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First *in-situ* SAXS studies of the mesostructuration of spherical silica and titania particles during spray-drying process

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Meso-organisation of SiO_2 and TiO_2 particles prepared by spray drying have been for the first time analysed through *in-situ* SAXS. Both processing and chemical parameters are critical to obtain meso-organised spheres.

Among different ways for the preparation of mesoporous materials, one of the most promising is the recently developed Evaporation Induced Self Assembly (EISA) process that involves progressive concentration of non-volatile species (organic template and inorganic oligomers).[1] Its advantages include a perfect control of the final stoichiometry in addition to the shaping as thin films (liquid deposition method), macrospheres (spray drying), and membranes (slow evaporation). Among these, aerosol generated spherical mesoporous particles are excellent candidates for applications in high technology domains such as pharmaceutical vectoring, catalysis, separation, and energy conversion (photovoltaic and fuel cells). This is attributed to the one-step control of the final multimodal porosity and to the possible crystallisation of transition metal oxide networks (TiO_2, ZrO_2).[2] Therefore it is of utmost importance to define the critical parameters. The final mesostructure is generally mainly governed by modulating the surfactant to inorganic ratio. Indeed, for CTAB-SiO_2 films, the entire range of mesostructures (from cubic to lamellar) has been obtained by increasing the CTAB/SiO_2 molar ratio.[3] However, in spray drying, the 2D hexagonal structure is systematically encountered in a wide range of CTAB/ SiO_2 ratios (0.8 to 0.28).[4] That this difference is very probably related to processing parameters is shown for the first time by the present *in situ* SAXS investigation.

Very recent work, dedicated to mechanisms involved in EISA applied to thin films, found that the final mesostructure effectively depends on chemical parameters but also on the diffusion of volatile species between the layer and the dip-coater atmosphere during evaporation.[3,5] In order to understand and to have a better control on EISA in spray drying, it is of paramount importance to be able to follow *in situ* the structure of these spherical particles in the carrier gas. However, the concentration of particles in the gas phase is very low (10^7 particles (6 μg dry matter) per cm^3, apparatus nominal value). Therefore, to reach a sufficiently high sensitivity, we designed an experiment that involves *in situ* SAXS characterisation, using high flux (8 keV) third generation synchrotron (ELETTRA-Italy). The experimental setup shown in Fig. 1 is composed of the aerosol generator (TSI 3076) from which drying droplets (1 μm initial mean diameter) are carried by dry air (3 l min^{-1}) first into an evaporation chamber, then into an oven and an X-ray transparent cell. The amount of matter analysed was raised to 5.10^{-8} g by lengthening the sampling cell to 70 mm (optimised distance to conserve a good resolution). The residence time of aerosol in the evaporation chamber was modulated from 0 to 270 s at 25 °C by varying its volume. Further evaporation and stabilisation took place in the heater at various temperatures ranging from 25 °C to 500 °C (2.5 s heating time). This thermal treatment is critical because it causes the hardening of the particle surface, preventing their coalescence. Depending on the system, a minimum heating temperature of between 125 and 250 °C is required.[2,4] Typical initial solutions contain CTAB : TEOS : H_2O : EtOH : HCl (molar ratio 0.14 : 1 : 5–41 : 0–20 : 0.13). 2 solvents compositions (water rich 0.14 : 1 : 41 : 0 : 0.13 or alcohol rich 0.14 : 1 : 5 : 20 : 0.13) were investigated. An additional Brij 58-TiO_2 system (molar ratio Brij58 : $TiCl_4$: H_2O : EtOH 0.08 : 1 : 10 : 40) was also studied. The following results show that the resting time in the evaporation chamber had no effect on the mesostructuration, while better organisation was obtained with alcohol-rich solvent systems. Overall, the self-assembly is critically influenced by the heater temperature.

