



# Synthesis and structure of cage-like mesoporous silica using different precursors

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## ABSTRACT

In this work the synthesis of cubic, FDU-1 type, ordered mesoporous silica (OMS) was developed from two types of silicon source, tetraethyl orthosilicate (TEOS) and a less expensive compound, sodium silicate ( $\text{Na}_2\text{Si}_3\text{O}_7$ ), in the presence of a new triblock copolymer template Vorasurf 504 ( $\text{EO}_{38}\text{BO}_{46}\text{EO}_{38}$ ). For both silicon precursors the synthesis temperature was evaluated. For TEOS the effect of polymer dissolution in methanol and the acid solution (HCl and HBr) on the material structure was analyzed. For  $\text{Na}_2\text{Si}_3\text{O}_7$  the influence of the polymer mass and the hydrothermal treatment time were the explored experimental parameters. The samples were examined by Small Angle X-ray Scattering (SAXS) and Nitrogen Sorption. For both precursors the decrease on the synthesis temperature from ambient,  $-25^\circ\text{C}$ , to  $-15^\circ\text{C}$  improved the ordered porous structure. For TEOS, the SAXS results showed that there is an optimum amount of hydrophobic methanol that contributed to dissolve the polymer but did not provoke structural disorder. The less electronegative  $\text{Br}^-$  ions, when compared to  $\text{Cl}^-$ , induced a more ordered porous structure, higher surface areas and larger lattice parameters. For  $\text{Na}_2\text{Si}_3\text{O}_7$  the increase on the hydrothermal treatment time as well as the use of an optimized amount of polymer promoted a better ordered porous structure.

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## 1. Introduction

Ordered mesoporous silica (OMS) with a cage like structure, tailored pore size [1] and amorphous walls can be used as adjuvant for specific antigen delivery [2], among other interesting applications. Also, OMS are appropriate hosts for catalytic purposes due to their morphological properties like high specific surface area, large pore size and uniform pore distribution. Ordered mesoporous structures can be obtained combining triblock copolymer templates with a silicon source. More hydrophobic templates are used to obtain cage-like structures. In particular, FDU-1 type of amorphous silica with a cage-like mesoporous  $\text{Fm}\bar{3}\text{m}$  cubic structure has outstanding figures such as its superficial area (ca.  $740\text{ m}^2\text{ cm}^{-1}$ ), wall thickness (2.9–7.4 nm), pore volume ( $-0.8\text{ cm}^3\text{ g}^{-1}$ ) and pore size ( $-12\text{ nm}$ ), that is larger than those of previously reported materials [3].

In this work the synthesis of FDU-1 type OMS was developed from two types of silicon source, tetraethyl orthosilicate (TEOS) and a less expensive compound, sodium silicate ( $\text{Na}_2\text{Si}_3\text{O}_7$ ), in the presence of a new triblock copolymer, Vorasurf 504 ( $\text{EO}_{38}\text{BO}_{46}\text{EO}_{38}$ ), produced by Dow Chemicals, in substitution of the former B50-6600 ( $\text{EO}_{39}\text{BO}_{47}\text{EO}_{39}$ ) [3–6]. The synthesis process using Vorasurf

504 is not yet fully optimized; therefore, this work aimed to find out the influence of some experimental conditions on the structural and morphological properties of the mesoporous material. For both silicon precursors the synthesis temperature was evaluated. For TEOS the effects of polymer dissolution in methanol and the acid solution (HCl and HBr) on the material structure were analyzed. For  $\text{Na}_2\text{Si}_3\text{O}_7$ , the influence of the polymer mass and the hydrothermal treatment time were the explored experimental parameters. The samples were examined by Small Angle X-ray Scattering (SAXS) and Nitrogen Sorption.

