



Synthesis and characterization of 2D-hexagonal, 3D-hexagonal and cubic mesoporous materials using CTAB and silica gel



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ABSTRACT

Highly ordered mesoporous materials SBA family (Santa Barbara Amorphous), with symmetry of two-dimensional (2D)-hexagonal SBA-3, three-dimensional (3D)-hexagonal $P6_3/mmc$ (SBA-7) and cubic $Pm3n$ (SBA-1) were synthesized by a simple and easy procedure, designed using silica gel as a silicon source, CTAB (cetyltrimethylammonium bromide) as a structure-directing agent, in highly acidic conditions. The effect of the variation of temperature and reaction time allowed us to obtain the optimum condition to prepare SBA-1, SBA-3 and SBA-7 materials. The sodium silicate generated “in situ” by dissolution of the silica gel, at different concentrations of NaOH and the variation of the synthesis temperature and reaction time are the three factors which allow obtaining different SBA phases. Thus, the best SBA-3, SBA-1 and SBA-7 materials with well-ordered mesoporous system can be obtained in the range of 0.8, 0.9 and 1.0 NaOH concentration and 30 and 25 °C and 45, 2880, 1440 min (for SBA-3, SBA-1 and SBA-7 respectively).

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1. Introduction

In recent years, physicists, chemists and engineers have focused their research on the design of new functional materials, whose characteristics depend on the specific organization of the inside of molecules. The methods applied, different from classical ones, generate changes in the material properties. By the introduction of new functional groups, features can be modified depending on cluster or grain, organization in several phases, molecular alignment and supramolecular nanoscale [1–3].

In addition, in the synthesis and control of materials in nanometer dimensions, the aim is currently directed towards the development of systems and devices that take advantage of chemical properties and physical principles where their causes lie in the nanometer scale. Investigations into mesoporous materials in Santa Barbara University have led to the development of SBA mesoporous materials [4]. These materials are highly regular in pore form system and arrangement, and their diameter is in the nanometer scale. The mesoporous materials are distinguished from microporous zeolites in their structural skeleton, since they are formed by completely amorphous silica. However, in each of these mesoporous materials, as well as in zeolites and zeotypes, pores have the same diameter and are disposed in a regular manner, i.e., the pore system maintains translational symmetry.

The synthesis of ordered mesoporous materials requires the use of surfactant molecules in aqueous solution. When the surfactant concentration in solution reaches a threshold value, the molecules form aggregates called micelles and supra-micelles. This is a function of the nature and chemical composition of the surfactant molecule, its concentration and temperature, while factors such as pH of solution [5] and total salt concentration also influence the micellar aggregation process. In the synthesis of the ordered mesoporous materials constituted by a skeleton of silica, silicate species in solution are assembled with micelles to give a solid product containing a high amount of surfactant occluded inside.

Two main routes can be followed to obtain mesoporous silica materials: precipitation from aqueous solution of sodium silicate [6,7] or hydrolysis of a silicon alkoxide [8,9]. The last route can provide an excellent material with a regular pore arrangement; yet, the silica precursor used is expensive and the “SiO₂” content is low. However, the silicon source commonly used for the synthesis of mesoporous materials is silicon alkoxide, tetraethylorthosilicate (TEOS) being the most widely used [10–12].

Much research has been conducted in recent years to reduce the cost of the synthesis of these mesoporous materials. Sodium silicate as a silicon source is being used with good results. Pinnavaia et al. exploring alternative routes of synthesis to reduce cost, have prepared mesoporous materials with different templates or surfactants [13,14], in which irregular silica was obtained. Xuelei et al. [15] have studied the influence of the morphology of mesoporous materials using inexpensive silica, by

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conducting a comparative study with materials obtained using TEOS as a silicon source.

Zhou Yun-yu et al. reported a rapid synthesis method of well-ordered mesoporous silica. They studied the effect of CTAB/sodium silicate ratio on the morphology of the mesoporous material and found that a higher weight ratio of CTAB/sodium silicate is beneficial to obtain mesoporous silica with a higher specific surface area and a narrower pore size distribution [16].

Yi Ding et al. [17] obtained ordered mesoporous silica SBA-15 rods with controllable size by using inexpensive sodium silicate as a silica source with no additives.

Although there are numerous investigations into the synthesis of mesoporous materials from an inorganic silicon salt, there are no studies on obtaining SBA-3 by this inorganic route and on the effect of the synthesis conditions on the structure of the material [17].

Ting et al. [18] studied the synthesis of SBA-1 using a template with a relatively short alkyl chain (C_{12} TMACl). They could obtain mesoporous SBA-1 cubic structures, with a high porous system, by using template of short-chain such as dodecyltrimethylammonium chloride. While they were able to determine that the morphology of the materials

obtained is a function of the temperature of the synthesis, Chao et al. [19] have prepared SBA-1 with different pore size using CnTMAX ($n = 14-18$, $x = Cl, Br$) and sodium silicate, synthesizing SBA-1 mesoporous materials employing dilute solutions with pH near 2. A recent study also showed that the formation of mesophases is affected by the presence of the counterions, and templates or surfactants can adopt one or other mesophase. Thus, Che et al. [20] found a phase shift from 2D-hexagonal cubic $p6mm$ into $Pm3n$.

