

# Bimodal Macro- Mesoporous Silica Network

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## ABSTRACT

Bimodal macro-mesoporous silica networks have been prepared in a simple one-pot synthesis using an inexpensive non-toxic surfactant and tetraethoxysilane as a silica precursor. These novel materials show high pore volumes with interparticle macropores and templated mesopores (average pore size 3.0 nm) in 20 nm thick walls. The key properties of these materials can be tailored by controlling the experimental conditions (temperature, pH, stirring and surfactant properties and concentration) to obtain surface areas over 1000 m<sup>2</sup>/g and total pore volumes of 2.0 cm<sup>3</sup>/g.

**Keywords:** bimodal porous silica, non-toxic surfactants, mesoporous

## 1 INTRODUCTION

Mesostructured solids have attracted much attention in the last years due to their wide range of applications in catalysis, controlled delivery, separation techniques, optical devices and sensors. [1-6] Surfactant-templated synthesis is a convenient widely used technique for the preparation of mesostructured materials.[2,3] This strategy allows for the precise control of porosity by adjusting key synthesis parameters. Surfactant-templated materials show some remarkable properties, such as high surface area and narrow pore size distribution [4-6]. Especially relevant is the case of ordered mesoporous silica, such as MCM-41 and related materials, firstly reported in the early 90's [8]. The principal feature of the MCM-41 is its periodic and ordered unimodal mesoporous structure. Although these properties have been suggested to be useful in catalysis, the poor acidity and stability of these materials have limited their applications [7-8]. Multimodal materials combine the benefits of high surface area micro- and mesoporosity with the accessible diffusion pathways of macroporous networks [9]. There are several reports on materials with various pore combinations: micro-mesopores, micro-macropores, meso-macropores, or trimodal micro-meso-macropores.[10].

In order to induce porosity, directing agents like tetraalkylammonium ions are typically used to produce microporous materials, like zeolites, block copolymers or long chain surfactants have been extensively used to prepare a wide variety of mesoporous solids, and hard templates, like polystyrene latexes, nanoparticles, or carbon black to make macroporous materials [6,10].

S. Mann and co-workers have synthesized macroporous sponge-like monoliths and mesoporous thin films using starch gels and sponges in combination with preformed silicalite nanoparticles.[10] Zhang et al. have described the synthesis of bimodal nanoparticulated silicas using a single non-ionic templating surfactant.[11] Cationic surfactants, like cetyltrimethylammonium bromide (CTAB), have been widely used to produce MCM-41 and other mesoporous materials. [12,13] In order to prepare materials with bimodal porosity two or more surfactants have been used simultaneously. [14,15] In many cases, the precise control of the pH is an important variable to finely tune the porous properties of these templated structures.

Using a modified synthesis of the so called "atraneroute", L. Huerta and co-workers have synthesized a novel bimodal mesoporous material with pore volumes in excess of 2.0 cm<sup>3</sup>/g. The strategy is based on the use of complexes like atranes or silatranes as hydrolytic inorganic precursors and surfactants as template [7]. L. Huerta and co-workers also shows that the pore and particle sizes in hierarchic porous silicas are highly dependent on the surfactant nature [7,9]. These materials, although prepared using a different strategy, show a similar structure to the ones that we have produced.

Herein we described the synthesis of a bimodal porous silica network prepared at room temperature in the presence of a cationic surfactant, namely the quaternary amine tallow tetramine. These materials have large surface area, high pore volume, and interparticle pores (20-100 nm) formed by mesoporous (3 nm) walls (20 nm thick). The key properties of these materials can be tailored controlling the experimental conditions (temperature, pH, stirring and surfactant properties and concentration) to produce materials with more than 1000 m<sup>2</sup>/g and total pore volumes of 2.00 cm<sup>3</sup>/g in a one-pot synthesis.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

The surfactant used as template was tallow tetramine, kindly supplied by Tomah3 Products Inc.

All reagents, tallow tetramine, tetraethoxysilane (98%, Aldrich, denoted as TEOS) and ammonium hydroxide (30%, Sigma-Aldrich, NH<sub>4</sub>OH) were used as received without further purification.