## 2. Materials and methods

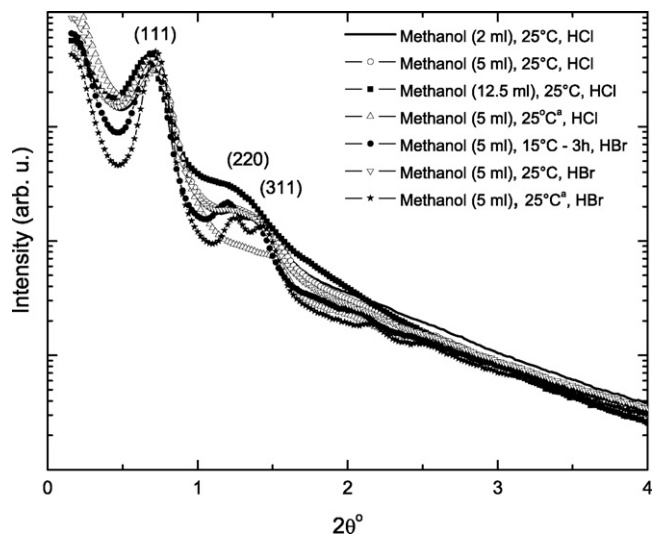
### 2.1. Synthesis

In the synthesis with TEOS, 2.5 g of Vorasurf 504 ( $\text{EO}_{38}\text{BO}_{46}\text{EO}_{38}$ ) was dissolved in analytical grade methanol (5 ml or 12.5 ml) and then, mixed with HCl or HBr ( $2\text{ mol L}^{-1}$ ). TEOS (8.9 ml) was added to the first solution after 15 min of intense magnetic stirring. The final solution stayed in magnetic stirring for 24 h. The temperature of the syntheses was tested, such that samples were prepared: (i) at constant ambient temperature of  $25^\circ\text{C}$ , (ii) at constant temperature of  $15^\circ\text{C}$  in the first 3 h of stirring and (iii) with the homogenized copolymer after a heat treatment for 1 h at  $50^\circ\text{C}$  before the alcohol dissolution. The hydrothermal treatment was performed in a pressure vessel inside a conventional oven at  $100^\circ\text{C}$  for 12 h.

The synthesis with  $\text{Na}_2\text{Si}_3\text{O}_7$  used different amounts of Vorasurf 504 (0.5–3.0 g) and fixed ethanol (2 ml) and water (40 ml) dilution. Small quantities of sodium silicate were added while the solution stayed in magnetic stirring for 6 h. At the last hour of stirring concentrated HCl (40 ml) was added to the solution. The synthesis temperature was also tested, such that samples were prepared: (i) at constant ambient temperature of  $25^\circ\text{C}$  and (ii) at constant temperature of  $15^\circ\text{C}$ . The hydrothermal

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**Fig. 1.** Small angle X-ray scattering (SAXS) patterns of OMS prepared with TEOS. <sup>a</sup> Polymer mass homogenization at 50 °C during 1 h.

treatment (HT) time was also checked, with the samples lasting for 24 or 48 h in a pressure vessel inside a conventional oven at 100 °C. An extra sample was prepared using an HT of 12 h at 100 °C plus 6 h at room temperature.

Tables 1 and 2 present the syntheses conditions, as well as the properties of the OMS. All the samples were washed with 2 L of distilled water to remove the chlorine ions and dried in air at 60 °C.

The polymer removal was made by calcinations in N<sub>2</sub> atmosphere up to 540 °C with a heating rate of 2 °C min<sup>-1</sup>. The samples were analyzed by small angle X-ray scattering (SAXS) and nitrogen sorption isotherms.

## 2.2. Small angle X-ray scattering (SAXS)

The SAXS measurements were carried out with a point focus copper source ( $\lambda = 0.15418$  nm), with the X-ray beam focalized by Gobbel mirrors and a bi-dimensional wire detector, provided by a Nanostar (Bruker) setup. All the data were corrected from absorption and parasitic radiation.