Kim and Ryoo [21] have reported that SBA-1 mesoporous material with 3D-cubic structure was synthesized by using cetyltrimethylammonium chloride (CTACl) as a template. Thus, they realized that they could obtain better cubic structures with lower temperature. Although there are few studies on the application of the structure of SBA-1, researchers were able to obtain significant results when incorporating Ti, Mn and zeolite assemblies into their structure [22–25].

At present, there are few studies of material synthesis and characterization of SBA-7 mesoporous material, with 3D-hexagonal structure $P63/mmc$. This structure has hexagonal channels in three directions. To obtain mesoporous materials, it is necessary to account for the dependence of crystalline phases that the surfactant can adopt. Recently,

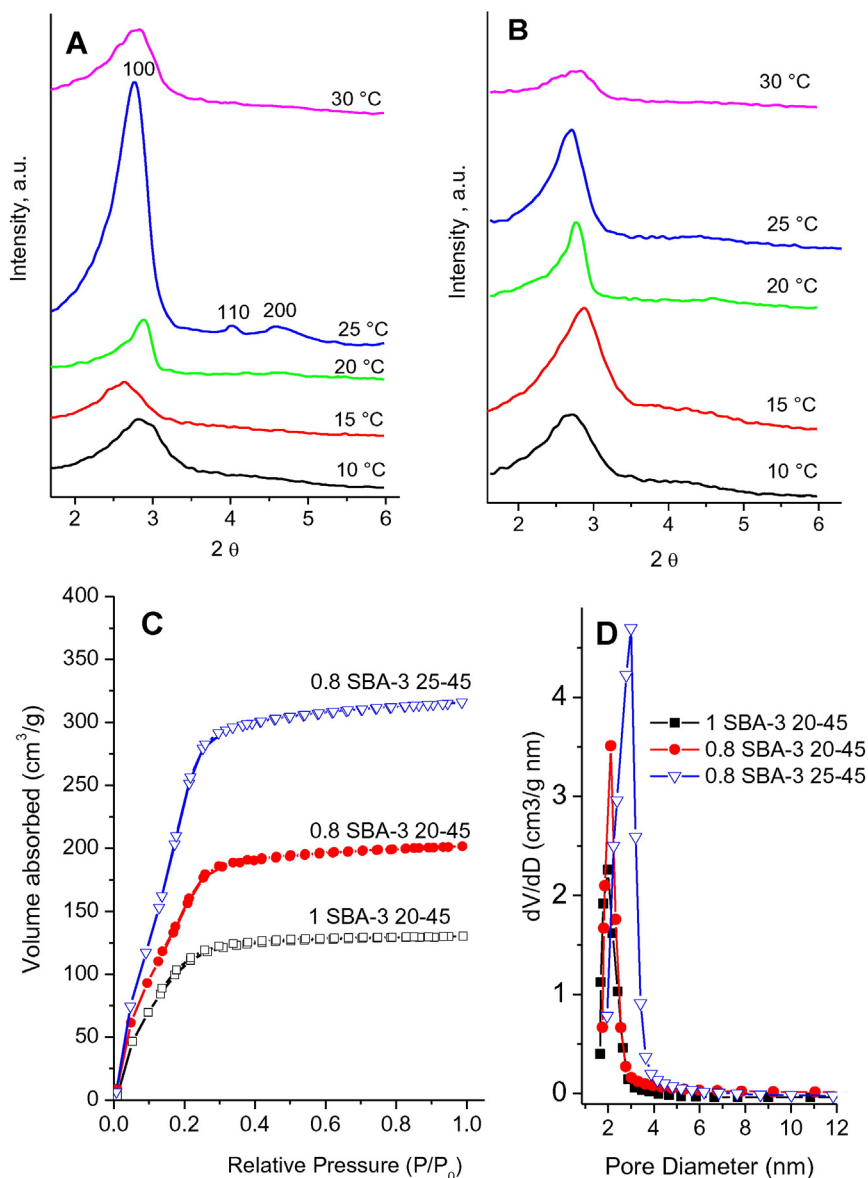


Fig. 1. XRD patterns of mesoporous silica at different temperatures for A) 0.8 M NaOH solution and B) 1 M NaOH solution, and C) and D) N_2 adsorption-desorption isotherms and pore size distribution of SBA-3 samples obtained at different conditions.

we have published results for the synthesis of SBA-3 with silica gel as a silica source [26].

Taking into account the concentration of sodium hydroxide solution, as a single variable, we have found that the formation of mesophase is a function of NaOH concentration in the dissolution of silica gel. Using different concentrations of sodium hydroxide, we obtained mesoporous materials with different pore structure of the hexagonal phase characteristic of SBA-3. However, studies of the influence of temperature and synthesis time are needed.

Thus, in this work, we investigated the influence of synthetic parameters such as temperature, aging time and NaOH concentration. The results for obtaining SBA-3 are therefore partial since more variables need to be further explored to synthesize mesoporous materials with 2D-hexagonal structure. The present study, unlike the previous one [26], also shows the procedure to obtain pure SBA-1 and SBA-7 mesoporous materials.

