

# Ion exchange columns for the synthesis of ordered mesoporous materials

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**Abstract** Structured mesoporous materials were successfully synthesized using an ion exchange column as protons source. Operating conditions were set in order to obtain mesostructured materials using short operation times. This method opens the door to the industrial synthesis of this kind of materials. The ordered mesoporous materials were obtained using sodium silicate solution as a precursor and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO<sub>19</sub>PO<sub>39</sub>EO<sub>19</sub> denoted as P84) was used as structure-directing agent. The influence of the composition variables (surfactant and precursor concentrations) was studied. The materials were characterized by TEM, SAXS and nitrogen adsorption–desorption isotherms to determine their specific surface area. A response surface was obtained, showing that in the studied range the ratio sodium silicate:water was the most significant parameter in order to obtain the materials with a well-structured pore arrangement. The use of sodium silicate solution as silica source instead of TEOS or TMOS, and the possibility of obtaining a material through an ion exchange column are important from the application point of view because of the relatively cheap raw materials and equipments. Presented results indicate that for every precursor:water:surfactant system an optimum experimental operating conditions must be selected once the reactants flow rate has been set.

**Keywords** Structured silica · Ion exchange column · Sodium silicate

## 1 Introduction

Ordered mesoporous materials have pore diameters in the 2–50 nm range and exhibit long-range order [1]. These materials possess unique structural characteristics and have a wide range of potential applications. While searching for new, high surface area, ultra-large pore catalytic materials, scientists at Mobil Corp discovered that some of their synthetic procedures yielded solid, powdery products characterized by the presence of regular, ordered pores with diameters from 1.5 to over 10 nm and high surface area [2, 3]. Different structures can be obtained by carefully choosing the template, and this means choosing the surfactant. Surfactants act as structure director agents. So a surfactant chain length variation may result in an increase or decrease in the mesopore sizes that are obtained. Two surfactant families are commonly used for the synthesis of mesostructured materials: nonionic surfactants and triblock copolymers. Both families give SBA-15 type materials [4].

Industrial viability of this synthesis has been discussed by several authors in the last decade [7–11]. Some authors consider that the process is not industrially viable because two critical reasons. The first is related to the precursor used as a silica source, which is usually TEOS or tetramethylorthosilicate (TMOS). As various authors have reported [7–11], these precursors are quite expensive and therefore their use represents a material cost disadvantage for producing mesostructured materials. Another problem with the use of TEOS is the production of ethanol as a reaction by-product, because ethanol breaks the surfactant structure leading to obtain non ordered mesoporous materials. In the last decade efforts have been made to reduce the cost by using inexpensive sodium silicate as a silica source to replace TEOS.

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When TEOS or TMOS is used, the formation of the silica network involves two consecutive reactions. An initiation reaction, the hydrolysis, leads to the formation of hydroxyl groups Si–OH. Then a successive reaction, the condensation, involves the formation of bridging oxygen. In strong acid conditions, hydrolysis and condensation occur synchronously, while at around  $\text{pH} = 2$ , the rate of condensation is far lower than that of hydrolysis [5–7]. Replacing TMOS or TEOS by sodium silicate, the silicate solution is composed of a variety of silica oligomers with different degrees of polymerization. In that case, the quality of materials depends strongly on the polycondensation, pH and ion concentration in the solution. To create favorable interactions between the surfactant and the silica species, the pH has thus been decreased by the addition, of an acid or by the resin proton source. As a result of a  $\text{S}^0\text{I}^0$  mechanism [11] leads to the mesopore ordering. The protonated water molecules are hydrogen bonded to the oxygen atoms of the oxyethylene groups of the surfactant.

The great advantage of the  $\text{S}^0\text{I}^0$  pathway [12, 13] is that it relies on H-bonding between  $\text{S}^0$  and  $\text{I}^0$  and circumvents charge matching constraints. Consequently the pathway affords more fully cross-linked framework structures in comparison to mesostructures formed through electrostatic  $\text{S}^+\text{I}^-$  and  $\text{S}^0(\text{H}^+\text{X}^-)$  pathways [14].