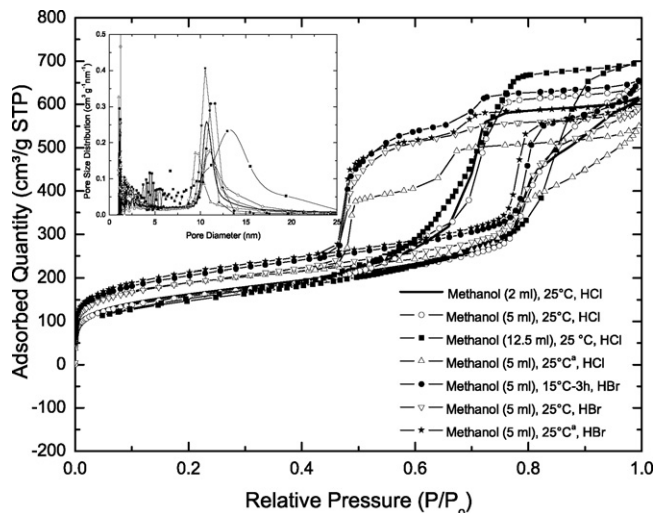
The relative ordered fraction was determined by the ratio of the integrated area under the (1 1 1) diffraction peak after background removal and the total integrated area at the same  $2\theta$  range.

## 2.3. Sorption isotherms

Sorption isotherms were measured at 77 K, using of 99.998% purity nitrogen, on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Measurements were performed in the range of relative pressure from 10<sup>-6</sup> to 0.99 liquid nitrogen on the samples degassed for approximately 10 h, under vacuum of about 0.133322 Pa, at 473 K. The specific surface area was evaluated using the BET method [1]. The total pore volume, VT (cm<sup>3</sup> g<sup>-1</sup>), was estimated from the amount adsorbed at the relative pressure of 0.99. Pore size distribution (PSD) was calculated using the BJH algorithm [7,8].

## 3. Results and discussion

The motivation to prepare cubic OMS with Vorasurf 504 using two different silicon precursors came from the fact that the ideal conditions to prepare this material with TEOS were not totally established and by the intention to obtain a lower cost process with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>. Fig. 1 displays the SAXS results obtained for the samples prepared with TEOS. The increase on the alcohol dissolution volume promotes an increase of lattice parameter, as well as pore diameter, but the surface area decreases. These results can be attributed to the alcohol hydrophobic nature, being located inside the direct micelle hydrophobic core. The best pore ordering was obtained with a dilution of the copolymer in 5 ml of methanol (sample B in Table 1); therefore, this volume was fixed for the other synthesis. The results also show that the use of HBr produces higher figures of porosity ordering (clear 2 2 0 and 3 1 1 diffraction peaks) and surface area, in comparison to HCl. The Cl<sup>-</sup> ions are more electronegative and have

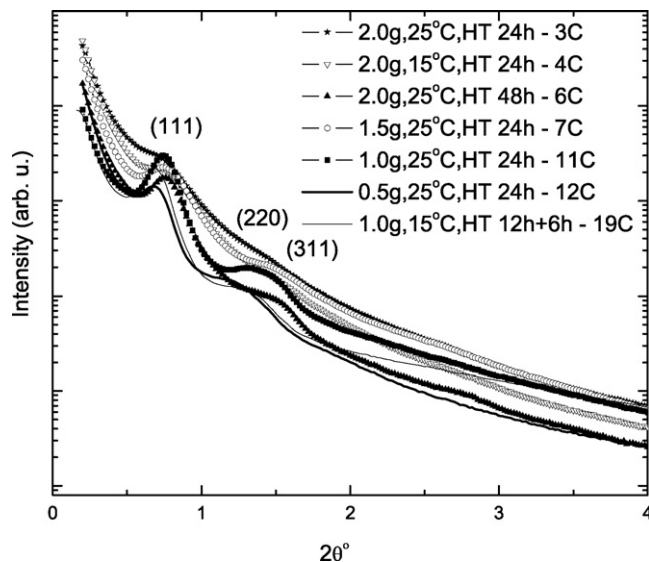


**Fig. 2.** Nitrogen adsorption isotherm at 77 K of OMS prepared with TEOS and pore size distributions of OMS prepared with TEOS. <sup>a</sup> Polymer mass homogenization at 50 °C during 1 h.

smaller ionic radius than Br<sup>-</sup>, allowing its permeation in the micelle corona, thus setting a less ordered porous network. The decrease on the synthesis temperature induced a better ordered porous structure, with higher surface area and large pore size (samples E and F in Table 1).

Fig. 2 depicts the adsorption isotherms and the PSD with micro- and mesopores. The samples prepared with HBr present isotherm profiles typical of a cage-like structure (type IV and H2 hysteresis loop) with smaller neck entrance [9] and sharp PSD, including the larger values of surface area (samples E, F and G in Table 1).