2. Experimental

SBA mesoporous materials were synthesized according to the procedure described by Martínez et al. [26]. First, we prepared several solutions of sodium hydroxide with different molar concentrations (0.6 to 1 M). Silica gel was then dissolved in the different solutions at 60 °C to obtain sodium silicate. The template was dissolved in an acidic solution. During the synthesis, the solution of the silicate was added dropwise to the template acid solution under continuous stirring. The syntheses were carried out by varying temperature and stirring time. After a given stirring time, the synthesis was stopped and the precipitate obtained was filtered, washed and placed in a drying oven.

The temperature of the synthesis was varied from 10, 15, 20, 25 to 30 °C with reaction times of 45, 120 and 1440 min.

The synthesized materials were named according to the following notation: NaOH concentration, phase type, temperature in Celsius degrees and synthesis time in minutes. Thus, for example, 1 SBA-3 25–120 sample designates: 1 M NaOH, SBA-3 phase; synthesis temperature of 25 °C and 120 min of time of the synthesis. The same notation was used for the other phases, SBA-1 and SBA-7.

2.1. Characterization

The materials obtained were characterized by different techniques: X-ray diffraction, nitrogen adsorption, scanning electron microscopy

(SEM) and transmission electron microscopy (TEM). The XRD pattern was obtained with a PANANALYTICAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and CuK α radiation source. Scans were performed between $2\theta = 1.5$ and 7° at an interval of 0.01 and a scanning speed of $2^\circ/\text{min}$. Nitrogen adsorption-desorption isotherms and pore size distribution were measured on a high-speed gas sorption analyzer (Nova 4000) and samples were first outgassed at 200 °C for 4 h. N₂ adsorption-desorption isotherms and surface area measurements were carried out at 0 °C 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 200 °C to a residual pressure below 104 atm. TEM micrographs were taken on a TEM Philips EM 301 instrument. Direct current electrical conductivity measurements were performed using pellets, improving contact with a silver layer.

3. Results and discussion

3.1. Influence of temperature of synthesis on the mesostructure

3.1.1. SBA-3 mesoporous material

In order to investigate the effect of temperature on the characteristics of SBA materials, samples were synthesized in the temperature range of 10 to 30 °C, taking intervals of five degrees between temperatures. X-ray diffraction was performed in the samples synthesized, where the synthesis temperature was varied and the other variables remained fixed. Fig. 1 A–B shows the diffraction patterns. For concentration of 0.8–1 M of NaOH, we found diffraction peaks at low angles around $2-3^\circ 2\theta$. These peaks are usually characteristic of mesoporous materials.

It is seen that the structure was not formed at temperatures of 10 °C. Signals were broad and peaks at 110 and 200 were not found. Surprisingly, when we perceived the diffraction patterns of materials synthesized at 15 °C, the best materials were obtained at higher concentrations of NaOH (0.8–1 M). A shoulder on the peak between $2-3^\circ$ of 2θ was found, probably due to the generation of another mesophase of the structure-directing agent. The sample obtained at 15 °C exhibits three well-resolved peaks in the range $2-3^\circ$ of 2θ . These peaks were indexed to 110, 002 and 101 diffraction planes, which are characteristic of 3D-hexagonal $P63/mmc$ mesophase. In the diffraction patterns of materials synthesized at 20 °C, we found the hexagonal mesophase characteristic of SBA-3 materials. We detected that, at this

Table 1

Properties of mesoporous samples with two-dimensional 2D-hexagonal (SBA-3), three-dimensional 3D-hexagonal (SBA-7) and cubic (SBA-1).

Sample	a_0 (nm)	S_{BET} (m ² /g)	V_{TOTAL} (cm ³ /g)	D_p (nm)
0.6 SBA-3 10–45	3.92	932	0.35	1.9
1 SBA-3 20–45	3.67	1068	0.53	2.1
0.9 SBA-3 20–45	3.75	964	0.49	1.9
0.8 SBA-3 20–45	3.74	1064	0.53	2.1
0.7 SBA-3 20–45	3.73	995	0.51	2.0
1 SBA-3 25–45	3.78	1250	0.53	2.5
0.8 SBA-3 25–45	3.95	1494	0.65	2.9
0.75 SBA-3 25–45	3.81	845	0.45	1.9
1 SBA-7 25–1440	4.27	962.2	0.72	2.1
0.6 SBA-7 25–120	4.06	948.6	0.72	1.9
0.8 SBA-7 15–45	3.72	887.3	0.71	1.7
0.7 SBA-7 20–120	3.76	892.6	0.71	1.7
1 SBA-7 30–45	3.75	951.0	0.73	1.9
0.75 SBA-1 25–120	8.18	1095.1	0.72	1.9
0.7 SBA-1 25–120	8.21	1081.1	0.71	1.9
0.7 SBA-1 25–1440	8.36	1062.5	0.70	2.3
0.7 SBA-1 25–2880	8.21	1083.4	0.71	1.9
0.9 SBA-1 25–1440	7.65	1165.0	0.71	2.0
0.9 SBA-1 25–2880	7.49	998.0	0.68	1.8
0.9 SBA-1 25–4320	7.11	995.3	0.68	2.2

a_0 : lattice parameter, S_{BET} : surface area, V_{TOTAL} : porous volume and D_p : pore diameter.

temperature, well-defined hexagonal structures were obtained for both concentrations. The studies performed showed that the best hexagonal mesoporous structures were produced using a sodium hydroxide concentration of 0.8 M at a temperature of 25 °C with 45 min of stirring. Under these conditions, it was possible to obtain SBA-3 mesoporous material similar to that achieved with alkoxides (TEOS) as a silica source.