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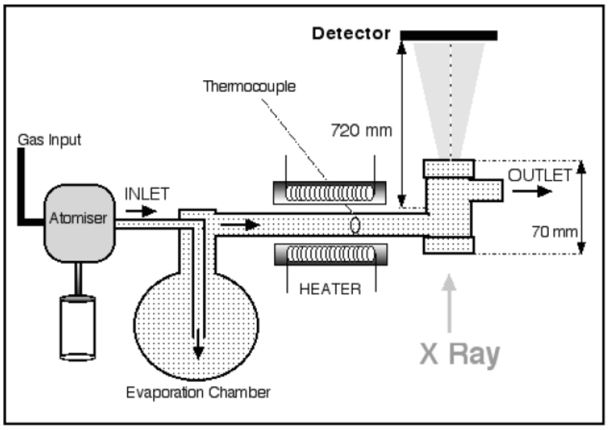

Fig. 1 *In situ* SAXS set up used for aerosol generated particle analysis.

In Fig. 2, X-ray diagrams and TEM pictures of silica spherical particles collected on a filter after heating at 350 °C correspond to the typical 2D hexagonal p6m structure. The poor diffraction peaks definition is due to the curved reticular plans forced by the particle spherical morphology (Fig. 2(d)).[4] *In situ* SAXS experiments were performed by progressively increasing the heating temperature up to 500 °C (100 s acquisition time). In the typical temperature resolved SAXS diagram shown in Fig. 3, the low quantity of analysed matter did not allow the observation of higher order correlation peaks. The appearance and evolution of the order with temperature are reported in Table 1 for each system. For alcohol-rich systems, order

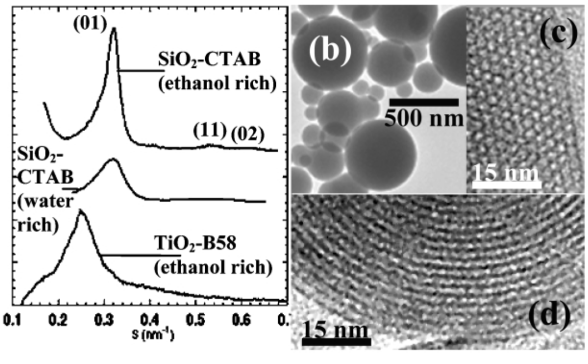

Fig. 2 SAXS diagrams of particles (350 °C) (a). TEM images of particles (SiO_2-CTAB ethanol rich): global (b), directions [001] (c) and [100] (d).

Table 1 Chemical and processing conditions used to prepare ordered mesoporous particles

Sol composition					Process:		Correlation shift		
Exp.	Metal	H_2O : M	EtOH : M	Ageing time/h	Drying time/s	Organisation temperature/°C	*d*-Spacing 1/Å	< Temperature/°C <	*d*-Spacing 2/Å
1	Si	5[a]	24	12	90	80	35	$120 < T < 240$	31
2	Si	5[a]	24	12	270	80	35	$120 < T < 240$	31
3	Si	41[a]	4	12	180	25	35	$120 < T < 260$	31
4	Ti	10	40	14	90	130	45	$230 < T < 310$	40

[a] For silica systems, 5 mol of water are systematically brought from [HCl] = 2 mol.l^{-1} solutions.

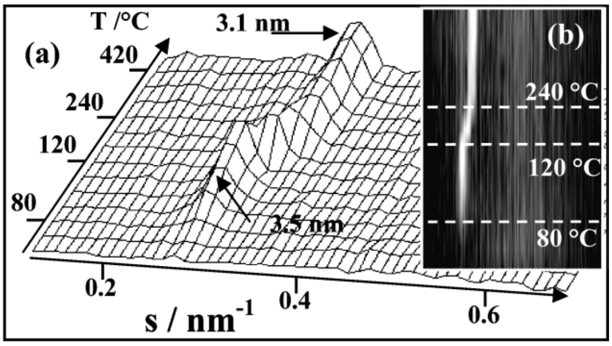

Fig. 3 a) 3D and b) 2D views of SAXS patterns recorded for the ethanol rich CTAB/TEOS system when increasing the heater temperature.

appeared above 80 °C. At higher temperatures, the correlation peak shifted systematically to higher angles and remained at a fixed angle above 250 °C. This shift may have two origins: phase transition and/or shrinkage. Indeed, epitaxial cubic⇆2D hexagonal phase transition, observed when the same solution is deposited in thin films,[6] can explain this shift. In addition, it is likely that high temperature induces shrinkage by evaporation–condensation. It is important to emphasise that organisation occurs above 80 °C, whatever the resting time in the evaporation chamber (Table 1), suggesting that temperature-assisted evaporation is one of the critical factors in this process. Exactly the same shift is observed for water-rich systems, except that the final structure is less ordered and the meso-organisation is present from 25 °C. As a result, the mesostructuration is influenced by the solvent nature and its evaporation rate which is enhanced at high temperature.

