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Aerosol generated mesoporous silica particles

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Organized mesoporous silica sub-micro spheres have been synthesized by spray drying solutions containing hydrated Si(OEt)₄ as silica precursor and surfactants as texturing agent. The resulting powder exhibits controlled organized 2-D hexagonal honeycomb-like porosity of 2.2 nm mean pore diameter, homogeneous size dispersion (the particle average diameter is around 0.3 µm and standard deviation σ = 1.89), and a high specific surface area (1000 m²/g). The long-range order porosity was achieved after controlling different parameters: surfactant type and surfactant/TEOS ratios, dilution, pH, temperature and relative humidity under laminar flux motion conditions of aerosol generation. Powders were characterized using X-ray diffraction, TEM, N₂ isotherm adsorption/desorption cycles and FTIR.

Introduction

During the last ten years that followed the discovery of meso-organised templated materials by Mobil & Co., many groups developed novel nano-textured inorganic and organic/inorganic hybrid materials by combining the sol-gel chemistry and the structuring effect of self assembling liquid-crystal surfactants. Most of those works, to which a number of reviews has been dedicated²-⁵, focused on the precipitation in solution of silica based oxide networks around a great variety of charged surfactants¹,⁹ such as Cetyltrimethylammonium Bromide (CTAB) or amphiphile block co-polymers such as PEO-PPO-PEO Pluronics⁶,⁷,⁸. Once the template is removed from the framework through thermal treatment or solvent extraction, the porosity stands at the former location of the nano-segregated micelles. This technique allows a perfect control of the pore size (typically between 2,1 and 10 nm in diameter depending on the surfactant molecular weight) and a controlled pore morphology and self organization within the material (spheres, cylinders or

![Fig. 01](image_url) The process of spray dried mesoporous silica particles. The initial droplet contains Cetyltrimethylammonium bromide (CTAB) as structuring agent, Tetraethoxysilane (TEOS) as silica precursor. The inorganic condensation is achieved via the sol-gel process, whose fundamental steps are showed in the low part of the picture. The role of solvent evaporation in the mesostructuration is put in evidence.
lamellae organized into mono-, bi-, or tri-dimensional arrays). In other words, surfactant micelles play the role of template of the porous network whose geometry is directly related to the surfactant molecule morphology and concentration in the medium.

Figure 01 illustrates the various steps involved in such a synthesis route. More recently, this technique was adapted to thin films, monoliths, and macro-spheres preparation through a controlled evaporation of initial isotropic mixtures of surfactant molecules and inorganic precursors in an appropriately highly volatile solvent. This new approach, addressed as the Evaporation Induced Self Assembly technique (EISA), has great advantages over the precipitation one. Indeed, firstly the surfactant/silica stoichiometry is retained along evaporation; secondly the shaping into spheres takes place with a control on the diameter (aerosol); thin layers have a controlled thickness (liquid deposition) and finally large objects with controlled dimensions (slow evaporation) are possible. While powder precipitation has been well developed, the EISA method was firstly directed to the preparation of variously mesostructured and porous silica thin films, which are interesting materials for applications in catalysis, separation, optoelectronic and chemical sensing.

The mechanisms involved during self-assembly were studied in details on thin films systems and are now well understood. Critical parameters that govern the mesoporosity are the surfactant volume fraction, the inorganic extent of condensation when processing, the evaporation conditions such as humidity and the post synthesis thermal treatment aiming at eliminating the surfactant and stiffening the inorganic network.

 Powders have indeed important applications in catalysis and separation domains but control on the primary particle dimension remains a challenge in precipitation synthesis. An alternative path stands in the simple, industrially already well developed and cheap aerosol generation of particles in which the particle dimension remains a challenge in precipitation synthesis. Evaporation Induced Self Assembly technique (EISA), has great advantages over the precipitation one. Indeed, firstly the surfactant/silica stoichiometry is retained along evaporation; secondly the shaping into spheres takes place with a control on the diameter (aerosol); thin layers have a controlled thickness (liquid deposition) and finally large objects with controlled dimensions (slow evaporation) are possible. While powder precipitation has been well developed, the EISA method was firstly directed to the preparation of variously mesostructured and porous silica thin films, which are interesting materials for applications in catalysis, separation, optoelectronic and chemical sensing.