In this work, ordered mesoporous materials were obtained using ion exchange resin columns. The synthesis of the mesoporous materials is based on a Cooperative Templating Mechanism (CTM). In the initial step, the interactions between silica micelles drive to the formation of an organic–inorganic mesophase in the resin column. Then, the condensation of the inorganic precursor at the external surface of the micelles occurs. The ordered mesophase is obtained after intermicellar condensation. Finally, the hydrothermal treatment at higher temperature completes the assembly of micelles and the polymerization of the silica source.

The influence of the composition variables (surfactant and precursor concentrations) on the material pore ordination and specific area were studied in order to determine the most favourable conditions to obtain mesostructured materials using cation exchange resin columns as source of  $\text{H}^+$ . The results were compared with the ones obtained using a batch reactor [11].

## 2 Materials and methods

### 2.1 Materials

The triblock copolymer of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) Pluronic P84,  $(\text{EO})_{19}(\text{PO})_{39}(\text{EO})_{19}$  was supplied by Sigma Aldrich.

Sodium silicate solution ( $\text{Na}_2\text{O} \approx 10.6\%$  and  $\text{SiO}_2 \approx 26.5\%$ ) 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  $\geq 1.7$  mmol/mL and particle size of 0.355–1.18 mm supplied from Merck was used in all the experiments. The ion exchange resin packing column was 23 cm height and 2.80 cm of diameter.

### 2.2 Methods

#### 2.2.1 Determination of breakthrough curves

First of all, 100 mL of HCl (2 M) were passed through the column in order to assure having the resin in acid form. Subsequently, the resin was washed with 200 mL of deionized water to remove the remaining HCl solution.

Sodium silicate: water solution was passed through the ion exchange column. Experiments were performed using three different sodium silicate solution:water mass ratios, and using a constant flow rate of 24.95 mL/min to maintain the same hydrodynamic conditions in all the experiments. pH measurements were performed over time in the lower outlet of the column until the final pH reached a value of approximately 95% of the initial pH of the solution.

When each experiment was finished, the remaining sodium silicate in the ion exchange column was removed by treating the resin with a NaOH (1 M). The resin was washed with deionized water, and the column was ready to be regenerated again with HCl solution.

Once breakthrough curves were obtained, maximum operation time is set due ordered mesoporous materials obtained by CSA method requires  $\text{pH} < 2$ , so the experiment must end before the silica:water:surfactant solution reaches  $\text{pH} = 2$  in the lower outlet of the column.

#### 2.2.2 Preparation of ordered mesoporous materials

Once ion exchange resin column breakthrough curves were obtained for every sodium silicate solution: water ratio, experiments were performed with the aim of obtaining ordered materials. The knowledge of breakthrough curves determines the maximum operating time for every flow rate in order to have a pH solution value lower than 2. Using this criterion, it was decided that 1:30 silicate solution:water ratio had a 8.5 min operation time, 2:30 ratio a 4.5 min and 3:30 ratio a 3 min time.

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. The final solution was allowed to cool to room temperature and the sodium

silicate solution (Na<sub>2</sub>O 10.6 % and SiO<sub>2</sub> 26.5 %) was added. The resulting solution was added to the column by a pump at constant flow rate and the outlet of the column was collected in a beaker.

Once the final operation time was reached, the column outlet was closed and the solution obtained from the column was introduced into a bottle to be left 24 h in the oven at 105 °C in order to achieve a white silica precipitate, i.e. the mesoporous material.

The bottle content's stove was filtrated using a vacuum pump and a Buchner funnel and the obtained silica material was left to dry at room temperature before being calcined. Finally, the material was calcined for 5 h at 550 °C to remove residual surfactant. The appearance of the material obtained was a white powder.

### 2.2.3 Characterization

**2.2.3.1 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, mesoporous material 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.

**2.2.3.2 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.

**2.2.3.3 N<sub>2</sub>-sorption analysis** The specific surface area of the mesoporous silica materials were determined by N<sub>2</sub>-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.