Fig. 3 displays the SAXS results obtained for the samples prepared with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>. The polymer mass was optimized through the analysis of the ordered fraction, surface area and total pore volume (samples 7C–12C in Table 2), being for the present proportions, around 1.0 g. High polymer contents produced a disordered porous network, since samples 8C, 9C and 10C did not show any diffraction peak. The ordered fraction values in Table 2 show that the decrease on the synthesis temperature (samples 3C and 4C), as well as the increase on the hydrothermal treatment time (samples 3C and 6C) promote a more ordered porous structure, favored



**Fig. 3.** Small angle X-ray scattering (SAXS) patterns of OMS prepared with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>.

**Table 1**  
Experimental parameters and properties of the OMS prepared with TEOS and Vorasurf 504.

Name/methanol	T °C	Acid	Ordered fraction	$d_{(111)}$ (nm)	Lattice parameter (nm)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
A/ 2 ml	25 °C	HCl	0.53	12.3	21.3	575	0.94	10.7
B/ 5 ml	25 °C	HCl	0.54	12.6	21.9	559	0.98	10.8
C/12.5 ml	25 °C	HCl	0.47	13.4	23.2	510	0.98	13.3
D/ 5 ml	25 °C <sup>a</sup>	HCl	0.44	11.9	20.7	661	0.82	9.6
E/ 5 ml	15 °C 3 h	HBr	0.69	13.0	22.5	724	0.99	11.4
F/ 5 ml	25 °C	HBr	0.54	12.6	21.9	666	0.90	11.0
G/ 5 ml	25 °C <sup>a</sup>	HBr	0.81	12.3	21.3	748	0.93	10.5

<sup>a</sup> Polymer mass homogeneization at 50 °C during 1 h.

**Table 2**  
Experimental parameters and properties of the OMS prepared with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> and Vorasurf 504.

Sample	Polymer mass (g)	Ordered fraction	$d_{(111)}$ (nm)	Lattice parameter (nm)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
3C <sup>a,d,f</sup>	2.0	0.04	12.3	21.3	508	2.10	12.4
4C <sup>a,e,f</sup>	2.0	0.11	11.6	20.1	495	2.40	11.3
6C <sup>b,d,g</sup>	2.0	0.35	11.6	20.1	409	1.49	11.2
7C <sup>c,d,f</sup>	1.5	0.26	11.6	20.1	549	2.00	11.3
8C <sup>c,d,f</sup>	2.0	–	–	–	–	–	–
9C <sup>c,d,f</sup>	2.5	–	–	–	–	–	–
10C <sup>c,d,f</sup>	3.0	–	–	–	–	–	–
11C <sup>c,d,f</sup>	1.0	0.51	11.9	20.7	598	1.06	10.8
12C <sup>c,d,f</sup>	0.5	0.30	12.6	21.9	342	0.72	11.3
19C <sup>a,e,h</sup>	1.0	0.45	13.4	23.2	794	1.11	10.3

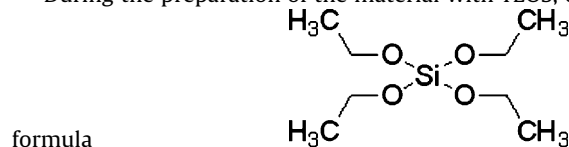
Polymer homogenization: <sup>a</sup>15 min, –50 °C, <sup>b</sup>60 min, –50 °C, <sup>c</sup>homogenized (1 L). Synthesis temperature: <sup>d</sup>–25 °C, <sup>e</sup>–15 °C. Hydrothermal treatment at 100 °C in autoclave: <sup>f</sup>24 h, <sup>g</sup>48 h, <sup>h</sup>12 h plus 6 h at 25 °C.

by the longer hydrolysis period leading to more stable silica walls. Fig. 4 shows the adsorption isotherms and the PSD plots. The shape of the isotherms for samples prepared with a Vorasurf 504 mass higher than 1.0 g is type IV, with the H3 type narrow hysteresis loop indicating the formation of slit like mesopores [10] with average pore diameter around 10 nm. The proper H2 type of hysteresis loop is obtained for a polymer mass of 1.0 g (sample 11C). The optimized synthesis conditions were used to prepare a sample, named 19C, which presented similar structural figures attained for the best OMSs prepared with TEOS and HBr, as shown in Tables 1 and 2. The PSD plots show that small mesopores were also formed (<3 nm).