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its viscosity (µ) at room temperature [Ref. 26, p.62] to be Re_t ≈ 250. Since Re_t < 2100, the particle transportation is done within the carrying gas into a laminar flux motion.

The particle generation follows a continuous regime since the Knudsen number has been evaluated to be (0.001 < Kn = 2λ/dp < 0.06; from Ref. 26, p.23), where dp is the experimental particle diameter which decreases from 2 to 0.3 µm by evaporation (in Figure 04 are reported the dried particle size distribution and a typical SEM picture of the particle is additionally provided) and λ is the nitrogen mean free path (λ = (kBT)/(21/2σ2πp) ≈ 0.0097 µm, p being the gas pressure inside the pipe of (105 Pa) and σ the nitrogen molecular cross section at room temperature). In the continuous regime, particles are large enough to fully follow the carrying gas motion. Despite these ideal conditions of particle generation, we assume that ~ 40% of the particles production rate (nominally given at 10^7 particles cm^-3) are lost within the system as a result of the gravitational force, the hydrophilic nature of the glass pipes, the thermophoresis phenomenon at the oven exit enhanced by the complexity of the piping pathway geometry (abrupt flow direction changes).

**Particle size distribution**

The initial droplet size distribution and mean average size are strictly bound to the solution viscosity and the atomizer characteristics (pressure, dimension of the membrane hole). Taking into account that the optimal initial solution contains weight ratios of 9% TEOS, 3% CTAB, 58% Ethanol, and 30% hydrochloric aqueous solution at pH 1.2 (TEOS/CTAB/Water/Ethanol = 1/0.18/40/30 molar ratios), and that the final particles are composed of SiO₂ microporous framework (p_(SiO₂) ≈ 1.8 g/cm³) and CTAB micelles (p_(CTAB) ≈ 1 g/cm³), the volume fraction of non volatile, condensed matter present in the solution is 4%. Since V_particle/V_drop = 0.04 = ds/dp, then the ds/dp = 0.34 suggests that any droplet is expected to reduce its size of a factor of 0.34 after drying, when keeping its integrity.

Figure 04 exhibits the SEM picture of a typical mesoporous silica powder prepared from a solution with the typical composition given above. The corresponding particle size distribution is also given. The lognormal mean particle diameter was evaluated at dₚ = 0.29 µm with a standard deviation σₚ = 1.89 µm [Ref. 26, p.29]. These values suggest that the initial mean particle diameter is 0.29/0.34 = 0.85 µm. The nominal initial droplet diameter is given to be around 2 µm for water solutions. Here, the lower theoretical value of 0.85 µm is likely related to the presence of 58% ethanol which reduces the solution viscosity. However, the value of dₚ ~ 0.29 µm remains in respect with the nominal characteristics of the our atomizer.

**Fig. 03** IR Spectra compared between CTAB 0.18 as made and calcined at 400°C in the region 1500 – 4000cm⁻¹. The high adsorption peaks (calcined sample) in the 1600 cm⁻¹ area are due to water condensation in the empty mesopores.

**Fig. 05** Diffraction pattern of sample mole ratios (a) CTAB/TEOS = 0.10 (worm-like structure) and (b) CTAB/TEOS = 0.18 (P6nm structure). The hexagonal and worm-like micelle models are shown. The inter-planar distance d₁₀ is given as well as the cell parameters a and b. Underneath, diffraction pattern intensities and Full Width at Half Maximum (FWHM) of samples shown in Table 2 show that the highest organization is reached in the central region of the graph, when the intensity is maximized and the FWHM is minimized.
Mesoscopic formation (influence of chemical parameters)

The starting solution conditions have been chosen by taking into account the behaviour of TEOS silica precursor in ethanol/water mixtures well known in sol-gel chemistry. From previous studies on films it was demonstrated that optimal conditions of hydrolysis condensation exist to promote well organisation during EISA. Following these, the initial solution pH was fixed at 1.2 in order to favour high hydrolysis and low condensation rates, which enable highly hydrophilic but small silica entities within the solution during the pulverisation period. The optimal solvent composition and dilution were fixed at TEOS/Water/Ethanol = 1/40/30 (molar ratios) as to minimize the loss of matter into the system and the pulverisation time, and to keep a good compromise between the extent of organisation, solution stability and concentration (based on a trial and error method). These optimal conditions are kept unchanged in the following study.