## 3 Results and discussion

Prediction or interpretation of the breakthrough curve is a key step in the engineering design of fixed beds. For a specified system, the stoichiometry, equilibrium and type of mechanism usually remain constant during scale-up. Generally, the breakthrough curves must be determined experimentally, due to the difficulty of prediction. Experiments were performed using three different sodium silicate solution:water mass ratios and constant flow rate in

order to model the reactor inside the ion exchange resin. Flow rate was chosen to assure enough operation time. Figure 1 shows the different curves obtained. The curves represent the pH at the outlet, and the breakthrough curve is obtained from the data between 5 and 95 % of the maximum variation of pH.

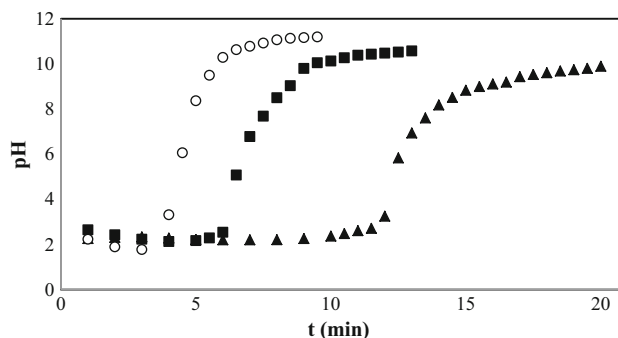
The time elapsed since the beginning of the operation in the column until the pH in the output current corresponds to the minimum pH + 5 % of the variation of pH is called rupture time or, more specifically, rupture time is when the maximum allowable pH is reached at the output current. Until the rupture time, ion exchange happens in the column and the pH of the output current is adequate for forming the material.

In comparison, it can be seen that the rupture time is less for the ratio 3:30, followed by 2:30 and finally the ratio 1:30 silicate:water ratio, as expected. For each silicate:water ratio, the column can be operated until its corresponding rupture time.

According to Michaels model [15] the exchange zone can be defined as the part of the column where ion exchange takes place and that moves down with time while the resin above the exchange zone is exhausted and the part below it remains fresh. The exchange zone length remains constant with time and can be calculated as follows:

$$Z_a = Z \frac{\theta_a}{\theta_A - (1-f)\theta_a}$$

where  $Z_a$  is the length of the exchange zone,  $Z$  the total length of the ion exchange resin column,  $\theta_A$  is the time needed to reach a concentration (or pH in this case) 95 % of the initial concentration at the treated solution,  $\theta_a$  corresponds to the time needed to pass from a concentration 5 to 95 % of initial one at the treated solution (which means the time required by the exchange zone to move down its own length,  $Z_a$ ) and  $f$  is the non saturated fraction of resin in the exchange zone and it is calculated from breakthrough curves.



**Fig. 1** Rupture curves for sodium silicate solution:water mass ratio 1:30 (black triangles), mass ratio 2:30 (black squares) and 3:30 (white circles) for a constant flow of 24.95 mL/min

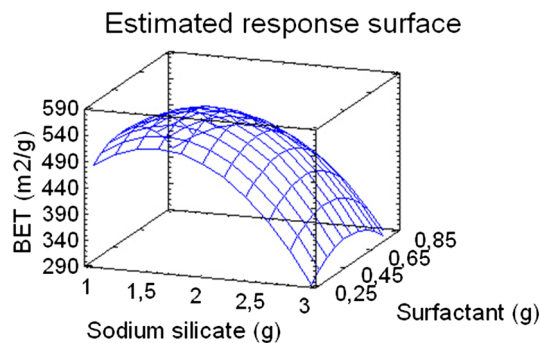
For the three silicate solution:water ratios the length of the exchange zone was the same in agreement with the Michaels model, and its value was around 5 cm, being the residence time of the fluid in that zone of 1 min for all experiments.

Several experiments were carried out (Table 1) in order to obtain the water/surfactant/sodium silicate solution range in which it is possible to get mesoporous materials with ordered mesopores. These experiments were done using a constant weight of water and different surfactant and sodium silicate solution weights.