It is well known that temperature is one of the factors that directly influence the synthesis of mesoporous materials; this is a key factor in determining the porous structure of the materials. Many investigations were conducted to understand the cooperative self-assembly between the surfactant and the sources of silicon to form the mesostructure [27].

Due to the effect of solvation and other entropic effects, it is difficult to predict the effect of temperature on the *g* factor (the effective surfactant ion pair packing parameter), without a better understanding of solvation and thermodynamic entropic forces in play. Moderate temperatures (20–25 °C) and higher NaOH concentration (0.8–1 M) accelerate the counterion binding and polymerization of the silicate framework; however, higher temperatures allowed the rearrangement and dissolution of the silicate framework.

Phase changes can be probably accounted for inducing changes in the *g* factor, because of temperature affecting the reorganization of the molecules of the template. In addition, this affects the silicate phase condensation and consequent change of hydration.

Using NaOH concentrations between 1 and 0.7 M, intense diffraction peaks were found in the region between 2–3° 2 θ (not shown), corresponding to diffraction plane 100. Two peaks less intense and broader between 4–5° 2 θ were also found. However, for NaOH concentration of 0.6 M, an intense and broad peak was found with a shoulder; this could be ascribed to the fact that, under these synthesis conditions, the surfactant forms another phase. The optimum temperature for synthesis of SBA-3, based on silica gel as a silicon source, is 25 °C. Under these conditions, we obtained the best material with a mesoporous structure characteristic of SBA-3.

Table 1 shows the structure parameters of samples obtained with structure of SBA-3 synthesized under different conditions. These samples exhibited a specific surface area in the range of 845–1494 m²/g, V_{total} in the range 0.35–0.65 cm³/g and D_p pore size ranging from 1.9 to 2.9 nm.

The N₂ adsorption-desorption isotherm for mesoporous materials is typical of SBA-3 structure (Fig. 1 C and D) and exhibits a significant uptake at $p/p_0 = 0.10$ –0.20. The isotherm can be classified as type IV showing a small hysteresis loop. We observed that the samples show a narrow and uniform pore distribution. A slightly increase in lattice parameter and pore size was observed for samples synthesized with a 0.8 M concentration; i.e., 0.8 SBA-3 25–45 revealed pore size from 2.9 nm, BET specific surface area of 1494.07 m²/g and pore volume in the range of 0.65 m³/g. The TEM image in Fig. 2 A–C corresponds to a SBA-3 mesoporous material with the typical hexagonal array for the samples, 1 SBA-3 20–45, 0.8 SBA-3 20–45 and 0.8 SBA-3 25–45. We could observe that all samples exhibited ordered mesoporous structure with longitudinal channels in a significant long range.

3.1.2. SBA-7 mesoporous materials

During research on how temperature affects the mesoporous structure, some samples showed a pattern of X-ray diffraction characteristic of 3D-hexagonal mesostructure.

Fig. 3A shows XRD patterns of SBA-7 mesoporous silica. Three well-resolved peaks were observed for SBA-7 in the range of 2 $\theta = 1.5$ –3°, indexed to 1 0 0, 0 0 2 and 1 0 1, and three weak peaks in the range of 3.5° to 6° were indexed to 1 1 0, 1 0 3 and 1 1 2 diffractions characteristic of 3d-hexagonal P63/*mmc* mesophase [28]. With the unit cell parameters, $a = 4.05$ nm and $c = 6.63$ nm, giving a c/a ratio of 1.637, close to the ideal c/a ratio of 1.633 for the hexagonal close-packed (hcp) structure of hard spheres. Fig. 3 B and C, show N₂ sorption isotherms and pore size distribution of SBA-7 samples. It can be observed that they