As already reported for such systems, the most important parameter that governs the formed mesophase is the CTAB/SiO2 volume ratio, since a high concentration in surfactant tends to form low curved interfaces while low surfactant concentrations lead to highly curved micelles that promotes extended interface of interaction between both phases.

TABLE 1 gives a list of the samples synthesised at different surfactant ratios together with their corresponding structural characterisation deduced from XRD and N2-BET investigations. Figure 05 displays the X-ray diffractions of (a) a typical worm-like structure, and (b) a typical 2D-Hexagonal structure (space group p6m) composed of cylindrical micelles which in the second case are organised into a compact hexagonal array. Peaks have been attributed to the (10), (11) and (20) Miller indices of the hexagonal structures. The compact hexagonal structure is confirmed on the whole particle by TEM.

<table>
<thead>
<tr>
<th>CTAB/TEOS mole ratio</th>
<th>FWHM (Δ2θ)</th>
<th>d(002) (nm)</th>
<th>Specific pore volume (cm3/g)</th>
<th>Specific surface area (BET) g/cm2</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.42</td>
<td>4.29</td>
<td>-</td>
<td>-</td>
<td>Worm-like</td>
</tr>
<tr>
<td>0.10</td>
<td>0.67</td>
<td>3.77</td>
<td>0.5</td>
<td>934</td>
<td>Worm-like</td>
</tr>
<tr>
<td>0.12</td>
<td>0.63</td>
<td>3.81</td>
<td>0.6</td>
<td>1058</td>
<td>Worm-like</td>
</tr>
<tr>
<td>0.16</td>
<td>0.40</td>
<td>3.74</td>
<td>0.6</td>
<td>1184</td>
<td>2-D Hex</td>
</tr>
<tr>
<td>0.18</td>
<td>0.31</td>
<td>3.53</td>
<td>0.7</td>
<td>1222</td>
<td>2-D Hex</td>
</tr>
<tr>
<td>0.25</td>
<td>0.36</td>
<td>3.45</td>
<td>-</td>
<td>-</td>
<td>Worm-like</td>
</tr>
<tr>
<td>0.30</td>
<td>0.72</td>
<td>3.07</td>
<td>-</td>
<td>-</td>
<td>Worm-like</td>
</tr>
<tr>
<td>0.35</td>
<td>1.65</td>
<td>3.23</td>
<td>-</td>
<td>-</td>
<td>Worm-like</td>
</tr>
</tbody>
</table>

As shown by the [001] and [110] view planes of Figures 06 (b,c and d) respectively, where one observes that the elongated micelles tend to align with the spherical particle surface in the hexagonal organisation, while they are randomly oriented in the worm-like structure (Figure 06 (a)). This was already observed in thin films where cylindrical micelles tends to align with both surface and substrate interfaces during evaporation.

A typical CTAB templated N2-BET adsorption-desorption isotherm is shown in Figure 07 (a). It reveals that the material is highly mesoporous with narrow pore size distribution centred at 2.2 nm in agreement with TEM observations. The
present above the critical point of 0.43 P/P_0 (where N_2 critical pressure, and that bottlenecks between pore arrays are not), capillary condensation and evaporation do not take place at temperature, humidity) before being collected on the filter, does not outmost importance since it prevents the particles to coalesce when they found themselves in contact on the filter, and allows the particles to keep the spherical shape such a coalescence phenomenon occurred for temperatures below 200°C. In terms of micellar organisation, a too high temperature leads to less organised particles. The best organisation (highest and narrowest diffraction peaks) was found by allowing the particles to pass inside a first furnace at 150°C before entering the second furnace at 350°C, suggesting that a progressive heat treatment is favourable to the meso-organisation. A too high temperature tends to reduce the degree of organisation (see Figure 08), which is attributed to a too extended condensation of the inorganic phase. In view of these results, one may say that the heat treatment is necessary to obtain discrete particles with well organised mesoporosity (low dispersion in pore size distribution). The optimal temperature conditions are the following: a progressive temperature up to 350°C leads to the formation of the hard shell around the particles leaving the inside flexible enough to complete the organisation. The silica condensation inside the particle is naturally achieved by ageing.