Operation time was obtained from breakthrough time. Silica condensation occurs at  $\text{pH} < 2$  because in the range of  $\text{pH} 2\text{--}4$  the silica polymerization is very slow [16]. To assure that the column outlet solution had  $\text{pH}$  lower than 2 the operation time was set 80 % of the time that produced  $\text{pH} 2$ . So, for the sodium silicate solution:water mass ratio 1:30 it was 8.5 min, 4.5 min for the ratio 2:30 and 3 min for the ratio 3:30.

Specific surface area was measured for mesoporous material obtained from each experiment and results were analysed by Statgraphics 5.1 in order to calculate the surface response graphic (Fig. 2).

Obtained materials presented specific surface areas between  $230 \text{ m}^2/\text{g}$  and  $575 \text{ m}^2/\text{g}$ , being mostly with specific surface areas greater than  $400 \text{ m}^2/\text{g}$ . SBA-15 materials have specific surface areas between  $400 \text{ m}^2/\text{g}$  and  $850 \text{ m}^2/\text{g}$  [17]. In this way, we can say that obtained materials using the ion exchange column and sodium silicate, although they are in the lower range of the specific surface area of SBA-15 materials, they achieve the requirements of SBA-15 with the advantage of the use of much cheaper precursor (sodium silicate) than SBA-15, which uses TEOS.



**Fig. 2** Surface response graphic for specific surface area of the mesoporous materials obtained

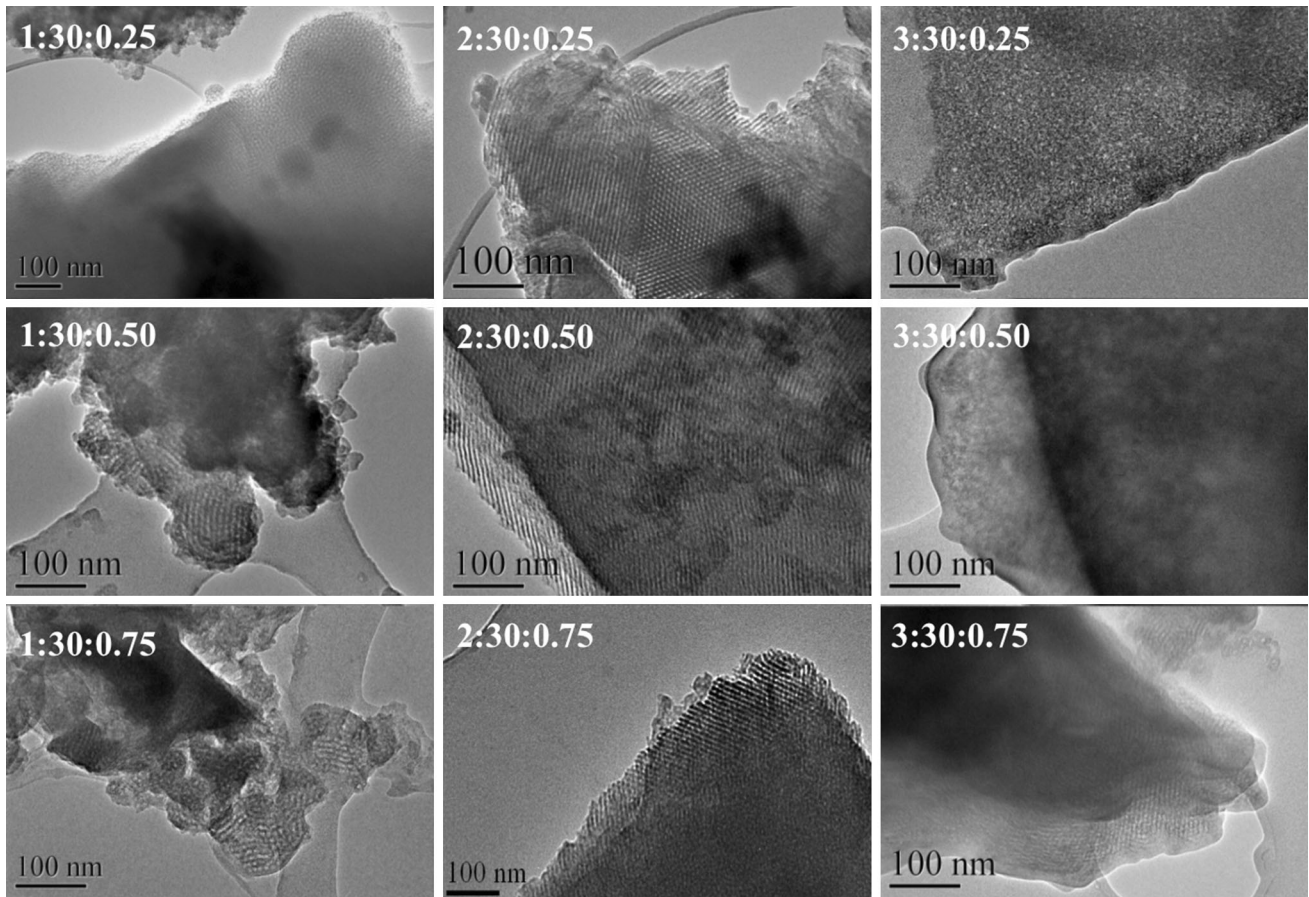
As it can be observed, sodium silicate concentration is the most significant variable regarding the influence in specific surface area, in the range studied. Surface area presented a maximum in the studied range. Figure 3 shows TEM images for the materials.