## 2.2 Synthesis

In a typical synthesis, 0.275 g of tallow tetramine was magnetically stirred (400 rpm) overnight in 25 ml of deionised water. Alternatively, orbital stirring (60 rpm) was used also overnight. Then, the pH was adjusted to 9.75 with  $\text{NH}_4\text{OH}$  (30%). At this value a viscous solution was obtained. Then, the copolymerization of 1.36 g of TEOS was carried out by base-catalyzed hydrolysis in the presence of tallow tetramine. After a 15h of orbital stirring at room temperature, a white suspension was obtained and the resulting solid was washed first with water and then with ethanol, filtered out, and air dried. Finally, the surfactant was removed by calcination at 550 °C for 8h.

The two different stirring methods (magnetic 400 rpm versus orbital 60 rpm) play a key role in the properties of the final material. More severe stirring (magnetic) produces a clear solution, which suggests that the surfactant was completely dissolved after overnight stirring. On the contrary, milder orbital stirring (60 rpm) does not allow for a complete dissolution of the surfactant after the same amount of time, producing a turbid suspension. The bimodal silica networks have been denoted as BSN1 and BSN2, where 1 and 2 refers to magnetic and orbital stirring of the surfactant, respectively.

## 2.3 Characterization

The morphology of the bimodal silica networks was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM analysis was performed using a JEM-2010 electron microscope (JEOL, Japan). The instrument, operated at 200 kV, has a resolution of 0.14 nm. Samples for TEM studies were prepared by dipping a sonicated suspension of the sample in ethanol on a carbon-coated copper grid. Scanning Electron Microscopy (SEM) analysis of all the samples was carried out using a JEOL JSM-840 microscope.

$\text{N}_2$  adsorption/desorption isotherms were obtained at 77 K in a Quantacrome Autosorb-6 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 523 K for 4 h at  $5 \times 10^{-5}$  bars. The pore size distribution was calculated from desorption branch of isotherms using the BJH method.

## 3 RESULTS AND DISCUSSION

### 3.1 Sample Morphology: TEM and SEM Analysis

Representative TEM micrographs of BSN1 (magnetic) and BSN2 (orbital) silica materials are shown in Figures 1a and 1b, respectively. The insets in Figures 1a and 1b are a detail of BSN1 and BSN2 obtained at higher magnification. BSN1 and BSN2 materials show a tortuous open structure which form irregularly-shaped intraparticle pores. At higher magnification, non-ordered mesopores are observed inside

the network walls which are 20 nm thick (see inset in Figure 1a and 1b). The intraparticle mesopores are only a few nanometers in diameter whereas the interparticle pores are significantly larger. In all cases, the samples were highly homogeneous. No dense phases were observed.

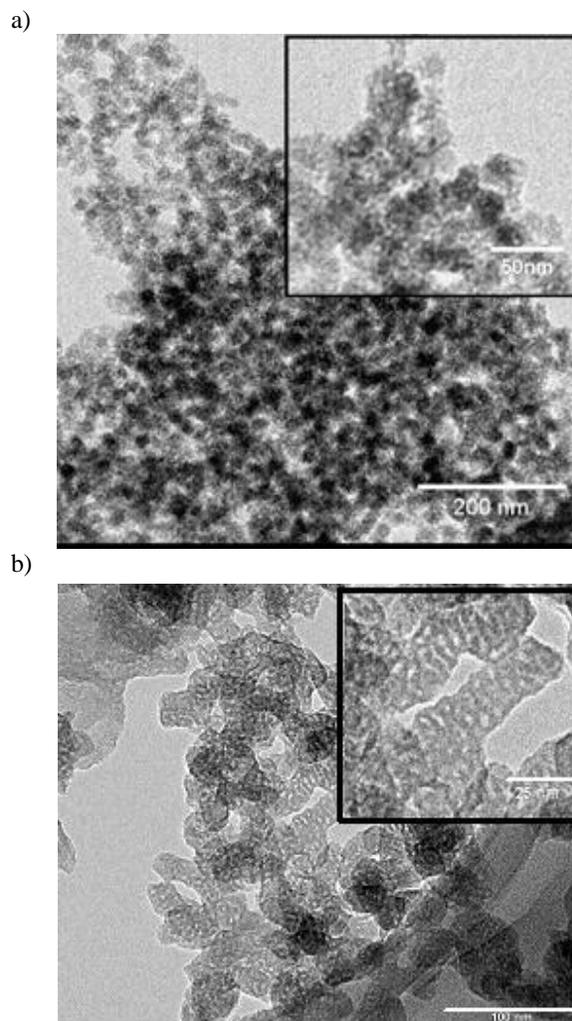


Figure 1: Representative TEM micrographs of calcined bimodal silica materials showing a very open network with both interparticle macro- and intraparticle mesopores: (a) BSN1 (magnetic) and (b) BSN2 (orbital). The detail shown as an inset in (b) was obtained at higher magnification for BSN2 (scale bar represents 25 nm).