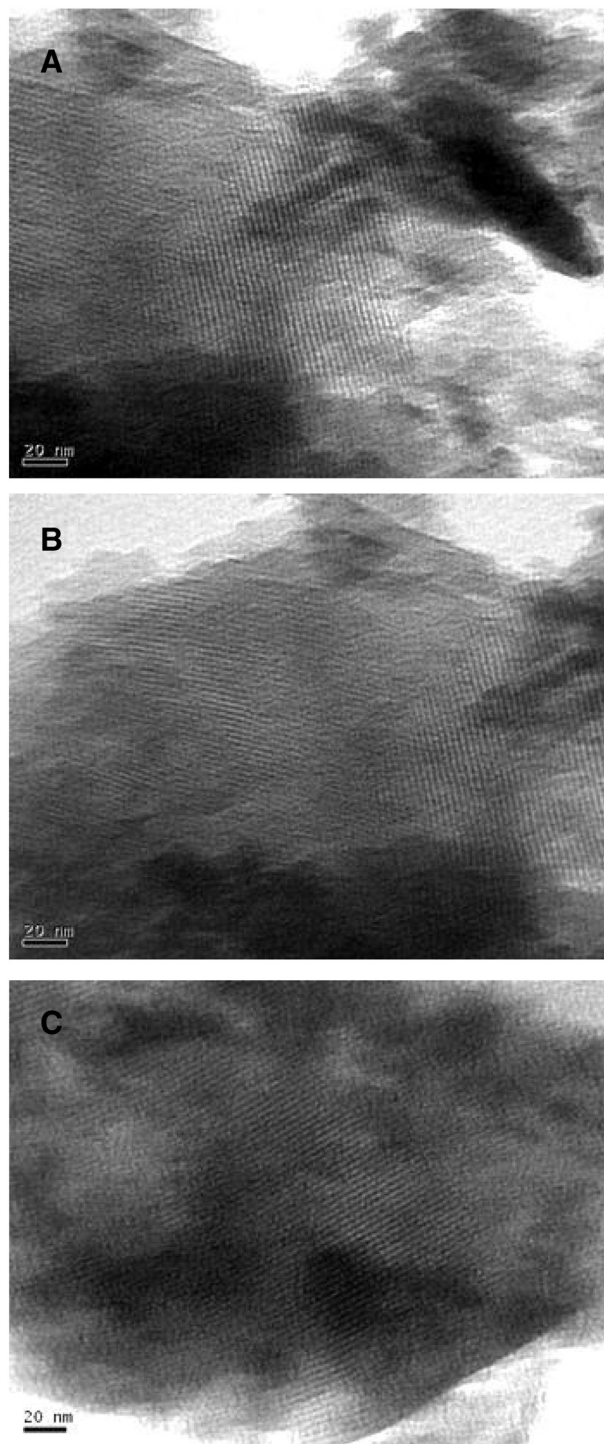


Fig. 2. TEM microscopy of SBA-3 mesoporous materials synthesized at different reaction conditions. A) 0.8 SBA-3 25–45, B) 0.8 SBA-3 20–45 and C) 1 SBA-3 20–45.

are type IV isotherms. The graphics show one well-defined step typical of type IV isotherms, which can be attributed to capillary condensation of nitrogen inside the mesopores, exhibiting a wide capillary condensation step from relative pressure 0.2–0.5. We could not observe a significant hysteresis loop or curve shape; this represents a narrow and uniform pore distribution, which indicates that the materials obtained have a good structural quality. The average pore size is within the range of 1.7 and 2.1 nm.

Table 1 shows that the SBA-7 phase, sample 1 SBA-7 25–1440, has a surface area of 962 m²/g, a pore volume of 0.72 cm³/g, with a pore