TEM images for silicate solution:water:surfactant ratio 1:30:0.25 do not show any order but when surfactant concentration raises to 0.50 and 0.75 some order appears. When the silicate solution:water ratio is 2:30 all the materials, regarding the surfactant ratio, presented ordered zones. This behaviour was also observed in a previous work where materials were obtained in a batch reactor [11]. The 2:30 silicate solution:water ratio corresponds to the maximum observed in the surface response graphic (Fig. 2). So, the more ordered structure of the material, the more specific surface is obtained. For materials with a silicate solution:water ratio 3:30 the structure of the pores disappears and the BET area decreases.

Figure 4 shows the nitrogen adsorption–desorption isotherms for different experiments. Only some isotherms are shown as examples. It can be observed that for the ratio

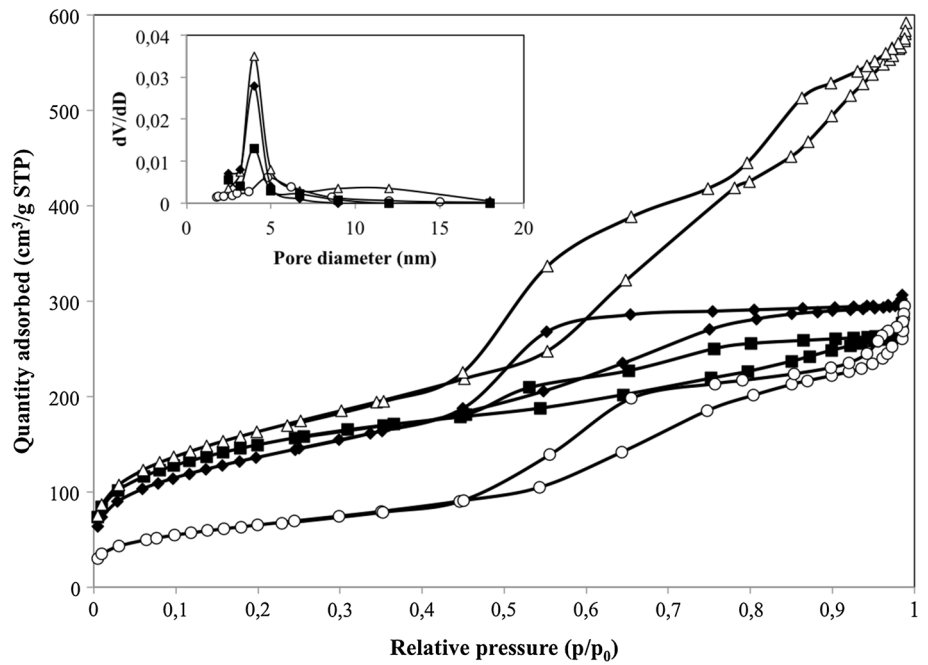
**Table 1** List of the carried out experiments: specific surface area ( $S_{\text{BET}}$ ) and pore diameter ( $\phi$ ) as a function of the surfactant quantity and sodium silicate amount

