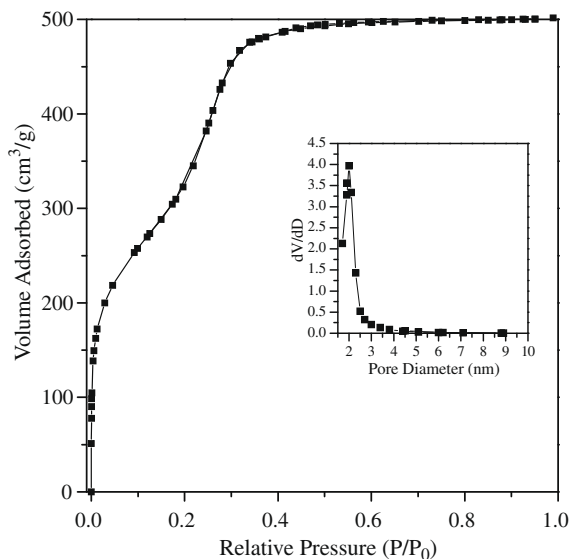
Fig. 5. Nitrogen adsorption/desorption isotherms and pore size distribution (inset) of the calcined sample produced by method **B** from a reaction mixture stirred at room temperature for 4 h and then heated at 70 °C for 3 h under stirring. The pore size distribution is calculated by plotting the derivative of the pore volume and the pore radius (dV/dP against the pore diameter).

ring for 3 h at 70 °C) are shown in Fig. 5. The sample exhibits type IV isotherm according to the IUPAC classification which is typical of mesoporous materials. The curves present a sharp inflection at a relative pressure around $P/P_0 = 0.15$–0.25 and a narrow and

Fig. 6. XRD pattern of a sample produced by method **B** from a reaction mixture stirred at room temperature for 4 h and then heated at 70 °C for 3 h under stirring: (a) 'as-synthesized' and (b) after post-synthesis thermal treatment for template removal ('calcined sample').

strong band in the pore size distribution curve. This feature is typical of well-ordered materials with narrow and uniform pore size distribution [37,38]. The pore volume was calculated from the isotherm by the adsorption at $P/P_0 = 0.95$ [39] and the pore size distribution was calculated from the desorption branches of isotherms using the standard Barret–Joyner–Halenda procedure [40]. The pore volume (V_p) and the pore diameter (D_p) for the sample are 0.906 cm³/g and 2 nm, respectively.

3.2.3. Influence of surfactant removal treatment

In these materials, the thermal treatment to remove the template usually results in a contraction of the inorganic network and is parallel to the exothermic processes associated with such organic elimination. These two linked processes can seriously deteriorate the mesostructure. However, it is interesting to note that the MCM-41 structures obtained by us resulted very stable upon post-synthesis treatments. Thus, Fig. 6 shows the XRD pattern of a sample produced by method **B** 'as-synthesized' and after post-synthesis thermal treatment for template removal ('calcined sample'). As it can be seen, the surfactant removal by heating the sample at 500 °C under N₂ flow and subsequent air flow significantly increased the peak intensities, allowing the resolution of the secondary peaks between 4° and 6° as well. This improvement in the degree of the structure ordering could be attributed to the formation of new Si–O–Si bridges and additional network cross linking [41–43] upon the thermal treatment. In addition, a lattice contraction of 5% associated with this process was also observed.

4. Conclusions

Two basically different synthesis methods have been evaluated in order to optimize the process conditions which allow to obtain a well-defined mesoporous silica phase. We propose an energetically favorable procedure by which a highly ordered MCM-41 structure with high surface area can be synthesized in 6–7 h. This material, prepared by stirring at 70 °C for 3 h a reaction mixture which was previously stirred at room temperature, resulted also stable upon post-synthesis thermal treatments for template removal. In addition, the structural distortion observed when ethanol is used to dissolve the surfactant would be probably caused by an increase

in the surfactant packing parameter 'g' due to the presence of the alcohol at the silicate-surfactant interface. Furthermore, we have also found that the presence of Na plays an important role in the synthesis process. This cation, probably because of its smaller size, allows silica species to approach and sufficiently polymerize to achieve a long-range ordered structure.

Acknowledgements

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