The SEM micrographs of BSN materials shown in Figure 2 are typical of an open and irregular structure formed by nanosized particles. These materials are highly homogeneous independently of the stirring method used (see Figure 2a and b).

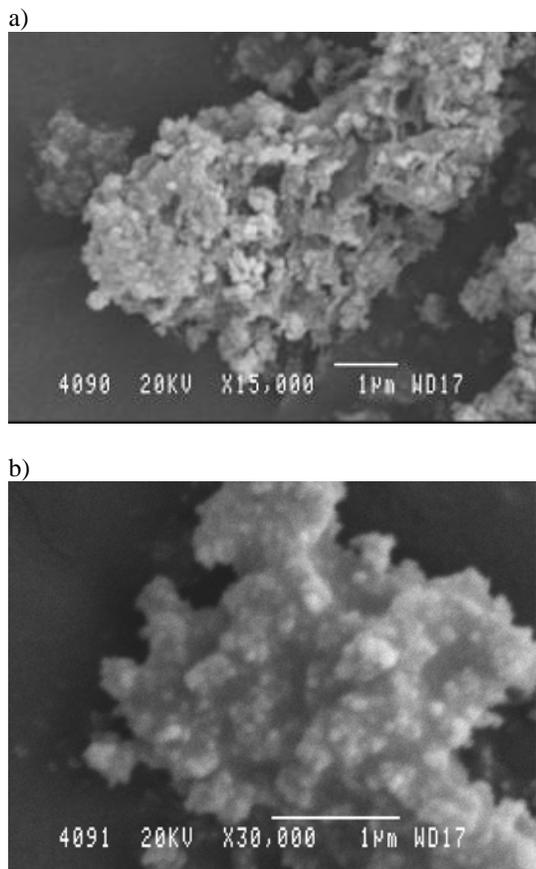


Figure 2: Representative SEM images of calcined silica bimodal material BSN2 (orbital) at two different magnifications.

### 3.2 Nitrogen physisorption isotherms

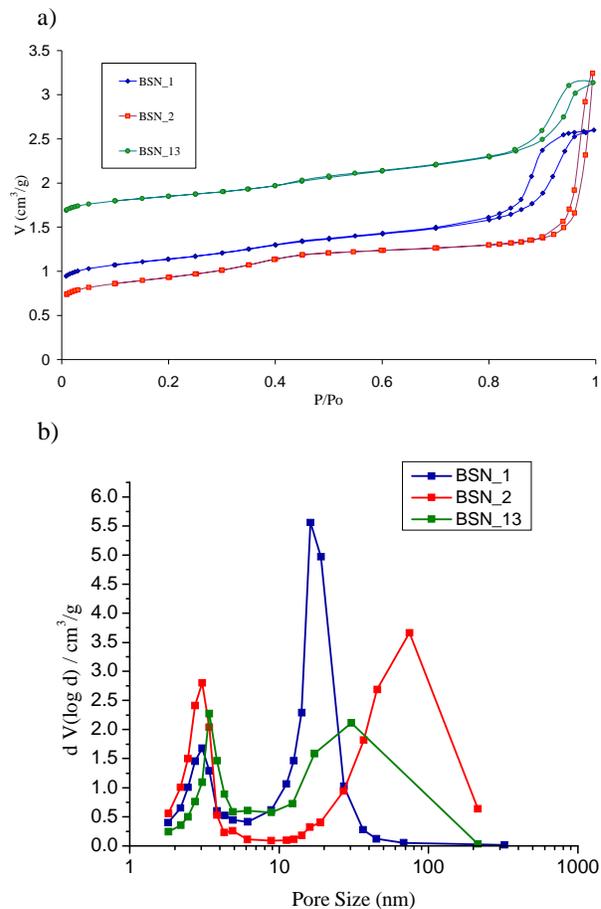


Figure 3: (a) Nitrogen adsorption isotherms of various mesoporous silicas prepared using tallow tetraamine as template (curves are shifted 0.5 cc/g for clarity) and b) Pore size distribution plot, obtained using the BJH method for the desorption branch.