Experiment	Operation time (min)	Final pH	Weight [g]			$S_{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	$\phi$ [nm]
			Sodium silicate	Water	Surfactant		
1	8.5	1.63	1	30	0.25	450	5.2
2	8.5	1.60	1	30	0.50	398	4.6
3	8.5	1.64	1	30	0.75	419	4.7
4	4.5	1.54	2	30	0.25	481	4.1
5	4.5	1.68	2	30	0.50	575	3.9
6	4.5	1.59	2	30	0.75	508	4.7
7	3	1.72	3	30	0.25	345	6.6
8	3	1.70	3	30	0.50	232	7.2
9	3	1.68	3	30	0.75	355	5.0



**Fig. 3** TEM images for the obtained materials with different sodium silicate:water:surfactant mass ratio

**Fig. 4** Evolution of the nitrogen adsorption–desorption isotherm and pore size distribution for different sodium silicate: water: surfactant ratios: 2:30:0.25 (black diamonds), 2:30:0.50 (white triangles), 2:30:0.75 (black squares) and 1:30:0.50 (white circles)

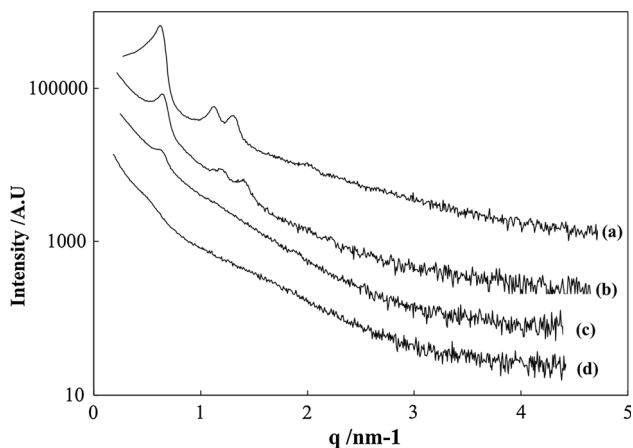


2:30:0.50 the isotherm shape is of type IV, typical from the mesoporous materials, with a broad hysteresis cycle.

It can be observed that the isotherms obtained with materials prepared with ratios of 1:30:0.50 and 2:30:0.75 show lower hysteresis than the one obtained with 2:30:0.50. Here again, we can conclude that there is an optimum sodium silicate concentration, which gives structured mesopores leading to a maximum surface area.

Moreover, TEM images and SAXS data show that the most ordered structure was obtained when 2 g of sodium silicate was used (2:30:0.50) as can be observed in Figs. 3 and 5.

Figure 5 shows SAXS results for some of the obtained materials. SAXS pattern confirmed TEM images conclusions about mesopores structure. For the material with the ratio 1:30:0.50 the pattern presented no peaks indicating it was a disordered material although TEM image presented some ordered zones. It seems that the materials prepared with 1:30:0.50 and 1:30:0.75 combine ordered and disordered zones and SAXS analysis shows a global vision of the samples, which is not capable to detect partial order. The same results were obtained for all the materials with ratios of sodium silicate: water 1:30 and 3:30. For the material synthesized using a ratio silicate:water:surfactant 2:30:0.50 two peaks were detected in addition to an initial sharp peak. The presence of these two peaks suggests a hexagonal organization of the channels. This arrangement was given by the surfactant used, P84, and it has been studied in previous works [11, 18, 19]. The pore order was progressively lost while surfactant concentration changed. For the material with the same sodium silicate: water ratio and a lower surfactant ratio the order of the pores is kept and a hexagonal structure can be seen. When the surfactant ratio is increased, at sodium silicate solution:water:surfactant ratio 2:30:0.75, only one peak is detected indicating



**Fig. 5** SAXS pattern for materials with different sodium silicate: water: surfactant ratios (a) 2:30:0.50 (b) 2:30:0.25 (c) 2:30:0.75 and (d) 1:30:0.50

that although the TEM image of this material (Fig. 3) showed an ordered material this structure should be local, and not all the material presented an ordered pore structure.