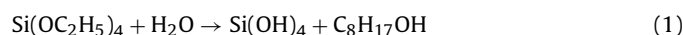
It was expected that with the Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> precursor it would be more difficult to achieve a well ordered porous structure, since this compound precipitates at lower pH, a condition necessary to form the polymer micelles. Therefore, the aggregation of Si(OH)<sub>4</sub> to the

polymeric network would be more difficult leading to disordered pores and thinner silica walls after calcination. Indeed, the relative ordered fractions attained with TEOS and HBr are larger than those obtained with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> at optimized synthesis conditions.

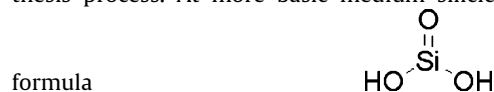
During the preparation of the material with TEOS, of chemical



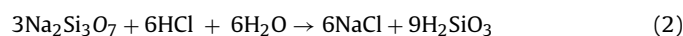
the silanol radicals are immediately formed in the acid medium (pH –2), close to the isoelectric point, where the hydrolysis of TEOS is favored, such that reaction (1) occurs.



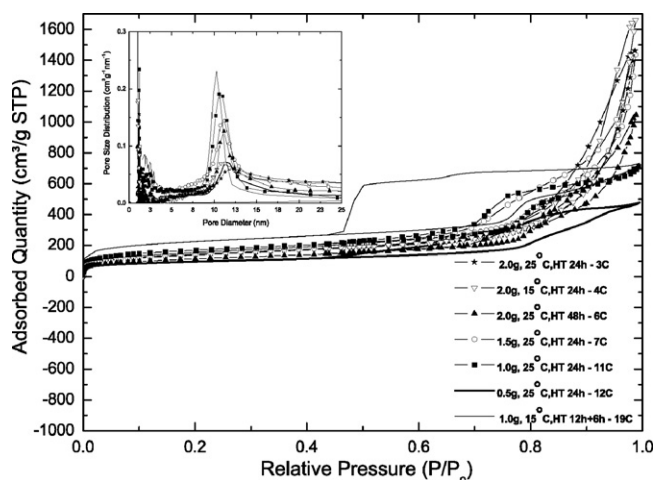
On the other hand, the silicate precursor precipitates at low pH, which has to be avoided in the beginning of the synthesis process. At more basic medium silicic acid of chemical



is formed, according to reaction (2).



By decreasing the pH, the silanol groups are formed, consistent with reaction (3), showing that for the Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> silicon source, the preparation of the material is slow and requires two chemical transformation steps.



**Fig. 4.** Nitrogen adsorption isotherm at 77 K of OMS prepared with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub> and pore size distributions of OMS prepared with Na<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>.

#### 4. Conclusions

In this work the optimized synthesis conditions to prepare Fm3m cage-like type of ordered mesoporous silica network were established, considering the evaluated experimental parameters and two silicon sources, TEOS and  $\text{Na}_2\text{Si}_3\text{O}_7$ . For both precursors the decrease on the synthesis temperature from ambient,  $-25^\circ\text{C}$  to  $-15^\circ\text{C}$  improved the ordered porous structure. For TEOS, the SAXS results showed that there is an optimum amount of hydrophobic methanol that contributed to dissolve the polymer but did not provoke structural disorder. The use of different acid medium showed that the large and less electronegative  $\text{Br}^-$  ions, compared to  $\text{Cl}^-$ , induced the formation of a more ordered porous structure with high surface area. For  $\text{Na}_2\text{Si}_3\text{O}_7$  the proper hydrothermal treatment, as well as the use of an optimized amount of polymer, promoted a better ordered porous cage like structure. Similar values of BET surface area were obtained with both silica sources. As expected, a better ordered porous network was achieved for the material prepared with TEOS and HBr, since for  $\text{Na}_2\text{Si}_3\text{O}_7$  the silanol formation occurs in a two-step process.

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