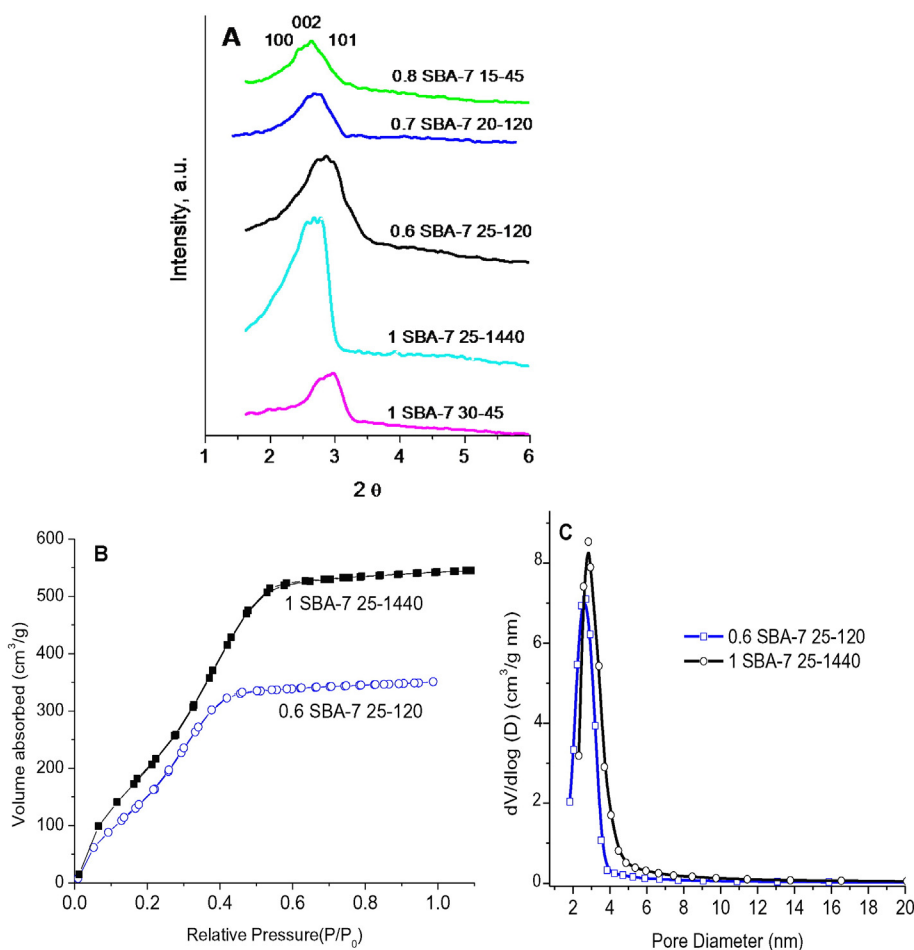


Fig. 3. A) XRD patterns of SBA-7 mesoporous silica at different conditions, B) and C) N_2 sorption isotherms and pore size distribution of SBA-7 samples.

diameter of 2.1 nm. This material has good structure according to X-ray pattern and properties analysis.

We can observe that the as-made silica/surfactant composites can be spontaneously packed into ordered hexagonal mesostructures ($p6mm$) with uniform large bimodal mesopores. We attribute the formation of this quasi-stable mesostructure to the synergistic effect between the assembly speed of the preformed spherical micelles as the building mesoblocks and hydrolysis and condensation of the silica precursors. Hence, few protons are located around the micelles, leading to low curvature with the formation of $P6_3/mmc$ phase and increasing the charge density of the head of the surfactant.

3.2. The effects of crystallization time

It is well known that the surfactant used for this synthesis has a phase diagram in which three structures can be obtained: hexagonal, cubic, lamellar.

When the synthesis time was varied, different behaviors were observed in the materials obtained. The times used were 45, 120 and 1440 min. Fig. 4 A and B depicts the materials obtained when synthesis time varied towards higher values.

The materials obtained at 25 °C exhibit different structural arrangement of SBA-3 hexagonal mesoporous (Fig. 4C). XRD patterns show well-defined structures such as SBA-7 at a concentration of 0.6 M; at concentrations higher than 0.6 M, the mesoporous structures observed were SBA-1 type. When the synthesis temperature was 30 °C, no formation of hexagonal mesoporous structures was observed. It should be noted that, at this temperature and time, SBA-7 type materials were

obtained. A loss of porous structural order was observed when time was increased at 25 °C. Fig. 5 depicts XRD patterns of SBA-1 materials obtained at 25 °C and different times. The SBA-1 samples show three well-resolved sharp XRD peaks in the region of $2\theta = 2\text{--}3.0^\circ$, which are indexed to the 200, 210 and 211 diffractions, corresponding at the cubic system according to P. Srinivasu et al. [29].

Transmission electron microscopy confirms the mesophase obtained by XRD of SBA-1 material. Fig. 5B shows the micrograph of the 0.9 SBA-1 25–2880 sample, displaying the three-dimensional arrangement characteristic of mesostructured SBA-1 materials. The image shows high degree of periodicity over large areas.

Fig. 5C–D shows N_2 isotherms and pore size distribution for SBA-1 materials. The isotherms obtained can be classified as type I. Isotherms show a small hysteresis loop and a pore size below 2.3 nm for all samples.

Many studies report the synthesis procedure to obtain SBA-1 type material, using CTAB (cetyltrimethylammonium bromide) under various synthesis conditions. Che et al. [30] obtained SBA-1 materials using this type of surfactant in highly acidic conditions. Goletto et al. [31], obtained SBA-1 mesoporous materials using the same surfactant employing a mixture of sources of silicon (TEOS + phenyl-containing silane) during the synthesis process. They determined that the mixture is important to maintain the cubic structure desired. Table 1 summarizes the properties of SBA-1 mesoporous silica. All SBA-1 samples have large BET surface area ($\sim 1000 \text{ m}^2/\text{g}$) and pore volume of 0.68–0.75 cm^3/g .

The effect of synthesis time creating the mesostructures can be understood by considering the properties of the surfactant CTAB, which