| Sample                | Surface area <sup>a</sup><br>(m <sup>2</sup> g <sup>-1</sup> ) | Pore size <sup>b</sup><br>(nm)<br>(small pore) | Pore size <sup>b</sup><br>(nm)<br>(large pore) | Pore Volume <sup>c</sup><br>(cm <sup>3</sup> g <sup>-1</sup> )<br>(small pore) | Pore Volume <sup>c</sup><br>(cm <sup>3</sup> g <sup>-1</sup> )<br>(large pore) | Total Pore Volume <sup>c</sup><br>(cm <sup>3</sup> g <sup>-1</sup> ) |
|-----------------------|--|--|--|--|--|--|
| 1- BSN1 <sup>d</sup>  | 1015.26  | 3.05   | 16.2   | 0.72   | 1.18   | 1.90   |
| 2- BSN2 <sup>e</sup>  | 1034.95  | 3.04   | 74.7   | 0.74   | 2.01   | 2.74   |
| 3- BSN13 <sup>f</sup> | 804.02   | 3.41   | 30.4   | 0.63   | 1.00   | 1.64   |

a The surface area was obtained using the BET method.

b Pore size was obtained using the BJH on the desorption branch of the isotherm.

c Pore volume was obtained from the isotherm. For the small mesopores the pore volume was measured at P/Po = 0.6 and for the total pore volume at P/Po = 0.99. The pore volume of the large mesopore was estimated subtracting both values.

d Magnetic stirring  $t = 15$  h.

e Orbital stirring.  $t = 15$  h.

f Magnetic stirring  $t = 48$  h.

Table 1: Textural parameters of different bimodal macro- mesoporous silica networks.

Nitrogen physisorption at 77K was used to study the porous properties of our materials. Figure 3a shows the isotherms of calcined BSN1, BSN2, BSN13. These isotherms have two distinctive gas uptakes. The first one, which is related to nitrogen condensation in small mesopores, appears at intermediate relative pressures ( $P/P_0 = 0.2 - 0.4$ ). The second noticeable gas uptake occurs at higher relative pressures ( $P/P_0 = 0.8 - 1.0$ ) and it is due to the filling of much larger mesopores or even macropores. In all cases, only the second uptake shows a hysteresis loop, indicating an irregularly shaped interparticle porosity. Their pore size distributions, obtained using the BJH method, show two distinct peaks at 3 nm (surfactant templated mesopores) and at 20-80 nm (interparticle porosity) as shown in Figure 3b. Table 1 contains some relevant textural parameters of these samples. These data is consistent with the electron micrographs, and with a very open bimodal network.

The formation of these bimodal materials has been related to the competition between kinetic and thermodynamic parameters. While intraparticle mesopores are due to the template effect of the surfactant aggregates, the large mesopores and the macropores appears as a consequence of a nucleation and growth of the primary mesoporous nanoparticles, forming an open and disordered network. Moreover, the proposed macropores formation mechanism involves the collision and aggregation of primary nanoparticles, which produces a disordered open network [7,9,16,17].

According to Amorós et al. [7,9], these structures seem to be formed by nanoparticle aggregates in the form of large clusters with fractal structure. In our case, the dimensions of the silica forming nanoparticles are between 40-70 nm, depending on the sample and the mesopores are around 6-7 nm in both BSN1 and BSN2-like network silica.

The combination of templated mesoporosity and interparticle meso- and macroporosity in these materials is expected to increase the accessibility of bulky molecules to the interior of this very open structure.

## 4 CONCLUSIONS

A simple one-pot synthesis of novel bimodal porous silica networks has been described using tallow tetramine surfactants. The judicious control of the pH conditions allows for the preparation of materials with very high pore volumes and open structures. Two different stirring methods have been studied at different reaction times obtaining the large pore volumes for orbital stirring and the sharp pore size dispersions results for magnetic stirring, during 15 hours.

The main advantages of the preparation herein described are its simplicity, the low cost and toxicity of the surfactant used (tallow tetramine), and the use of the pH as structure directing parameter. The materials produced are

macro- mesoporous bimodal, show a large surface area and pore volumes and a very open structure.

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