In the present aerosol process, the concentration of particles in the carrying gas is fixed, suggesting that evaporation stops when liquid/gas partial pressure equilibrium is reached. Since temperature greatly influences the evaporation rate through a variation of vapour pressure, the chemical composition of the particle inside the heater is temperature dependent. Indeed, saturated vapour pressures of pure ethanol and water at 26 °C are 0.09 and 0.033 atm. respectively, and increase to 1.00 and 0.47 atm. at 80 °C. Because no organisation is observed before 80 °C with the ethanol-rich system, one would expect the evaporation not to be completed before the heater and thus the mesostructuration to be promoted by the fast and almost total departure of ethanol above 80 °C. This structure is therefore allowed by elimination of the ethanol co-surfactant perturbing effect, concomitantly with the increase of medium polarity.[7] On the other hand, the lower saturated vapour pressure of water and its strong interactions with silica and CTAB polar head groups make it more difficult to evaporate than ethanol. The residual amount of water at 80 °C promotes self-assembly (Fig. 3).[5] This effect is confirmed for the water-rich system, where the meso-ordering readily takes place at room temperature, as a result of the high water to ethanol ratio. Final particles prepared from alcohol-rich solution exhibit better organisation than those prepared from water-rich solution (Fig. 2). Since a competition between condensation and self-assembly describes the EISA process, this lower order is due to a higher degree of silica condensation, favoured in aqueous medium, which prevents complete self assembly into highly ordered structure.[3] The role of ethanol is confirmed with the titania-Brij 58 system. Here, structure and peak shift are observed at higher temperatures than with silica (exp. 4). These variations are related to the different physico-chemical properties of this system: slower Brij 58 segregation kinetics, slower titania oligomer condensation rate, higher hygroscopicity, and higher chloride concentration.[2] However, the same solvent diffusion effect can be assigned to this different system. The self-assembly of aerosol generated templated particles is controlled by the diffusion of water and ethanol out of the particles during drying. After the first evaporation step, the proportion of water and ethanol that remains within the wet particles depends on the initial solution composition and on the corresponding saturated vapour pressures. During the following thermal treatment, the latter constants increase with the temperature, inducing further evaporation. The meso-ordering was observed from room temperature for water-rich systems, and from 80 °C for ethanol-rich systems, suggesting that the self-assembly requires the total elimination of ethanol but the presence of a slight amount of water, which can be achieved by adjusting the temperature. After self-assembly, initial structures obtained with all studied systems, undergo phase transition and/or shrinkage at higher temperatures, suggesting that the structure is still flexible.

Finally, the higher silica condensation degree, favoured in water-rich solvent, leads to a lower final extent of meso-ordering when compared to ethanol-rich systems. Indeed condensation must be limited in the sol state (control of H_2O : M and H_2O : EtOH ratios, pH, T) and during processing (control of relative humidity, T) to avoid the quenching of the self-assembly arrangement by the kinetically controlled inorganic growth. Note that for a given surfactant to metal ratio, highly ordered mesoporous particles are only obtained for a tuned solvent composition, if particles dry long enough in the proper atmosphere at a specific temperature, and if they undergo a final thermal stabilisation before filtering.

We demonstrate in this work that the critical parameters are both chemical and processing in nature and must be perfectly controlled. These *in situ* SAXS experiments shed a lot of light on the complex mechanisms occurring at the curved hybrid interfaces of spray-dried droplets during their mesostructuration, and open a land of possibilities for the reproducible design of inorganic or hybrid spheres having hierarchical structure.

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