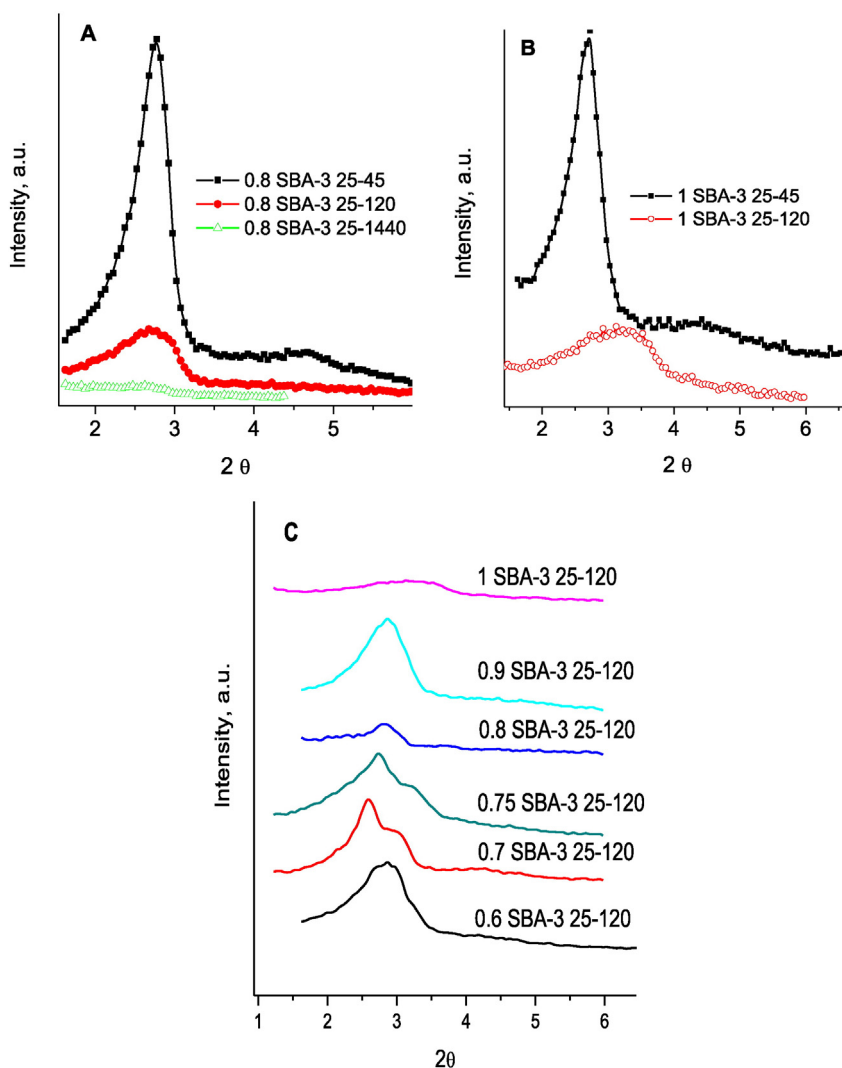


Fig. 4. A, B) XRD of SBA-3 obtained at different synthesis for 0.8 and 1 M NaOH and C) XRD of materials synthesized at constant temperature but different NaOH concentration and reaction time.

has a hydrophobic tail and a hydrophilic head group. This type of surfactant has the ability to self-assemble when its concentration exceeds the critical micelle concentration. The surfactant is packed to fill space in a manner that maximizes the Van Der Waals force between hydrophobic tails and minimizes the repulsive forces between the heads with positively charged group.

It is known that the cooperative assembly between organic surfactants and inorganic precursors results in organic/inorganic mesostructured composites. Mesoporous materials are obtained after removal of template from as-synthesized organic-inorganic composite. Without these surfactants the mesostructured materials could not be obtained.

Under acidic conditions, Stucky et al. [32,33] proposed the synthetic route $S^+X^-I^+$ (S^+ = surfactant cations, I^+ = inorganic precursor cations, and X^- = anionic counterions), where counterions are required. In our case, X^- is halogen ion (Cl^-). In a strongly acidic medium, the initial $S^+X^-I^+$ interaction through Coulomb forces or, more exactly, double-layer hydrogen bonding interaction, gradually transforms into $(IX)^-S^+$. The anions affect the structure, regularity, morphology, thermal stability and porosity of mesoporous silica. The synthesis of mesoporous materials is faster at a low pH of the synthesis solution. The higher concentrations of HCl induce the increased precipitation rate. When HCl concentrations are higher and $pH < 1$ is achieved, the best results are obtained, since at pH between 1 and 2, minor precipitation rates are obtained, probably due to proximity to the isoelectric point of silicon.

Many researchers have shown that sodium metasilicate (Na_2SiO_3) can be used as a silicon precursor as it can generate small oligomers of silicon in the synthesis process in acid medium. This precursor has the ability to form monomers and oligomers leading to irreversible polymerization under highly acidic conditions [34–36]. Similarly, in the process of mesostructure synthesis, sodium salts are generated, which favor the formation of mesostructures. With the addition of inorganic salts, Yu et al. [37] found that high-quality SBA-15 can be synthesized even at low temperatures ($10^\circ C$) and low triblock copolymer P123 concentrations. In the solution synthesis, the reaction temperature is relatively low. The most convenient temperature is room temperature. Two factors were important: Critical Micellar Temperature (CMT) and Cloud-Point (CP) to select temperature. The temperature is normally higher than the CMT values of the surfactants. The CMT values are relatively low for cationic surfactants. In the templating cases of the cationic surfactant, the assembly rate of the templating surfactants slows down with the decrease in the synthesis temperature, facilitating the preparation of high-quality mesoporous silicates. Heating is unnecessary and room temperature of preparation is feasible [38].