From the results obtained it can be assumed that if the sodium silicate ratio is too small there is no enough silicate to surround all the structure created by the surfactant in a properly way, resulting in disordered materials. It can be observed that an excess of precursor decreases the specific area of the material. This behaviour was previously reported by Stébé et al. [20] 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.

Results obtained in the present work were compared with the ones previously reported [11]. It can be observed that using an ion exchange column along which solution flows in order to exchange  $\text{Na}^+/\text{H}^+$  specific surfaces areas are generally greater than the ones obtained using a batch reactor where ion exchange resin is dispersed. When a column is used,  $\text{Na}^+/\text{H}^+$  exchange progressively takes place along the exchange zone,  $z_a$ , approaching to a tubular reactor flow. However, a faster exchange occurs when a batch is used, the protons instantly acidify the media and allow the silicate condensation around the surfactant micelles, which occurs very fast. So, condensation takes place more slowly when a column is used, allowing the silicate to slowly surround the surfactant structure and resulting in more pore ordination and more specific surface.

Regarding influence of surfactant ratio in the obtained materials, it can be appreciated that a maximum in specific surface is obtained too. This maximum is not so evident as that obtained for the silicate influence. In a previous work [11] it was established that the obtaining of mesoporous materials was influenced by the surfactant solution:water ratio, which presented an optimum in the studied range. According to the results, 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 depends on the surfactant concentration. When the concentration of surfactant is too high, at fixed sodium silicate and water, many condensation nuclei appear simultaneously and very fast, so they probably cannot grow very much, and only short cylinders can be formed that cannot arrange in an ordered way.

Mesoporous materials preparation in ion exchange resin columns may be a solution to the problem of their industrial production. Ion exchange resin columns presented an

easy scale-up as long as the relationship between volumetric flow and column dimensions was set constant.

Obtained materials may not possess, in some cases, a complete ordination in the pore structure, but for some applications this order is not always needed. Sometimes high enough specific surface and a selective pore diameter (pore diameters that ease the entrance of desired molecules and avoid the bigger ones) are the main criteria factors to choose the material.

#### 4 Conclusions

In this work mesoporous materials have been obtained using an ion exchange column as a  $H^+$  source. Precursor used was sodium silicate as silica source, which is much cheaper than others used traditionally, like TEOS or TMOS. The use of sodium silicate solution is easier for the operation of the column and from the industrial point of view because TEOS or TMOS reacts with the humidity of the air and it makes difficult the process.

The most relevant point of this work is the use of an ion exchange column to obtain mesostructured materials. The silicate solution travels along the column progressively exchanging ions as it crosses the exchange zone. So condensation occurs approaching to a tubular reactor flow, in contrast to the mixed reactor used in a previous work. Resulting materials possess high specific surfaces areas, placing them in the SBA-15 mesoporous materials range. As long as hydrodynamic conditions of the column were set constant it could be scaled-up. Moreover, that system prevents the presence of free ions in the media and, consequently, no washing is required.

The study of the influence of composition variables in the specific area and order shows that an optimum of sodium silicate: water ratio exists. For too high silicate concentrations a part of the silica cooperates with the surfactant to form the ordered structure and the excess of silicate precipitates in an amorphous way over the material resulting in a non-ordered material. For smaller silicate concentrations there is not enough precursor to surround all the surfactant structure, so the material results in a disordered one.

Surfactant solution:water ratio also seems to have a maximum of surface area in the studied range, although statistical analysis did not show a significant influence of this variable in this range. For too low surfactant concentrations, the material cannot grow into an ordered structure because there are not enough micelles. For too high surfactant concentrations there was an excess of surfactant micelles nuclei that disturbed the one-dimensional growth, forming too short cylinders or just agglomerates that could not arrange in an ordered way.