Humidity. The versatility of the technique allows to change the composition of the carrying gas in the system. Recent studies on similar system as thin films demonstrated the critical role of the water relative pressure in the environment during evaporation. At high humidity, water diffuses inside the system, promoting self assembly of the micelles by adjusting the micellar interfacial interaction with the inorganic matrix. This later wet condition can be applied to the aerosol generation by filling part of the drying chamber with water. In the present conditions of production, a relative humidity of 70% was measured in the chamber. The corresponding XRD diagram is given in Figure 08 and confirmed the positive role of water on the organisation during EISA, since it provided the most intense diffraction peak.

Conclusion
Preparation of mesoporous silica sub-micro spheres exhibiting high surface area, narrow pore size distribution, and hexagonal organization of cylindrical pores with CTAB or compact body centered cubic organization of spherical pores with copolymer blocks is possible by spray drying. Control on the pore size and organization is achieved by selecting the appropriate surfactant and by adjusting its composition. Also, careful control on the chemical parameters (initial sol composition, and pH) and on the processing parameters (temperature and humidity) is required to promote self-assembly and to retain the spherical shape. The optimal conditions involved pH = 1.2, CTAB/TEOS = 0.18, the presence of water and ethanol in the solution, a progressive heat treatment up to 350°C and a high relative pressure of water in the carrying gas.

References

In order to create larger pores, we have used Pluronics as structuring agents and a tri-dimensional micellar Cubic structure was found, as shown by the corresponding TEM image in Figure 06 (e). The N_2-BET adsorption-desorption isotherm of the P123 sample, shown in Figure 07 (c), is of type IV showing the presence of a large hysteresis loop of type H_2, indicating that capillary condensation and evaporation do not take place at the same pressure, and that bottlenecks between pore arrays are present above the critical point of 0.43 P/P_0 (where N_2 critical liquefaction can occur). The isotherm idicates a high pore structure is verified for CTAB/Si ratios ranging from 0.15 to 0.25 with an apex in the organisation degree located at 0.18 as illustrated in Figure 05. This optimal system will then be used to study the influence of the processing conditions on the organisation degree.

Mesostructure formation (influence of processing parameters).

The processing conditions, that is to say the successive residence time of the particles in a certain environment (temperature, humidity) before been collected on the filter, does influence the final morphology and the mesostructural organisation of the micelles. The diffraction diagrams corresponding to various studied conditions are given in Figure 08.

**Furnace temperature.** The role of the furnace is to allow for the particle to solidify by condensation. As a result of the short period of time in the furnace (typically less than 10s), the heat is mainly located at the particle surface since it is diffusion limited inside the particle. A peripheral condensed layer (outer shell) is then formed by condensation at the periphery. This shell is of outmost importance since it prevents the particles to coalesce when they found themselves in contact on the filter, and allows the particles to keep the spherical shape. Such a coalescence phenomenon occurred for temperatures below 200°C. In terms of micellar organisation, a too high temperature leads to less organised particles. The best organisation (highest and narrowest diffraction peaks) was found by allowing the particles to pass inside a first furnace at 150°C before entering the second furnace at 350°C, suggesting that a progressive heat treatment is favourable to the meso-organisation. A too high temperature tends to reduce the degree of organisation (see Figure 08), which is attributed to a too extended condensation of the inorganic phase. In view of these results, one may say that the heat treatment is necessary to obtain discrete particles with well organized mesoporosity (low dispersion in pore size distribution). The optimal temperature conditions are the following: a progressive temperature up to 350°C leads to the formation of the hard shell around the particles leaving the inside flexible enough to complete the organisation. The silica condensation inside the particle is naturally achieved by ageing.

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**References**
73 A. Sayari, Chem. Mater., 1996, 8, 1840-1852
75 A. Corma, Chem. Rev., 1997, 97, 2373-2419
76 U. Ciesla, F. Schuth, Microporous mesoporous mater., 1999, 27, 131-149