4. Conclusions

Obtaining best mesoporous structures with a specific porous system has become a challenge, particularly when researchers not only seek the

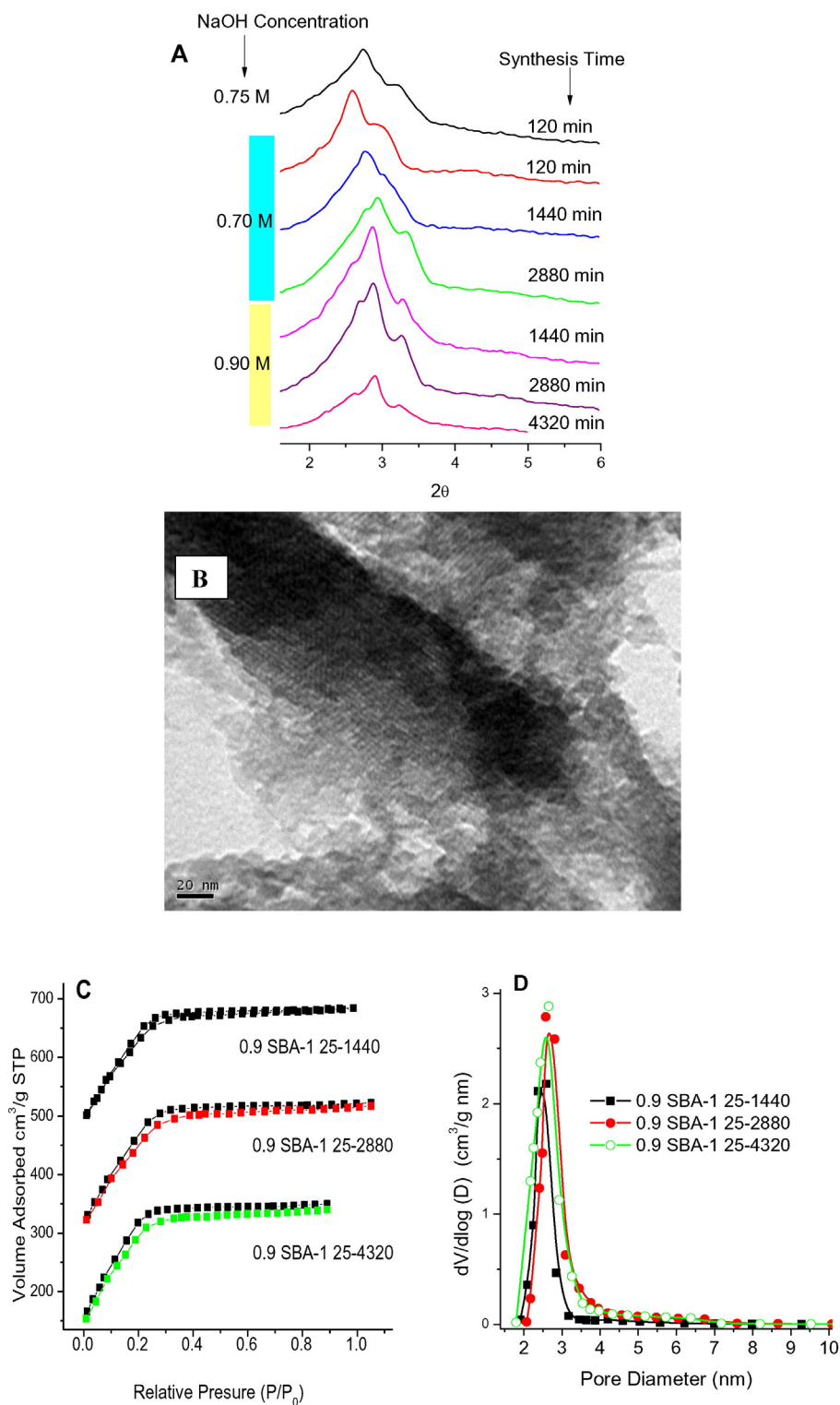


Fig. 5. A) XRD of SBA-1 materials synthesized at 25 °C and different reaction conditions, B) TEM microscopy of SBA-1, sample 0.9 SBA-1 25-2880 and C) and D) N_2 sorption isotherms and pore size distribution of SBA-1 samples. The isotherm profiles of the samples are vertically shifted by 150 cm^3/g , 325 cm^3/g , and 500 cm^3/g , respectively.

best mesophases, but also accomplish a lower production cost to take it to the industrial scale. SBA-3 material was obtained starting from silica gel (filling chromatographic columns) as a silicon source instead of expensive TEOS. This study allowed us to determine that the optimum synthesis conditions were 25 °C, concentration of sodium hydroxide of 0.8 M and 45 min of synthesis time. The typical SBA-3 mesostructure yielded was evidenced by XRD, N_2 isotherms and TEM. Similarly, during

the variation of synthesis conditions, we obtained two additional structures: such as SBA-7 materials with porous structure well-ordered 3D hexagonal and SBA-1 materials with cubic mesophase. SBA-7 ($P6_3/mmc$) was obtained under certain conditions of temperature and time. As the synthesis time was increased, a change was evidenced in the arrangement of the micelles of surfactant, from cubic to hexagonal structure itself. When the stirring time increased from 45 min to 24 h, SBA-1

structures were observed with a good cubic system. In this research, we were able to obtain mesoporous structures of high structural system, using CTAB as a template agent and Silica gel as a silicon source.

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