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#### References

1. W.J. Koros, Y.H. Ma, T. Shimidzu, Terminology for membranes and membrane processes. *J. Membr. Sci.* **120**, 149 (1996)
2. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* **359**, 710 (1992)
3. S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCulle, J.B. Higgins, J.L. Schlender, A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* **114**, 10834–10843 (1992)
4. D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **279**, 548–552 (1998)
5. Y. Wan, D. Zhao, On the controllable soft templating approach to mesoporous silicates. *Chem. Rev.* **107**, 2821–2856 (2007)
6. V. Meynen, P. Cool, E.F. Vansant, Verified syntheses of mesoporous materials. *Microporous Mesoporous Mater.* **125**, 170–223 (2009)
7. D. Pan, L. Tan, K. Qian, L. Zhou, Y. Fan, C. Yu, X. Bao, Synthesis of highly ordered and hydrothermally stable mesoporous materials using sodium silicate as a 381 precursor. *Mater. Lett.* **64**, 543–545 (2010)
8. J. Kim, G.D. Stucky, Synthesis of highly ordered mesoporous silica materials using sodium silicate and amphiphilic block copolymers. *Chem. Commun.* **13**, 1159–1160 (2000)
9. E. Santamaría, M. Cortés, A. Maestro, M. Porras, J.M. Gutiérrez, C. González, Micro-meso and macroporous materials obtained from highly concentrated emulsion of decane/brij 35/water and decane/brij 700/water. *Chem. Lett.* **41**, 1041–1043 (2012)
10. J. Shah, S. Kim, T.J. Pinnavaia, A versatile pathway for the direct assembly of organo-functional mesostructures from sodium silicate. *Chem. Commun.* **5**, 572–573 (2004)
11. E. Santamaría, A. Maestro, M. Porras, J.M. Gutiérrez, C. González, A novel approach to the industrial preparation of mesostructured silica: use of ion exchange resin and study of the effect of composition variables. *Chem. Eng. J.* **226**, 7–12 (2013)
12. P.T. Tanev, T.J. Pinnavaia, Mesoporous silica molecular sieves prepared by ionic and neutral surfactant templating: a comparison of physical properties. *Chem. Mater.* **8**, 2068–2079 (1996)
13. T.R. Pauly, T.J. Pinnavaia, Pore size modification of mesoporous hms molecular sieve silicas with wormhole framework structures. *Chem. Mater.* **13**, 987–993 (2001)
14. Q.S. Hue, D.I. Margolese, U. Ciesla, P.Y. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schuth, G.D. Stucky, Generalized synthesis of periodic surfactant/inorganic composite materials. *Nature* **368**, 317–321 (1994)
15. A.S. Michaels, Simplified method of interpreting kinetic data in fixed-bed ion exchange. *Ind. Eng. Chem.* **44**, 1922–1930 (1952)
16. V.N. Romannikov, M.S. Melgunov, A.N. Shmakov, M.E. Malyshev, A.N. Vodennikov, V.B. Felonov, Physicochemical features of formation of silicate porous mesophases. *Russ. Chem. Bull.* **57**, 29–35 (2008). **International Edition**
17. M. Kruk, M. Jaroniec, Characterization of the Porous structure of SBA-15. *Chem. Mater.* **12**, 1961–1968 (2000)

18. E. Santamaría, A. Maestro, M. Porras, J.M. Gutiérrez, C. González, Controlled release of ibuprofen by meso–macroporous silica. *J. Solid State Chem.* **210**, 242–250 (2014)
19. E. Santamaría, A. Maestro, M. Porras, J.M. Gutiérrez, C. González, Preparation of structured meso–macroporous silica materials: influence of composition variables on material characteristics. *J. Porous Mater.* **21**, 263–274 (2014)
20. F. Michaux, M.J. Stébe, J.L. Blin, Systematic investigation of the synthesis parameters driving the preparation of mesoporous materials using nonionic fluorinated surfactant. *Microporous Mesoporous Mater.* **151**, 201–210 (2012)